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TRANSITION METAL NITROSYL COMPLEXES

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I. Introduction[1]

This chapter describes the synthesis of transition metal nitrosyl complexes with particular reference to routes that involve common reagents (e.g., NO and $NOBF_4$). Methods for their characterization by spectroscopic and structural techniques are critically reviewed. The application of ^{15}N NMR for distinguishing among linear, bent, and bridging nitrosyls are emphasized. The bonding in metal nitrosyl complexes is reviewed from a molecular orbital and valence-bond point of view. Finally, the reactions of transition metal nitrosyl complexes are discussed.

In recent years transition metal nitrosyl compounds have attracted considerable interest, and several review articles have been published (*1–11*). This interest has been directed towards three main areas.

1. The factors that influence the mode of bonding of nitric oxide. These are important as part of the more general study of how small molecules bond to, and are activated by, transition metals. In this respect the coordination chemistry of nitric oxide exhibits greater versatility compared with that of many other simple molecules, including carbon monoxide and dinitrogen.
2. Concern over the role of nitrogen oxides in air pollution. This has stimulated the development of catalysts for the removal of nitrogen oxides from exhaust gases. Nitric oxide is thermodynamically unstable with respect to decomposition to its elements at 25°C and 1 atm:

$$2NO \longrightarrow N_2 + O_2 \qquad \Delta G^\circ = -174 \text{ kJ mol}^{-1}$$

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[1] A list of abbreviations appears at the end of this chapter.

However, it is kinetically inert and requires a catalyst for this and many other of its reactions. Generally, heterogeneous catalysts such as CuO and Rh_2O_3 are used, though homogeneous catalysis has been reported for some reactions of nitric oxide. For example, a number of platinum metal complexes, as well as metals and metal oxides, can catalyze the oxygen transfer reaction:

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

The catalytic implications of the alternative coordination modes of nitric oxide in transition metal complexes were first noted by Collman (*12*). He argued that the *linear* → *bent* transformation, concomitant with a change in the formal oxidation state of nitrogen from (III) to (I), results in the withdrawal of electron density from the metal center and facilitates the coordination of another ligand into a vacant site. Thus, the mixed carbonyl nitrosyl complex $[Co(CO)_3(NO)]$ undergoes thermal CO substitution by an associative mechanism, whereas the isoelectronic, homoleptic carbonyl $[Ni(CO)_4]$ reacts by a dissociative pathway (*13*).

3. The synthesis of organonitrogen compounds from nitric oxide and unsaturated organic molecules. Such reactions, catalyzed by transition metal compounds, provide the opportunity of converting nitric oxide from an unwanted pollutant into a feedstock for the chemical industry. Surprisingly little research has been undertaken in this area, though several interesting stoichiometric reactions involving NO are known. For example, Becker *et al.* (*14*) have reported the synthesis of *vicinal*-diamino compounds from alkenes and nitric oxide using $[\{Co(\eta\text{-}C_5H_5)(NO)\}_2]$. Metal nitrosyl complexes are also involved as intermediates in the catalyzed air oxidation of alkenes to epoxides by transition metal nitro compounds and air (*14*).

Although previous reviews have discussed the synthesis and reactions of nitrosyl complexes (*1–11*), they have not emphasized the characterizational aspects. Therefore, this review will attempt to correct this imbalance.

II. Synthesis of Transition Metal Nitrosyl Compounds

A variety of methods are available to the inorganic chemist for the synthesis of nitrosyl complexes. Some examples of the most widely used routes are discussed next; more exhaustive accounts have been given by Connelly (*2*), Caulton (*4*), and Gladfelter (*11*).

A. Addition Reactions

If we pass gaseous nitric oxide through a solution of a coordinatively unsaturated transition metal complex, simple addition may occur. Since nitric oxide contains an unpaired electron, this method is most commonly applied to paramagnetic starting materials. Some examples of this reaction (*16, 17*) are

$$[CoCl_2(PPh_3)_2] \xrightarrow{NO} [CoCl_2(NO)(PPh_3)_2]$$

$$[Cr(N^iPr_2)_3] \xrightarrow{NO} [Cr(N^iPr_2)_3(NO)]$$

Alternatively, the addition of the nitrosonium ion, generally as the tetrafluoroborate or hexafluorophosphate salt, provides a convenient synthetic route to nitrosyl complexes. Examples of such reactions include (*18, 19*)

$$[RuCl(NO)(dppbp)] \xrightarrow{[NO]BF_4} [RuCl(NO)_2dppbp]BF_4$$

$$[RuCl(NO)(PPh_3)_2] \xrightarrow{[NO]BF_4} [RuCl(NO)_2(PPh_3)_2]BF_4$$

$$[Os_4H_3(CO)_{12}]^- \xrightarrow{[NO]BF_4} [Os_4H_3(CO)_{12}(\mu_2\text{-}NO)]$$

Reduction of the nitrosyl group occurs in certain cases, providing an effective method for the synthesis of nitrido clusters. For example (*19*):

$$[Ru_4H_3(CO)_{12}]^- \xrightarrow{[NO]BF_4} [Ru_4H(\mu_4\text{-}N)(CO)_{12}]$$

B. Substitution of Two-, Three-, Four-, and Five-Electron Ligands

Nitric oxide replaces ligands such as CO, tertiary phosphines, and alkenes as in the following reactions (*20–22*):

$$[Rh(\eta\text{-}C_7H_8)(PPh_3)_2]^+ \xrightarrow{NO} [Rh(NO)_2(PPh_3)_2]^+$$

$$[Mn(CO)_3(NO)(PPh_3)] \xrightarrow{NO} [Mn(NO)_3(PPh_3)]$$

$$[Cr(CNR)_6]^{2+} \xrightarrow{NO} [Cr(NO)(CNR)_5]^{2+}$$

In addition, odd-electron ligands can be substituted to yield diamagnetic complexes (*23*):

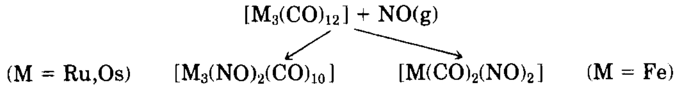
$$[\mathrm{IrH(CO)(PPh_3)_3}] \xrightarrow{\mathrm{NO}} [\mathrm{Ir(CO)(NO)(PPh_3)_2}]$$

These methods have also been applied to the synthesis of nitrosyl cluster compounds (*24, 25*):

$$[\mathrm{V}(\eta\text{-}\mathrm{C_5H_5})_2] \xrightarrow{\mathrm{NO}} [\{\mathrm{V}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{NO})_2\}_2]$$

$$[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_3] \xrightarrow{\mathrm{NO}} [\mathrm{Mn_3}(\eta\text{-}\mathrm{C_5H_5})_3(\mu_2\text{-}\mathrm{NO})_3(\mu_3\text{-}\mathrm{NO})]$$

The reactions of nitric oxide with metal cluster compounds themselves are complicated by the possibility of metal—metal bond cleavage. In the next example, the tri-iron compound shows very different reactivity from its ruthenium and osmium analogs (*26–28*):



$$[\mathrm{M_3(CO)_{12}}] + \mathrm{NO(g)} \longrightarrow (\mathrm{M = Ru,Os})\ [\mathrm{M_3(NO)_2(CO)_{10}}] \quad;\quad [\mathrm{M(CO)_2(NO)_2}]\ (\mathrm{M = Fe})$$

The nitrosonium ion, which is isoelectronic with CO, has also been used in substitution reactions (*29*):

$$\mathrm{OsCl(CO)(NO)(PPh_3)_2} \xrightarrow{[\mathrm{NO}]\mathrm{BF_4}} [\mathrm{OsCl(NO)_2(PPh_3)_2}]\mathrm{BF_4}$$

$$[\mathrm{Rh(NO)(PPh_3)_3}] \xrightarrow{[\mathrm{NO}]\mathrm{BF_4}} [\mathrm{Rh(NO)_2(PPh_3)_2}]\mathrm{BF_4}$$

A common reaction of nitrosonium ion with low-valent transition metal compounds results in 1-electron oxidation of the complex, with the evolution of NO(g). Thus, nitrosyl complexes were not isolated in the following reactions (*30*):

$$[\{\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\}_2] \xrightarrow{[\mathrm{NO}]^+,\mathrm{MeCN}} [\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]^+$$

$$[\mathrm{Pt(PPh_3)_4}] \xrightarrow{[\mathrm{NO}]^+} [\mathrm{Pt(PPh_3)_4}]^{2+}$$

C. Reductive Nitrosylation

Reaction of nitric oxide with high oxidation state metal halides can lead to reduction to low-valent nitrosyl compounds, with elimination of nitrosyl halide. This route has been used particularly for early transition metal compounds and some examples from molybdenum chemistry are (*31, 32*)

$$[MoCl_5] \xrightarrow{NO} [MoCl_2(NO)_2]_x$$

$$[MoCl_5] \xrightarrow{NO,MeCN} [MoCl_3(NO)(MeCN)_2]$$

Reductive nitrosylation also occurs on reaction of hydroxylamine with transition metal oxo- compounds (*33–35*):

$$[TcO_4]^- \xrightarrow{NH_2OH,NaSCN} [Tc(NO)(SCN)_5]^{2-}$$

$$[MoO_4]^{2-} \xrightarrow[NH_2OH]{HCl,NaSCN} [Mo(NH_2O)(NCS)_4(NO)]^{2-}$$

$$[OsO_4] \xrightarrow[NH_2OH,NaSCN]{HCl} [Os(SCN)_5(NO)]^{2-}$$

D. USE OF ORGANONITROSYL REAGENTS

A versatile reagent is *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (MNTS), which effects the replacement of a metal hydride bond and a labile ligand by a metal nitrosyl bond. For example (*36*):

$$[RuH_2(PPh_3)_4] \xrightarrow{MNTS} [Ru(NO)_2(PPh_3)_2]$$

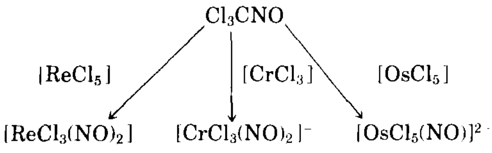
The reaction has also been applied to carbonyl anions (*37*):

$$[V(\eta\text{-}C_5H_5)(CO)_3]^{2} \xrightarrow{MNTS} [V(\eta\text{-}C_5H_5)(CO)(NO)_2]$$

Other nitroso derivatives have also been used, and the reactions are summarized in the following examples (*38–41*), where dppe is 1,2-bis(diphenylphosphino)ethene and THF is tetrahydrofuran:

$$[Mo(N_2)_2(dppe)_2] \xrightarrow[THF]{MeN(NO)(CONH_2)} [Mo(NCO)(NO)(dppe)_2]$$

$$[W(N_2)_2(dppe)_2] \xrightarrow[THF,MeOH]{Et_2NNO} [WH(NO)(dppe)_2]$$



E. REDUCTION OF COORDINATED NITRITE OR NITRATE LIGANDS

These synthetic methods are based on oxygen transfer reactions, which are an important general feature of transition metal nitrosyl chemistry. The following reactions illustrate this route (*15, 42*):

$$[PtCl(NO_2)(NH_3)_2] \xrightarrow{HCl} [PtCl_3(NO)(NH_3)_2]$$

$$[Ni(NO_3)_2(PEt_3)_2] \xrightarrow{CO} [Ni(NO_3)(NO)(PEt_3)_2]$$

An important recent development in this class of reaction has been the use of bis-(triphenylphosphine)iminium (PPN) nitrite. This reagent has proved to be particularly useful, especially in the synthesis of nitrosyl cluster compounds from the more readily available carbonyl clusters under mild conditions (*43, 44*):

$$[Mn(CO)_4(NO)] \xrightarrow{[PPN]NO_2} PPN[Mn(CO)_2(NO)_2]$$

$$[Ru_6C(CO)_{17}] \xrightarrow{[PPN]NO_2} [Ru_6C(CO)_{15}(NO)]^-$$

In certain cases simple substitution of carbonyl by nitrite ligand occurs such as (*43*):

$$[Co(CO)_3(NO)] \xrightarrow{[PPN]NO_2} PPN[Co(CO)_2(NO)(NO_2)]$$

Alternatively, reduction can occur with or without the isolation of nitrido-clusters. A comparison of the reactions of the hexanuclear rhodium and iridium clusters is shown (*45*):

$$[Ir_6(CO)_{16}] \xrightarrow{PPN(NO_2)} PPN[Ir_6(CO)_{15}(NO)] \xrightarrow{PPN(NO_2)} (PPN)_2[Ir_6(CO)_{15}]$$

$$[Rh_6(CO)_{16}] \xrightarrow{PPN(NO_2)} [Rh_6(\mu_6\text{-}N)(CO)_{15}]^-$$

The use of nitrite salts with mineral acids has been known for many years as a route to nitrosyl complexes, and some typical examples are the following (*46, 47*):

$$[Pt(NO_2)_2(NH_3)_2] \xrightarrow{NaNO_2,HCl} [PtCl(NO_2)_2(NO)(NH_3)_2]$$

$$FeSO_4 \xrightarrow{NaNO_2,(NH_4)_2S} [Fe_4S_3(NO)_7]^-$$

It is not known if anation by the nitrite ion is the initial step or if the nitrosonium ion is formed by the equilibrium

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

In the case of $[RuCl(bpy)_2(H_2O)]^+$ (bpy is 2,2′-bipyridine) no reaction with sodium nitrite is observed after an hour whereas in the presence of acid the following reaction occurs instantaneously (*48*):

$$[RuCl(bpy)_2(H_2O)]^+ \xrightarrow[NaNO_2]{HCl} [RuCl(NO)(bpy)_2]^{2+}$$

F. Reaction of Nitrosyl Halides

The nitrosyl halides can cause oxidative nitrosylation, as in the following examples (*49–51*):

$$[Cr(\eta\text{-}C_6H_6)(CO)_3] \xrightarrow{NOCl, THF} [CrCl_2(NO)_2(THF)_2]$$

$$[V(\eta\text{-}C_5H_5)_2] \xrightarrow{NOCl} [V(\eta\text{-}C_5H_5)_2Cl(NO)]$$

$$[RhCl_3 \cdot xH_2O] \xrightarrow[PPh_3]{NOCl} [RhCl_2(NO)(PPh_3)_2]$$

As with nitrosonium salts, 1-electron oxidation is a common side-reaction of nitrosyl halides with metal complexes, some examples of which are (*52*):

$$[Fe(CN)_6]^{4-} \xrightarrow{NOCl} [Fe(CN)_6]^{3-}$$

$$[Mo(CN)_5]^{2-} \xrightarrow{NOCl} [Mo_2(CN)_{10}]^{3-}$$

G. Nitrosyl Transfer Reactions

A number of transition metal nitrosyl complexes are capable of transferring a nitrosyl group to another metal center. For example (*53–55*),

$$[VH(CO)_4(dppe)] \xrightarrow{[\{CoCl(NO)_2\}_2]} [V(CO)_3(NO)(dppe)]$$

$$[V(\eta\text{-}C_5H_5)(CO)_4] \xrightarrow{[\{CoBr(NO)_2\}_2]} [V(\eta\text{-}C_5H_5)(CO)(NO)_2]$$

$$[Fe(NO)(diphos)_2]^+ \xrightarrow{[Co(dmgh)_2(NO)]} [Fe(NO)_2(diphos)]$$

Besides the preceding examples, the dinitrosyl complexes [$M(NO)_2(PPh_3)_2$] (M = Ru, Os) readily transfer a nitrosyl group (*56, 57*).

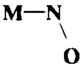
III. Characterization of Transition Metal Nitrosyl Complexes

A. INTRODUCTION

Two extreme modes of bonding are found in mononuclear nitrosyl compounds. There are many examples of complexes with a terminal, linear coordination geometry (**1**), but there are fewer examples of complexes with the bent structure (**2**), and it is very difficult to predict *a priori* the preferential geometries for the whole range of complexes. The bending of the nitrosyl ligand and the concomitant changes in electron density are of considerable importance in understanding the chemistry of nitrosyl compounds and the catalytic processes in which they are active.

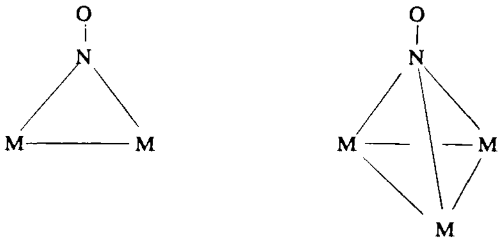
$$M—N—O$$

(1)



(2)

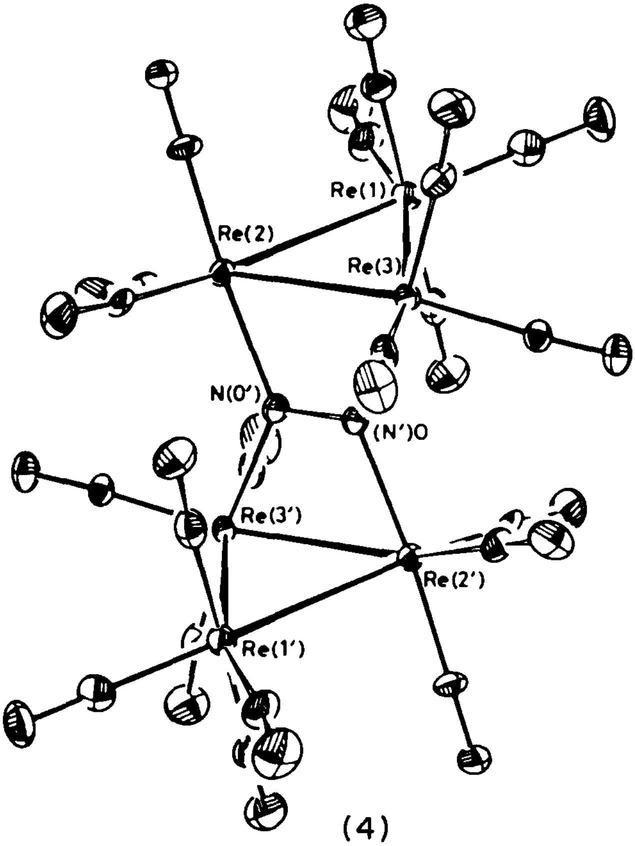
In polynuclear complexes, nitric oxide can also act as a bridging ligand between two or three metal centers, as illustrated in (**3**).



(3)

The only structurally characterized example of a M-O-N interaction, where M is a transition metal fragment, is in the polynuclear rhenium compound (**4**) (*58*).

A variety of spectroscopic and structural techniques are available for characterising transition metal compounds, and in the following sections those that have been used to determine which of the nitrosyl geometries is adopted are critically discussed.



(4)

B. VIBRATIONAL SPECTROSCOPY

The nitric oxide molecule shows one infrared stretching frequency at 1860 cm^{-1} and, on coordination to a metal center, a shift to lower frequency is observed. Typical frequency ranges for coordinated nitrosyl groups are summarized in Fig. 1 and in Table I. In many cases the ν_{NO} stretching frequency is considered diagnostic of the coordination mode of the nitrosyl ligand, but the considerable overlap indicated in the figure precludes any definitive structural formulation based on the stretching frequencies in the region 1600–1720 cm^{-1}. Indeed, stretching frequencies for linear nitrosyls occur as low as 1450 cm^{-1} for highly negatively charged complexes such as $[Mo_4S_4(NO)_4(CN)_8]^{8-}$ (*59*). Infrared spectroscopy is therefore not, in itself, a diagnostic tool, and incorrect structural assignments can be made, especially for bent nitrosyl groups. Large differences in ν_{NO} for the complexes $[MCl_2(NO)(PPh_3)_2]$

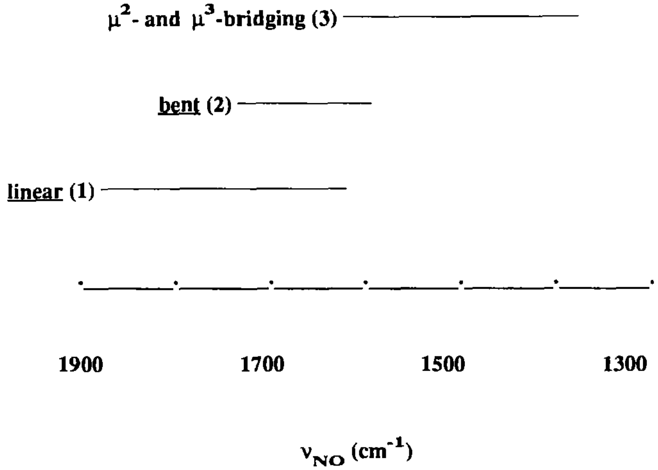


FIG. 1. The range of nitrosyl stretching frequencies observed in metal complexes.

(M = Rh, 1626 cm^{-1}; M = Ir, 1545 cm^{-1}) led to the incorrect conclusion that different solid-state structures are adopted by the two compounds (*60*). However, X-ray powder data showed the rhodium material to be isomorphous with the structurally characterized iridium complex, which in the solid state has a square-pyramidal geometry and a bent apical nitrosyl ligand (*61*).

Haymore and Ibers (*62*) have developed a series of corrections to the observed ν_{NO} stretching frequencies that take into account the position of the metal in the periodic table, the charge on the complex, the metal's coordination number, and the other ligands present. The resulting corrected ν_{NO} are more successful in predicting the nitrosyl geometry in transition metal complexes.

An area in which IR spectroscopy has been useful is in the identification of structural isomerism, both in the solid state and in solution. The complexes $[CoCl_2(NO)(PR_3)_2]$ (*63*) and $[V(\eta\text{-}C_5H_5)_2I(NO)]$ (*50*) both show two nitrosyl bands in their spectra, consistent with one isomer containing a linear nitrosyl group in equilibrium with another containing a bent ligand. In the vanadium compound, the linear nitrosyl structure would be formally a 19-electron complex and, as with $[Mo(\eta\text{-}C_5H_5)_2Me(NO)]$ (**5**) (*64*) and $[W(\eta\text{-}C_5H_5)_2(CO)_2]$ (*65*), an η^3-C_5H_5 ring is postulated. In the IR spectrum of $[Co(NCS)(NO)(dias)_2]^+$ (dias is dis(dimethylarseno)benzene), two bands are observed at 1587 and 1561 cm^{-1} (*66*); in this case these are assigned to cis and trans isomers of the complex, both of which contain bent nitrosyl ligands.

TABLE I

INFRARED DATA FOR SOME MONONUCLEAR NITROSYL COMPLEXES

	ν_{NO} (cm^{-1})	M-N-O (deg)
Linear complexes		
$[V(CN)_5(NO)]^{3-}$	1530	176[a]
$[Mn(CN)_5(NO)]^{3-}$	1700	174[b]
$[Mn(CO)_4(NO)]$	1763	180[c]
trans-$RuCl_3(NO)(PPh_3)_2$	1870	180[d]
$[Os(CO)_2(NO)(PPh_3)_2]^+$	1750	177[e]
trans-$[RhCl(NO)(P^iPr_3)_2]^+$	1842	180[f]
$[IrH(NO)(PPh_3)_3]^+$	1715	175[g]
Bent complexes		
trans-$[CoCl(NO)(en)_2]^+$	1611	119[h]
$[Co(S_2CNMe_2)_2(NO)]$	1630	135[i]
$[Rh(NO)(PPh_3)_3]$	1610	157[j]
$[IrCl(CO)(NO)(PPh_3)_2]^+$	1680	124[k]
$[IrCl_2(NO)(PPh_3)_2]$	1560	123[l]
$[NiN_3(NO)(PPh_3)_2]$	1710	153[m]
Dinitrosyl complexes		
$[Ru(NO)_2(PPh_3)_2]$	1605, 1655	175, 168[n]
$[RuCl(NO)_2(PPh_3)_2]^+$	1687, 1862	138, 178[p]
$[Os(NO)_2(PPh_3)_2]$	1615, 1665	179, 174[q]
$[Rh(NO)_2(PPh_3)_2]^+$	1714, 1759	169[r]
$[Ir(NO)_2(PPh_3)_2]^+$	1715, 1760	164[s]

[a] S. Jagner and N. G. Vannerberg, *Acta Chem. Scand.* 1968, **22,** 3330.

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[k] See ref. *183.*

[l] See ref. *61.*

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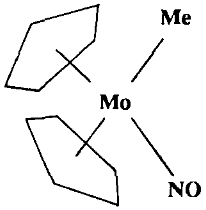
[r] J. A. Kaduk and J. A. Ibers, *Inorg. Chem.* 1975, **14,** 3070.

[s] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.* 1970, **9,** 1105.



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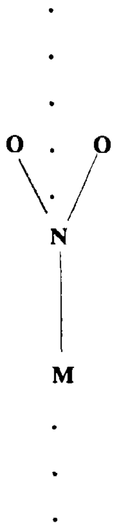
C. X-RAY CRYSTALLOGRAPHY

The most reliable method for the assignment of the coordination mode of nitric oxide in transition metal complexes in the solid state is single crystal X-ray crystallography. Crystallographic disorder can lead to characterization problems for bent nitrosyl groups. Both two-fold (**6**) and four-fold (**7**) crystallographic disorder have been observed and have led to some confusion and ambiguity about the identity of the ligands. The various positions for the oxygen atoms of the disordered ligands can usually be resolved, but the nitrogen atom positions can also be disordered (**8**), giving anomalously high mean-square vibrational amplitudes for these atoms if the disorder remains unresolved.



C_2 axis

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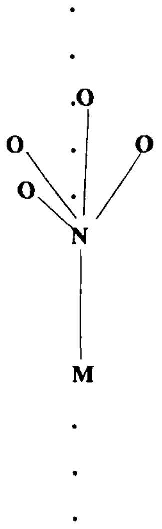

C_4 axis

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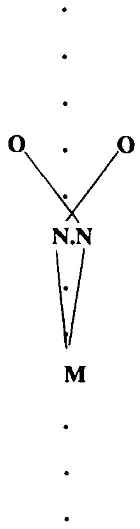
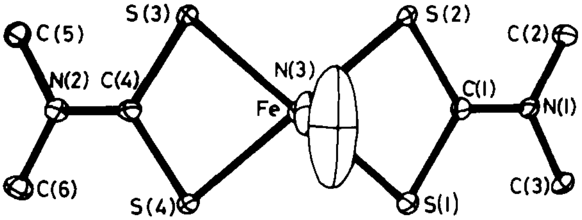


C_2 axis

(8)

This makes it impossible to define the nitrogen positions uniquely and leads to inaccurate bond lengths and angles for the coordinated nitrosyl ligand. The apparent molecular parameters reflect the way in which the crystallographic disorder has been modeled, and in a number of cases at least two models are consistent with the X-ray data. A number of 5-coordinate $[MNO]^7$ complexes with a square-pyramidal geometry and a bent apical nitrosyl group have shown these disorder problems in their crystal structure determinations, and the structure of $[Fe(S_2CNMe_2)_2(NO)]$ (**9**) illustrates the dilemma (*67*). A high vibrational amplitude along the *y*-axis of the structure led to ambiguity as to whether it contains a linear nitrosyl or a disordered ligand with an M-N-O angle of 160°. Such crystallographic problems can be overcome by the use of low-temperature techniques.



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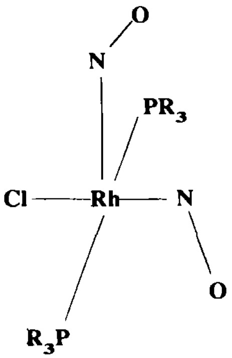
The product isolated from the reaction of $[RhCl(SO_2)(PR_3)_2]$ {R = Cy, *n*-butyl (^{n}Bu), *iso*-propyl (^{i}Pr)} with gaseous nitric oxide has proved difficult to characterize uniquely (*68*). Analytical data suggested the formulation $[RhCl(NO)_2(PR_3)_2]$ and the IR spectrum gave two stretching frequencies at 1638 and 1664 cm^{-1}, consistent with structure (**10**), which contains two bent nitrosyl groups. The crystal structures of both the tri-*n*-butylphosphine and tricyclohexylphosphine derivatives con-



(10)

firmed the square-pyramidal coordination geometry around the rhodium atom with basal phosphines, but both complexes showed considerable disorder. The apical nitrogen showed a two-fold disorder that was resolved sufficiently for assignment of this group as a bent nitrosyl ligand without ambiguity. The problems associated with the basal plane were more severe because the basal chlorine and nitrogen were 50% disordered with two oxygen atom sites around each position. Attempts to resolve the disorder by determination of the PCy_3 structure at low temperature failed to improve the situation markedly. The data were therefore ambiguous, consistent with either $[RhCl(NO)_2(PCy_3)_2]$ or $[RhCl(NO)(NO_2)(PCy_3)_2]$. The triphenylphosphine analog of the latter can be isolated from the reaction of Wilkinson's compound with nitric oxide (*69*):

$$RhCl(PPh_3)_3 \xrightarrow{NO} RhCl(NO)(NO_2)(PPh_3)_2$$

In a related problem, the crystal structure of *cis*-$[Fe(S_2CNEt_2)_2(NO)_2]$ was redetermined and the complex shown to be a nitro-nitrosyl compound (*70*).

Feltham and Enemark (*8*) have given an excellent summary of the results of X-ray crystallographic structural determinations on metal nitrosyl complexes. The following conclusions are particularly noteworthy:

1. The metal-nitrogen distances are rather short, indicating substantial multiple bond character between the nitrosyl and the metal. The average value for the N—O distance in a wide range of complexes is 1.159 Å. The M-N-O bond angles range from 180° to 109° with clustering near the values 120° and 180°.
2. The most common coordination number for mono-nitrosyl complexes is 6 and $\{M(NO)\}^n$ complexes with $n = 4, 5, 6, 7$, and 8 are known. The M-N-O group is linear (±10°) provided that $n < 6$. The range of bond angles for $\{M(NO)\}^7$ and $\{M(NO)\}^8$ is larger, but the average bond angles of 146(11)° and 126(9)°, respectively, show clearly the way in which n influences the M-N-O bond angle.
3. Comparisons of the differences in bond lengths for the cis- and trans-ligands in octahedral complexes with linear M-N-O groups with $\nu(NO) > 1800\ cm^{-1}$ have trans-M—L bonds slightly shorter (0.013–0.075 Å) than those of the cis-ligands. In contrast $[Cr(NO)(CN)_5]^{3-}$, a $\{M(NO)\}^5$ complex with $\nu(NO) = 1643\ cm^{-1}$ has a trans-M—C distance that is 0.042 Å longer than the cis-M—C distances. The 6-coordinate $\{M(NO)\}^8$ complexes (e.g., $[Co(NO)(NH_3)_5]^{2+}$) have a bent nitrosyl li-

gand and show a trans-Co—N distance 0.24 Å longer than the cis-Co—N distances.

4. The structures of mono-nitrosyl square-pyramidal complexes follow the same basic pattern as that established for octahedral complexes, with $n < 6$, having essentially linear geometries. For $n = 7$ the M-N-O bond angles vary from 127(6)° to 178(1)°. When $n = 8$, the mono-nitrosyl complexes have a strongly bent M-N-O group with the bond angles ranging from 141° to 109°.

5. $\{M(NO)\}^8$ trigonal-bipyramidal complexes have bond angles much closer to linearity and lie in the range 159°–180°. When no steric constraints are imposed, the NO group prefers the equatorial site of the trigonal bipyramid; however, with bulky ligands it is frequently observed in the axial site.

6. Four-coordinate $\{M(NO)\}^{10}$ complexes with three equivalent ligands have pseudotetrahedral coordination geometries and linear M-N-O groups (M-N-O lies between 174° and 180°). In complexes for which the symmetry deviates significantly from C_{3v}, the M-N-O bond angle may vary substantially from 180°.

D. PHOTOELECTRON SPECTROSCOPY

In X-ray photoelectron spectroscopy (XPES), the nitrogen and oxygen 1*s* binding energies can be measured, and it is found that the former correlate very well with the calculated charge on the nitrogen atom. Figure 2 illustrates the chemical-shift variation observed over a range of simple nitrogen compounds (*71–73*).

Since ν_{NO} is also affected by the electron density that is transferred to the nitrosyl group by the metal, a correlation can be expected between the nitrosyl stretching frequency and the N(1*s*) binding energy. For an isostructural series, the changes in binding energy of the N(1*s*) photoelectrons do correlate roughly with the changes in ν_{NO}, as shown in Fig. 3 (*74*).

The N(1*s*) binding energy correlates with the O(1*s*) binding energy in the spectra from a series of $[M(CN)_5(NO)]^{n-}$ complexes {M = V, Cr, Mn, Fe, and Mo} (*74*) (Fig. 4) as expected for back-donation by the metal into NO (π^*) orbitals. The N(1*s*) spectra of these compounds show two peaks: one in the region 398.3–399.0 eV, assigned to CN and a weaker band in the region 400.6–403.9 eV assigned to NO.

A number of workers have attempted to correlate the N(1*s*) binding energy with the M-N-O bond angle (*75, 76*). Generally, it is observed that bent nitrosyls have low binding energies whereas those of linear

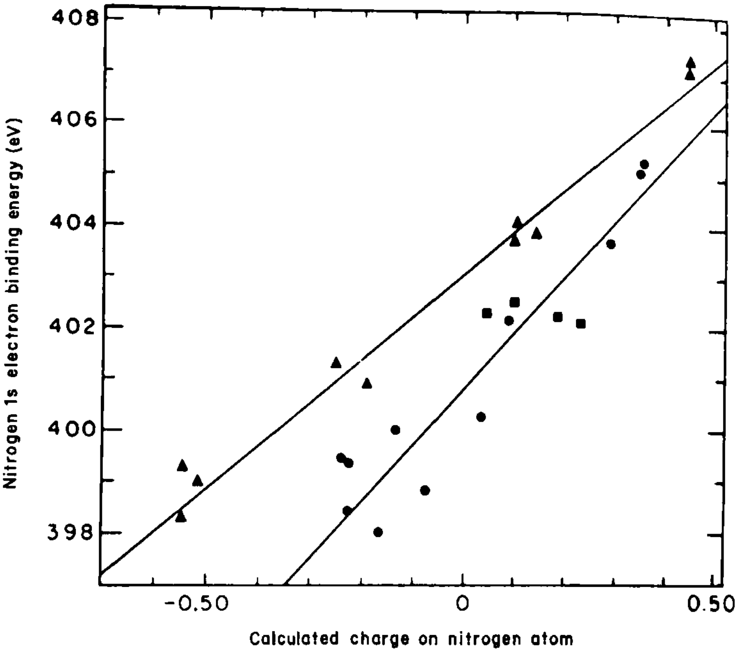


FIG. 2. Plot of nitrogen 1s binding energy versus CNDO calculated charges on nitrogen atoms: ▲, anions; ●, neutral molecules; ■, cations.

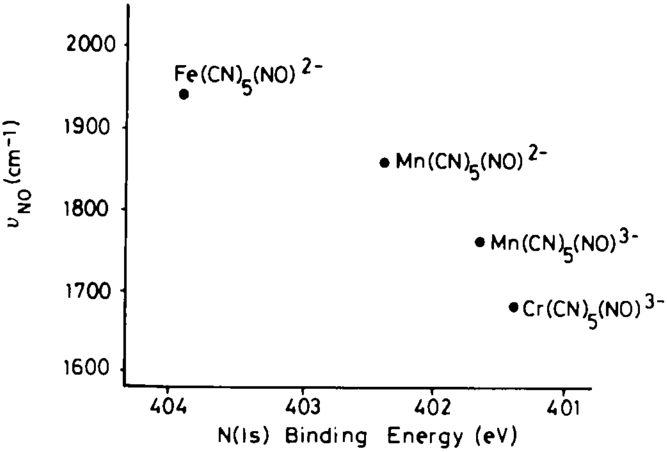


FIG. 3. Plot of nitrogen 1s binding energy versus ν_{NO} for various pentacyanonitrosyl complexes.

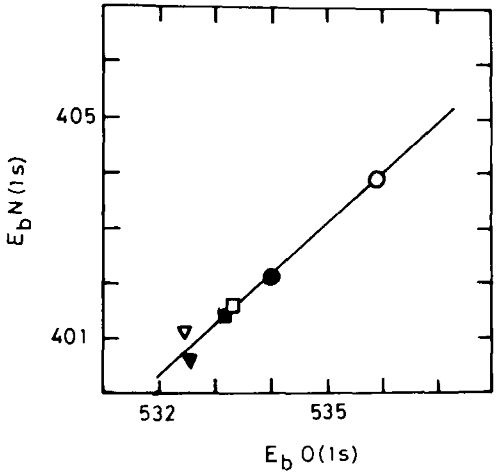


FIG. 4. The nitrogen 1*s* binding energy as a function of the oxygen 1*s* binding energy for nitrosyl complexes $[M(CN)_5NO]^{n-}$.

complexes are variable and dependent on the extent of back-bonding. However, the relative values of the O(1*s*) and N(1*s*) shifts have been found to be useful (*76*) because the effects of back-bonding from metal d_π orbitals on the individual shifts effectively cancel. The difference $\{E_bO(1s) - E_bN(1s)\}$ was found to be in the range 132 ± 1 eV for linear and 128 ± 2 eV for bent nitrosyls. The results are illustrated graphically in Fig. 5.

Jolly and other workers have attempted to define the bonding capabilities of nitric oxide and other diatomic ligands by studying XPES data. They concluded that NO was a stronger π-acceptor than CO, but the relative π-acceptor strengths of the diatomic ligands in $[Cr(\eta\text{-}C_5H_5)(CO)_2(NX)]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_2(CX)]$ {X = O or S} are still controversial (*77–79*). In comparisons of this type, it is likely that molecular properties such as electron relaxation energies differ, and the observed ionization energies are not therefore directly comparable. These correlations are based on the assumption that Koopmans' theorem is valid and that the shifts relative to the standards are reliable.

Another area in which XPES has proved effective, if used in conjunction with IR spectroscopy, is in observing more than one nitrogen site in a molecule (*72, 75, 80*). In polynitrosyl complexes such as $[RuCl(NO)_2(PPh_3)_2]^+$ two N(1*s*) bands are indeed observed; but in $[\{Cr(\eta\text{-}C_5H_5)(NO)_2\}_2]$, the difference in electron density is not sufficiently large to resolve two separate peaks for terminal and bridging nitrosyl ligands. A number of mononitrosyl complexes such as $[CoCl_2(NO)\text{-}$

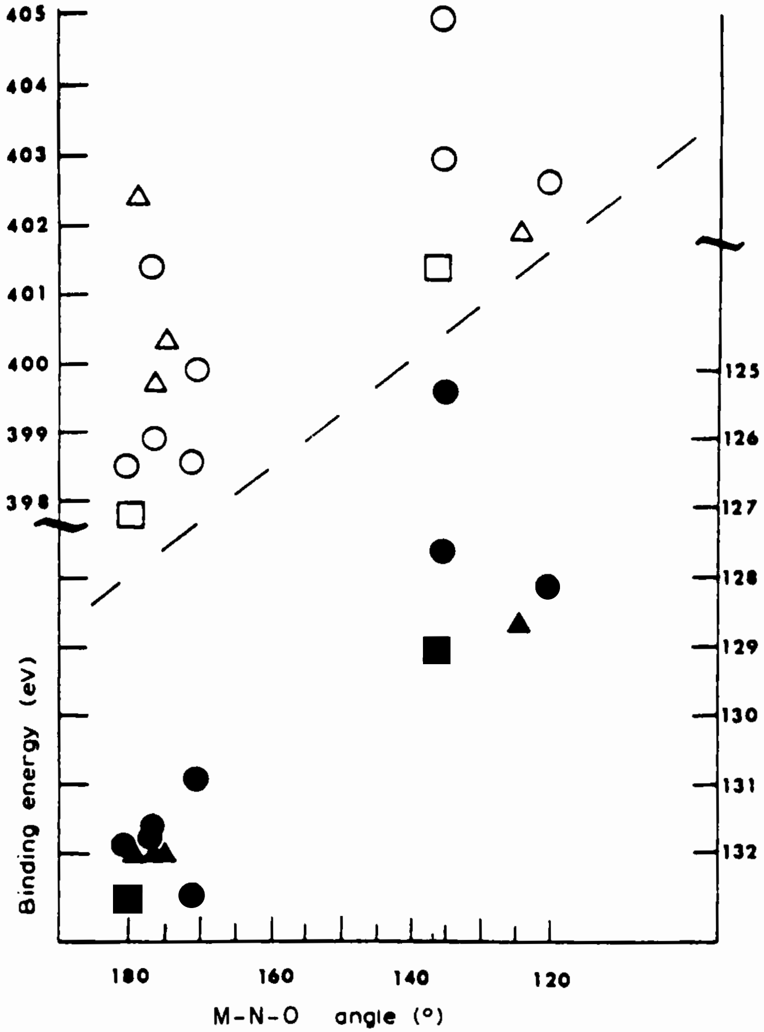


FIG. 5. Binding energy as a function of M-N-O bond angle. The left-hand ordinate and open symbols refer to N(1*s*) binding energies; the remainder refers to the difference between the O(1*s*) and N(1*s*) binding energies.

$(PR_3)_2]$ (Fig. 6) (*63*) and $[Fe(NO)(diars)_2]^{2+}$ also exhibit two N(1*s*) bands in their XPES spectra, which may be indicative of structural isomerism. In the latter case, only one ν_{NO} is observed, however, suggesting that the XPES splitting is due either to decomposition or to interactions with unpaired electrons (*81, 82*).

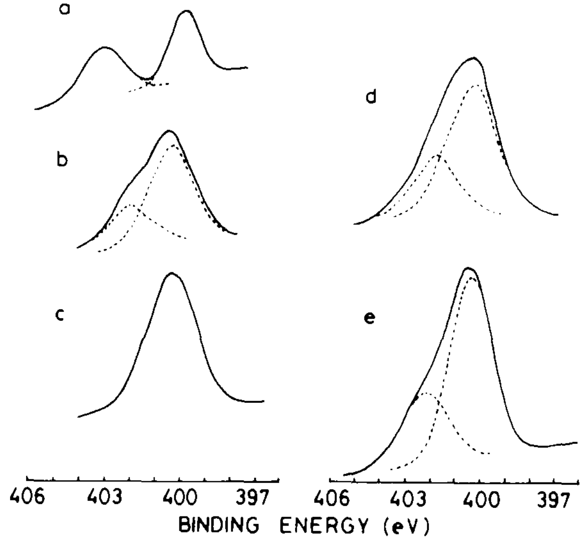


FIG. 6. N(1s) X-ray photoelectron spectra of $[CoCl_2(NO)(PR_3)_2]$. PR_3 is (a) PMe_2 and PMe_2Ph; (b) $PMePh_2$, room temperature; (c) PPh_3; (d) and (e) $PMePh_2$, low temperature.

E. MÖSSBAUER SPECTROSCOPY (*83–86*)

A number of transition metal nuclei can be studied by Mössbauer techniques (e.g., Fe, Ni, Ru, W, Os, Ir, and Pt). Of these, only ^{193}Ir, ^{99}Ru, and ^{57}Fe have been used to study nitrosyl bonding. The most detailed studies have been on the well-known iron complexes: $[Fe(CN)_5(NO)]^{n-}$ (*87, 89*) and $[Fe(NO)(dtc)_2]$ (*88–90*) (dtc is *N,N*-dialkyldithiocarbamato). In the latter, high-spin/low-spin equilibria can be followed by ^{57}Fe Mössbauer spectroscopy, and the Mössbauer parameters agree well with data from electron spin resonance (ESR) spectroscopy in determining the ground states of these complexes.

In both ^{99}Ru and ^{57}Fe spectroscopy, it is found that strong π-acceptor ligands such as CO or NO have a profound influence on the isomer shift. The more-positive value observed is indicative of a lower s-electron density at the nucleus due to an increase in shielding by the d electrons. This increase in shielding is usually caused by a greater positive charge on the metal center, consistent with the electron-withdrawing nature of the ligands. The most widely studied ruthenium nitrosyl systems are octahedral $[\{RuNO\}^6]^{3+}$ complexes, and here the isomer shift is similar to that found in Ru(III) compounds (Fig. 7) (*91–94*), though the formal oxidation state is Ru(II).

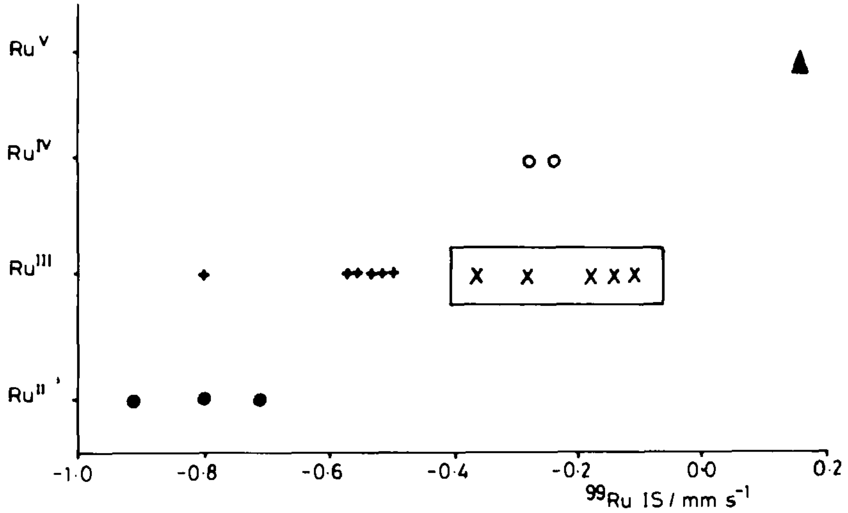
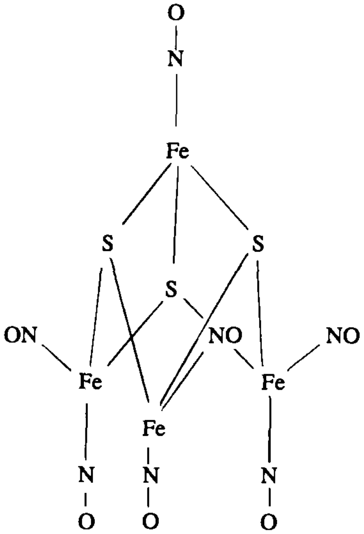


FIG. 7. Plot of ^{99}Ru Mössbauer shifts for some ruthenium nitrosyl and related complexes: ●, Ru^{II}; ▲, Ru^{V}; +, Ru^{III}; ○, Ru^{IV}; ×, Ru^{III} anomalous complexes.

Relatively few compounds have been studied with ^{193}Ir spectroscopy, but the isomer shifts of the complexes [Ir(NO)(PPh$_3$)$_2$L] {L = CO, PPh$_3$}, which formally contain Ir(-I), are very similar to those in complexes of the type [IrX(CO)(PPh$_3$)$_2$] {X = Cl, Br}, suggesting considerable electron withdrawal by the nitrosyl ligand (*95*) in the former complex.

For structural work Mössbauer spectroscopy is of limited value. No use has been made of partial isomer shift (IS) or quadrupole splitting (QS) values for distinguishing linear and bent coordination modes in nitrosyl complexes of Ir, Ru, or Fe. Nevertheless, Mössbauer spectral studies on complexes with inequivalent metal atoms are informative. For example, the family of iron-sulphur clusters containing terminal nitrosyl ligands has been studied, and in [Fe$_4$S$_3$(NO)$_7$]$^-$ (**11**), two iron sites are observed in the Mössbauer spectrum (*96*). The signal corresponding to lower *s*-electron density is assigned to the iron atoms in the equivalent equatorial sites since these have a larger quadrupolar splitting consistent with a lower site symmetry.

Mössbauer spectroscopy has proved useful in investigating the series of complexes [FeBr(NO)$_2$L] in which L is a sulphur donor ligand. A distinctly different Mössbauer isomer shift for the *o*-aminothiophenol (atp) compounds, compared with the monodentate thioester complexes (Table II), is evidence for a change from 4- to 5-coordination in the former (*97*).



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F. NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

No ^{14}N nuclear quadrupole resonance (NQR) studies have been reported for transition metal nitrosyl complexes. This technique is expected to show interesting differences between linear and bent nitrosyls since the values of the quadrupole coupling constant and the asymmetry parameter depend on the relative populations of the nitrogen s, p_x, p_y, and p_z orbitals. NQR spectroscopy has been used to study organic and inorganic nitroso compounds, and it is found that both

TABLE II

OBSERVED MÖSSBAUER ISOMER SHIFTS FOR SOME IRON COMPLEXES [$FeBr(NO)_2L$] CONTAINING THIOAMIDE OR SIMILAR LIGANDS

L	Mössbauer IS (mms^{-1})
$(H_2N)_2C{=}S$	0.51
$MeC({=}S)NH_2$	0.48
$PhC({=}S)NH_2$	0.53
atp	0.38
$FeBr(NO)_2(atp)_2$	0.38

TABLE III

NQR PARAMETERS FOR SOME NITROSO COMPOUNDS

	χ (MHz)	η	Geometry
NNO[a]	−0.27	0.0	linear
Me_2NNO[b]	−5.42	0.21	bent
CH_3NO[c]	−6.06	0.83	bent
NO_2^-[d]	−5.50	0.38	bent

[a] M. Sancho and M. D. Harmony, *J. Chem. Phys.* 1966, **45**, 1812.

[b] E. G. Sauer and T. Oja, *J. Chem. Phys.* 1973, **58**, 2710.

[c] D. Coffey, C. O. Britt, and W. E. Boggs, *J. Chem. Phys.* 1968, **49**, 591.

[d] T. Oja, R. A. Mario, and P. J. Bray, *Phys. Lett. A* 1967, **26**, 11; G. Petersen and P. J. Bray, *J. Chem. Phys.* 1976, **64**, 522.

constants are much greater for bent than for linear nitrosyls. Typical data are summarized in Table III.

^{14}N NQR studies have been made on a number of coordination complexes containing other nitrogen ligands such as *o*-aminobenzoic acid, pyridine, imidazole, cyanide, and thiocyanate (*98*). For the latter ligand it was possible to distinguish between N and S bonded ligands.

G. ELECTRON SPIN RESONANCE SPECTROSCOPY

A large number of paramagnetic transition metal nitrosyl complexes have been studied using electron spin resonance (ESR) spectroscopy. Information on the electronic ground state can be derived from the *g*-value and the hyperfine coupling constants, and many $[ML_5(NO)]^{n-}$ (see Table IV) and nitrosyl porphyrin complexes (*99*) have been studied in this way with a view to understanding their electronic structures.

Information on the nitrosyl ligand is available from $A(^{14}N)$, the ^{14}N hyperfine coupling constants, and large values are expected if unpaired electrons occupy M-N σ or $\sigma + \pi$ orbitals. In a number of 5-coordinate complexes such as [Fe(NO)(porphyrin)] (*100*) and $[Fe(NO)(dtc)_2]$ (see Table IV), couplings of the order of 12–17 G are observed, which is in agreement with the unpaired electron occupying an M-N σ^*-orbital. In many compounds the electron resides in an orbital that is nonbonding with respect to NO, in which case no hyperfine coupling to ^{14}N is expected; and Table IV shows that in a number of transition metal nitrosyl complexes, the hyperfine constants are low

TABLE IV

EXAMPLES OF ^{14}N HYPERFINE COUPLINGS IN PARAMAGNETIC TRANSITION METAL NITROSYL COMPLEXES

	Occupied orbital	A_{iso}
NO	π^*	7.0[a]
$^tBu_2NO$	π^*	15.18[b]
$[PhNO_2]^-$	π^*	13.65[c]
Six-coordinate complexes		
$[Fe(CN)_5(NO)]^{3-}$	$d_z^2 + n_N$	14.8[d]
$[Cr(CN)_5(NO)]^{3-}$	d_{xy}	5.83[e]
$[Cr(NH_3)_5(NO)]^{2+}$	d_{xy}	6.98[f]
$[Cr(H_2O)_5(NO)]^{2+}$	d_{xy}	5.83[g]
$[CrCl(NO)(diars)_2]^+$	d_{xy}	5.0[h]
$[Mn(CN)_5(NO)]^{3-}$	d_{xy}	3.80[e]
Five-coordinate complexes		
$[FeTPP(NO)]$	$d_z^2 + n_N$	17.3[i]
$[Fe(S_2CNMe_2)_2(NO)]$	$d_z^2 + n_N$	12.6[j]
$[Fe(S_2C_2Ph_2)_2(NO)]$	$d_x^2 - y^2$	Not resolved[k]

[a] B. A. Goodman, D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A* 1966, p. 1547.

[b] M. Edelstein, A. Kwok, and A. H. Maki, *J. Chem. Phys.* 1964, **41,** 179.

[c] W. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc. A* 1966, p. 448.

[d] M. D. B. Bloom, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc., A* 1971, p. 3843.

[e] P. T. Manoharan and H. B. Gray, *Inorg. Chem.* 1966, **5,** 823.

[f] P. T. Manoharan, H. A. Kuska, and M. T. Rogers, *J. Am. Chem. Soc.* 1967, **89,** 4564.

[g] B. A. Goodman, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* 1968, p. 1973.

[h] R. D. Feltham and J. H. Enemark, *Inorg. Chem.* 1965, **4,** 1332.

[i] B. B. Wayland and L. W. Olsen, *J. Am. Chem. Soc.* 1974, **96,** 6637.

[j] J. Gibson, *Nature (London)* 1962, **196,** 64.

[k] J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscomb, *J. Am. Chem. Soc.* 1967, **89,** 6082.

or even unresolvable, indicating little delocalization of spin density onto the nitrosyl group. Nonzero hyperfine coupling to ^{14}N, in cases where the coupling constant is expected to be zero, is observed and has been explained (*101*) in terms of configuration interaction between the ground state and some excited state of the complex. Alternatively (*102*), it has been suggested that the interaction is due to polarization of electrons in M—NO bonding orbitals by the unpaired electron. In addition, small deviations from axial symmetry, as observed in

$[Cr(NH_3)_5(NO)]^{2+}$ (*103*), introduce nonzero overlap between the unpaired electron and the nitrogen σ-orbitals, which also makes a contribution to the ^{14}N hyperfine coupling constant.

If spin-polarization contributions to the hyperfine couplings are ignored, the components of the ^{14}N hyperfine tensor give information on the hybridization of the nitrogen atom, but such analyses are limited by the unresolvable hyperfine couplings often found in nitrosyl complexes. A related example is the spectrum of NO_2 in crystalline potassium nitrate. The hyperfine tensor gave a value for the nitrogen ($\%2p/\%2s$) character of 2.5, suggesting slightly more p character than sp^2 for the orbitals containing the unpaired electron. Consistent with the ESR data, microwave spectroscopy suggests that the O-N-O angle is 134° (*104*). A similar analysis has been carried out on a limited number of transition metal nitrosyl compounds. In $[Fe(NO)(CN)_5]^{3-}$, the nitrogen($\%p/\%s$) character from the hyperfine coupling is 1.6, consistent with a considerably bent nitrosyl ligand (*105*), whereas $[Fe(NO)(ox)_2]^{2-}$ gives a value of 1.03, indicating sp hybridization and an essentially linear group (*106*). Interestingly, addition of $SnCl_4$ to a solution of the latter increases the nitrogen $\%p/\%s$ character to 1.47.

The ^{14}N coupling can be used to study solvent effects. In $Fe(NO)(S_2CNEt_2)_2$, the change in $A(^{14}N)$ as a function of solvent is consistent with interaction of the Lewis base with the a_1' orbital in the vacant axial coordination site.

ESR spectroscopy is a powerful tool for studying unstable radicals in solution. Reactive complexes obtained by electron capture after γ-irradiation, such as $[Cr(CN)_4(NO)]^{4-}$, $[Mn(CN)_5(NO)]^{2-}$, and $[Fe(CO)_2(NO)_2]^-$ (*107–108*), have been studied; and the product of photolysis of $[Fe(CO)_5]$ with NO(g) has been identified as $[Fe(CO)(NO)_3]$ by ESR spectroscopy coupled with $^{14}N/^{15}N$-labeling studies (*109*).

The iron compounds $[\{Fe(NO)_2X\}_2]$ {X = halide}, which are diamagnetic in the solid state, give solution ESR spectra consistent with the formation of complexes of the type $[FeBr(NO)_2(solvent)]$ (*97, 110*). Hyperfine coupling to the halide nuclei is observed: Thus, the iodide complex in tetrachloromethane gives a six-line pattern attributable to $[FeI(NO)_2(CCl_4)]$. Another application of ESR is the study of the interaction of nitric oxide with solutions of Fe(II) salts, in which the structures of the complexes formed can be inferred from the hyperfine couplings. Initial reaction gives an ESR signal only when the $pH > 4$ due to the formation of the complex $[Fe(NO)_2(OH)_2]^-$, though in ethanolic solution an intense broad signal is obtained that is attributable to $[Fe(NO)_2(H_2O)_2]^+$. Addition of bromide ion to this solution gives spectra consistent with the formation of two species: $[FeBr(NO)_2(H_2O)]$ and $[FeBr_2(NO)_2]^-$ (*111, 112*).

H. Nitrogen NMR Spectroscopy

1. *Introduction*

^{15}N NMR spectroscopy has been a particularly useful technique for defining the coordination mode of the nitrosyl ligand in both solution and the solid state (*113–116*). In this introductory section, the potential of this technique and the difficulties associated with it will be discussed. Extensive reviews have been recently published on nitrogen NMR, with a particular emphasis on its biological applications (*117–123*).

Both ^{14}N and ^{15}N have low magnetogyric ratios (Table V) and therefore, from the following relationship,

$$\text{receptivity} = \text{natural abundance} \cdot \nu^3 \cdot I(I+1) \cdot B_0^2$$

have low NMR sensitivities (i.e., about one-tenth that of ^{13}C in the case of ^{15}N). ^{15}N has the advantage over ^{14}N of having spin $\frac{1}{2}$ but suffers from very low natural abundance, negative nuclear Overhauser effect (NOE) factors, and very long relaxation times. ^{14}N has a high natural abundance but is quadrupolar, though the quadrupole moment is relatively small. Before the advent of wide-bore high-field NMR spectrometers and sensitivity enhancement techniques, most NMR studies on nitrogen were carried out on ^{14}N, though recently the availability of

TABLE V

Comparison of Nitrogen with Other NMR Active Nuclei

Nucleus	I	a (%)	Receptivity[a]	ν	Q[b]	$T_{1(\max)}$ (sec)[c]
^{2}H	1	0.015	0.0082	4.106	2.73	10
^{11}B	$\frac{3}{2}$	80.42	754	8.579	35.5	1
^{14}N	1	99.63	5.69	1.933	16.0	0.3
^{15}N	$\frac{1}{2}$	0.37	0.0219	−2.712	—	170
^{17}O	$\frac{5}{2}$	0.037	0.061	−3.626	−26.1	0.2
^{23}Na	$\frac{3}{2}$	100	525	7.076	120	0.06
^{29}Si	$\frac{1}{2}$	4.70	2.09	−5.315	—	150
^{31}P	$\frac{1}{2}$	100	377	10.83	—	55
^{51}V	$\frac{7}{2}$	99.76	2150	7.036	−52	0.05
^{95}Mo	$\frac{5}{2}$	15.72	2.88	1.743	120	0.2
^{119}Sn	$\frac{1}{2}$	8.58	25.2	−9.976	—	2.0
^{195}Pt	$\frac{1}{2}$	33.8	19.1	5.741	—	1.3

[a] Receptivity at natural abundance relative to ^{13}C.

[b] Nuclear quadrupole moment ($\times 10^3$).

[c] Higher value of observed range of T_1.

inexpensive isotopically enriched starting materials have made NMR spectra of low abundance nuclei more accessible.

2. ^{14}N NMR Spectroscopy

Although the ^{14}N quadrupole moment is relatively small, ^{14}N NMR spectroscopy is dominated by quadrupolar relaxation. The linewidths of the signals vary greatly because they depend on the nitrogen bond type and the molecular mobility. High-resolution work is possible only if the local electronic symmetry and the mobility are both high.

The electric field gradient (EFG) is small ($\chi < 1$ MHz) for linear or planar nitrogen if the ligands are of comparable electronegativity, but it dramatically increases if the nitrogen carries a lone pair. A comparison of the values for MeCN and R_3N with those for $[NO_3]^-$, MeNC, and $[R_4N]^+$ in Table VI illustrates this point.

When the lone pair becomes utilized in coordination or is delocalized into a conjugated system (e.g., in anilines and amides), the EFG decreases, and the linewidth, which is sensitive to changes in χ, also

TABLE VI

EXPERIMENTAL ^{14}N NUCLEAR QUADRUPOLE COUPLING CONSTANTS AND LINEWIDTHS AT AMBIENT TEMPERATURES

	χ^a (MHz)	$W_{1/2}{}^b$ (Hz)
MeCN (liq)	3.74	78.0
MeNC (liq)	0.27	0.26
$NaNO_3$ (H_2O)	0.745	—
Me_3N (liq)	5.20	100
$[Me_4N]I$ (D_2O)	0.0	—
pyridine-*N*-oxide (CCl_4)	1.1	28.3
NH_3 (liq)	4.08	—
$[Co(NH_3)_6]^{3+}$ (H_2O)	3.62	370
$[Fe(CN)_6]^{3-}$ (H_2O)	—	1040
$[Co(CN)_6]^{3-}$ (H_2O)	3.62	370

[a] $\chi = e^2qQ/h$ is the nuclear quadrupole coupling constant, which can be obtained from microwave, NQR, or NMR spectroscopy.

[b] $W_{1/2} = 3\chi^2(1 + \eta^2/3)\tau_q/8\pi$, where $W_{1/2}$ is the linewidth of the Lorentzian curve at half-height, τ_l is the effective rotational correlation time of the nuclear quadrupole, and $\eta = (q_x - q_y)/q_z$ is the asymmetry parameter.

decreases. A direct dependence of linewidth on viscosity is also observed for a wide range of molecules, and line-broadening can be sharply reduced by warming the sample.

3. ^{15}N NMR Spectroscopy

Working with ^{15}N presents certain problems: Low natural abundance and low sensitivity make high-resolution work difficult and time-consuming; a negative NOE presents problems with proton decoupling; and long relaxation times (Table VII) require slow pulsing with Fourier transform spectrometers. Low sensitivity can be improved markedly by isotopic labeling, but the most significant problem is often relaxation.

A number of processes contribute to ^{15}N relaxation. Intra- or intermolecular dipole–dipole interactions with ^1H nuclei are less efficient for ^{15}N than for ^{13}C due to a ν^2 dependence of the relaxation rate. Spin rotation processes, which are especially important for small molecules and ions such as ND_3, $[NO_3]^-$, and N_2, are more effective at higher temperatures. Shielding anisotropy, which is important for linear or planar nitrogen groups, such as in dinitrogen complexes, becomes more effective at higher fields, and paramagnetic impurities present in

TABLE VII

EXAMPLES OF ^{15}N SPIN–LATTICE RELAXATION TIMES AT AMBIENT TEMPERATURES[a]

	T_1 (sec)[b]	ζ_{obs}[c]
$PhNO_2$ (liq)	420	−1.6
$Ca(NO_3)_2$ (D_2O)	300	0.0
(H_2O)	180	−2.0
ND_3 (liq)	413	−0.5
NH_3 (liq)	186	−3.7
N_2 (liq, 77 K)	15	—
(liq, 126 K)	1.5	—
pyridine (liq)	85	−0.4
(liq, with 0.05-M Cr(acac)$_3$)	3.7	—
$[Co(^{13}CN)_6]^{3-}$ (D_2O)	35	—
mer-$OsCl_2(N_2)(PMe_2Ph)_3$ (THF)		
Nα	23	−1.2
Nβ	31	−0.9

[a] Note the effect of the presence of protons on the relaxation rate and observed NOE factor.

[b] Spin-lattice relaxation time in seconds.

[c] Approximate NOE factor on proton decoupling.

the solution also make a significant contribution and are often added as paramagnetic relaxation agents.

The NOE factor for ^{15}N is given by the following equation:

$$\zeta_{\mathrm{obs}} = \frac{\nu(^{1}\mathrm{H})}{2\,\nu(^{15}\mathrm{N})} \cdot \frac{T_{1(\mathrm{obs})}}{T_{1(\mathrm{dd})}}$$

The maximal value (−4.93) compares favorably with that of ^{13}C (2.99), but the negative sign means that the signal can be lost totally if the relaxation rate is only 20% by the ^{15}N-^{1}H dipolar mechanism. In addition, since higher magnetic fields can result in a reduction of the maximal NOE factor (*124*), the NOE becomes less advantageous with higher field machines. The negative NOE factor can be overcome by using reverse-gated proton decoupling (*117*).

The sensitivity of ^{15}N NMR spectroscopy can be improved by the use of low temperatures, high fields, wide-bore spectrometers, and proton decoupling (if the NOE is favorable). More dramatic enhancements can be achieved by using magnetization transfer pulse sequences, usually with proton magnetization (*125*), though transfer from ^{19}F (*126*) and ^{31}P (*127*) has also been reported. The enhancement is the product of the $\nu(\mathrm{X})/\nu(^{15}\mathrm{N})$ ratio (in which X is the heteronucleus), which is approximately 10 for $\mathrm{X} = {}^{1}\mathrm{H}$, and a factor due to the ability to pulse at a rate determined by the relaxation of X. Thus, for slowly relaxing nitrogen, the enhancement may be by a factor of the order of a hundred. In solution, cross-polarization techniques transfer magnetization by scalar couplings such as in the INEPT, SEPT, DEPT, and SINEPT pulse sequences. Such methods are increasingly being used for natural abundance work; the main disadvantage is that the resulting enhancement depends on the coupling constant between the ^{1}H and the ^{15}N nucleus. This must be known accurately and be of the order of 10 Hz (on a 250-MHz machine), or else sensitivity is reduced by relaxation during the pulse sequence, though methods that do not require the presence of NH protons are being developed (*128*).

4. Nitrogen Chemical Shifts (129)

^{14}N and ^{15}N chemical shifts are interchangeable because primary isotope effects are very small and of the order of experimental uncertainties (*130*). Figure 8 shows the range of chemical shifts exhibited by nitrogen compounds related to transition metal nitrosyl complexes. Chemical shifts in nitrogen NMR spectroscopy are dominated by the paramagnetic term, which arises from mixing of excited states with

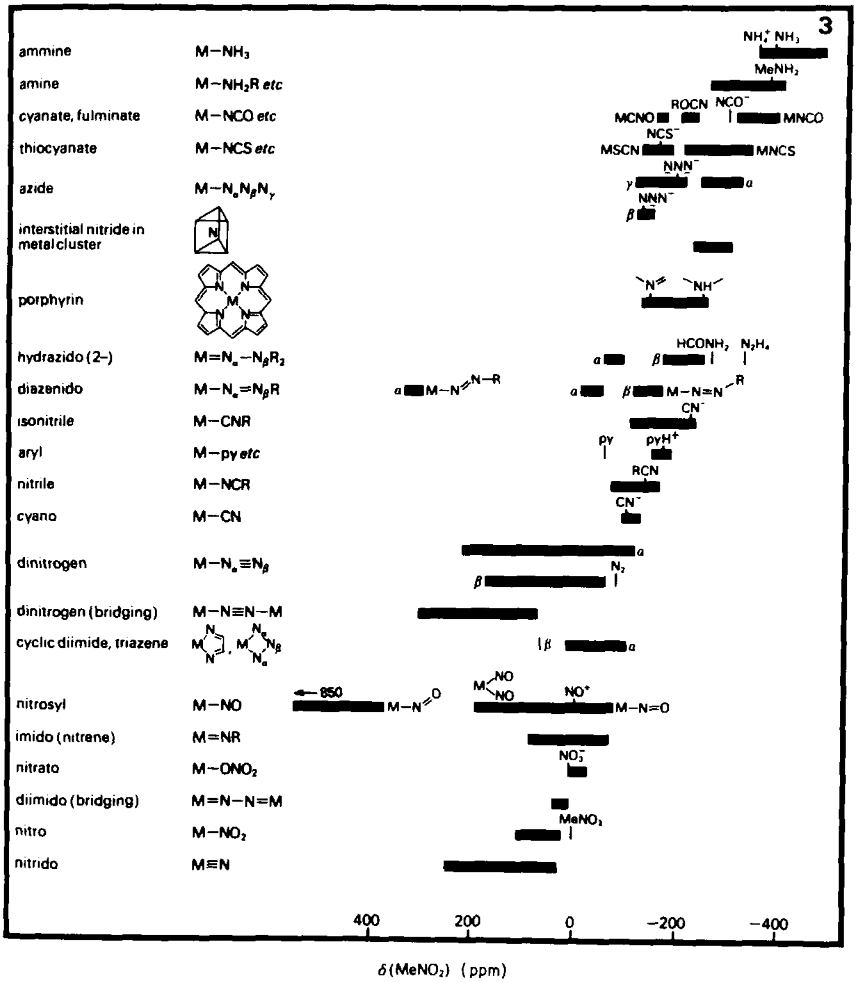


FIG. 8. Range of nitrogen chemical shifts observed for nitrosyl complexes and related compounds.

the ground state under the perturbing influence of a magnetic field. These second-order effects are mediated by the magnetic dipole operator and involve changes in the orbital angular momentum associated with the rotation of electronic charge around the nucleus. Such electron density currents interact with the magnetic dipole of the nucleus, giving rise to changes in the effective field experienced by that nucleus, which are measured as changes in the shielding. The interaction can be simplified by using a one-center approximation to the shielding tensor, which restricts terms to those centered on the nucleus in question. The resulting equation for the paramagnetic contribution to the shielding (σ^{p}) is very useful for studying trends in chemical shifts empirically in a wide range of compounds (*130*):

$$\sigma^{\mathrm{p}} = -\mu_0\mu_{\mathrm{B}}\cdot\langle r^{-3}\rangle_{np}\cdot\frac{\Sigma Q}{\Delta E}$$

(Here ΣQ represents the imbalance of the electrons in the valence p orbitals of the atom, $\langle r^{-3}\rangle_{np}$ is an average radial term, where r is the distance of the np electrons from the nucleus, and ΔE is the lowest energy transition of the allowed type or some average of the lowest lying transitions.)

As one moves across a period there is a strong correlation between the chemical-shift sensitivity of a nucleus, measured by the range of observed shifts, and the size of the respective radial factor (*131*). Thus, the nitrogen chemical-shift range is almost three times larger than that for carbon, attributable to a larger value of $\langle r^{-3}\rangle_{2p}$, though there is also a contribution due to the large asymmetries that occur when nitrogen carries a lone pair (see later).

The importance of the energy term $(\Delta E)^{-1}$ in nitrogen NMR is due to the fact that the $n_{\mathrm{N}} \rightarrow \pi^*$ electronic transitions in compounds with nitrogen lone pairs dominate the paramagnetic term. This leads to correlations between the chemical shift δ and λ, the wavelength of the $n_{\mathrm{N}} \rightarrow \pi^*$ absorption band. A notable example has been observed in alkylnitroso compounds (RNO) (*132*), in which the nitrogen shielding increases as the electronic absorption band moves to longer wavelengths (Fig. 9). Similar trends have been observed for 1,2-diazene (R_2N_2) (*133*) and diazo(RNN) (*134*) compounds. In addition, δ may correlate with the inverse of the lone-pair ionization energy (*135*) and also with the N(1*s*) binding energy from electron spectroscopy for chemical analysis (ESCA) experiments (*136*). The nitrogen deshielding increases in the following series:

imines < diazenes < nitroso compounds

The increase is due to the stabilization of the π^* lowest unoccupied molecular orbital (LUMO) relative to the n_{N}, the latter being destabilized by the presence of a lone pair on the partner atom. The correlation of low nitrogen shielding in alkylnitroso compounds with low energy $n_{\mathrm{N}} \rightarrow \pi^*$ circulations is supported by the observation of significantly increased nitrogen shielding (about 140 ppm) in organic compounds

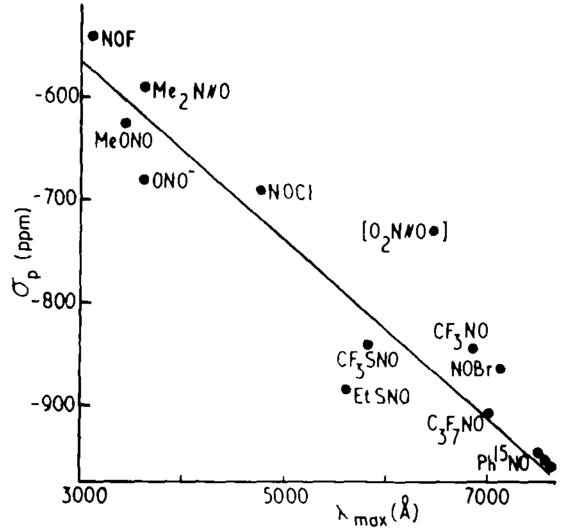


FIG. 9. Plot of σ_p versus λ for some organic nitroso compounds.

when alkyl groups on the α-carbon are replaced by fluorine or perfluoroalkyl groups (*114*).

5. *Nitrogen Spin–Spin Coupling*

^{14}N resonances are commonly too broad for resolution or accurate measurement of spin–spin coupling. Nevertheless, the nitrogen coupling constants are valuable because of their sensitivity to the presence and orientation of lone pairs on the nitrogen atom. Thus the value of $^1J(^{13}C\text{-}^{15}N)$ can be used to distinguish the geometrical isomers in oximes (*137*). Coupling constants to nitrogen atoms carrying a lone pair are expected to be small because the contribution from the Fermi contact term is opposite in sign but similar in magnitude to the term from the bonding electrons; the two thus tend to cancel. In pyridine and methylamine, $^1J(^{13}C\text{-}^{15}N)$ is calculated to be 0.6 and 2.6 Hz, respectively whereas in the pyridinium ion and formamide, the corresponding values are 12.5 and 10.7 Hz (*137*). These relationships are expected to carry over to the NMR spectra of nitrogen ligands in metal complexes: Those in which the nitrogen carries a lone pair are expected to exhibit smaller coupling constants than those containing no such lone pair.

If both coupled atoms carry a lone pair, the coupling constant between them is very sensitive to the dihedral angle between the orbitals containing the lone pairs. Model calculations have shown a strong dependence of $^1J(^{15}N\text{-}^{15}N)$ in hydrazines (NR_2NR_2) on conformation. For cis geometries the calculated coupling constant is -11 Hz whereas for the trans arrangement a large positive value is expected (*138, 139*).

6. *Application of ^{15}N NMR Spectroscopy to Nitrosysl and Related Compounds*

The sensitivity of nitrogen chemical shifts and coupling constants make ^{15}N NMR a very important tool in determining the structures of complexes containing nitrogen ligands both in solution and in the solid state. Ligands that can exhibit linear → bent isomerism at nitrogen show sizeable deshielding as the bond angle at nitrogen decreases. In diazenido complexes of Rh or Ir, with M-N-N angles of the order of 125°, N_α can be deshielded by about 350 ppm relative to similar complexes of Mo, W, or Re, in which the M-N-N angle is close to 180° (*140*). Similarly, in the bent triazene ion, $[TsN—N—NTs]^-$, the central nitrogen is deshielded by 286 ppm compared with the linear azide ion (*141*). A comparable bending, and thus deshielding, is possible in imido complexes.

The flattening of pyramidal nitrogen, concomitant with interaction of the lone pair with a delocalized system, also involves deshielding of the nitrogen atom. In complexes of the hydrazido(2-) ligand ($M—NNH_2$), the nitrogen chemical shift of the $—NH_2$ group (about −230 ppm) resembles that of an amide (e.g., −265 ppm for $HCONH_2$) rather than that of hydrazine (−320 ppm), consistent with a planar geometry for this group (*142*). On the other hand, utilization of the lone pair in protonation is known to result in increased shielding of the order of 100 ppm; for example, protonation of N_β in tungsten dinitrogen complexes increases the shielding by 135 ppm (*142*).

^{15}N NMR spectroscopy has been used extensively in the study of dinitrogen complexes, and a large body of data now exists on these compounds (*143*). It has also been used to study reactive intermediates: Attempts, so far unsuccessful, have been made to identify the unknown ion $[HN_2]^+$ in the diazotization of NH_3 with $H^{15}NO_2$ (*144*). The cyclic anion $[CN_7]^-$ and the isomers of $[HCN_7]$ formed in its protonation have been examined (*145*). Cluster compounds containing encapsulated nitrogen atoms (*146*) and mononuclear nitro complexes have also been studied (*147*) by both ^{15}N and ^{14}N NMR spectroscopy. The latter show a range of shifts from 66 to 174 ppm.

The first nitrogen NMR work for nitrosyl compounds was reported in the 1960s for ^{14}N. This work showed that linear complexes resonate at medium field; but due to the problems of quadrupolar broadening, it did not prove possible to obtain ^{14}N NMR spectra for bent nitrosyls (*148*). At that time the difficulties associated with ^{15}N NMR spectroscopy had not been overcome, and it was not until 1979 that ^{15}N NMR signals for nitrosyl ligands in transition metal complexes were observed. Legzdins and co-workers (*149*) reported the natural abundance ^{15}N NMR spectra of some linear cyclopentadienyl nitrosyl complexes of Cr, Mo, and W, which were measured on a wide-bore 180-MHz machine, but it proved impossible to measure the spectra of bent nitrosyls under similar conditions. The first low-field lines attributable to bent nitrosyl ligands were observed by Larkworthy and co-workers (*116*) with 99% ^{15}N enrichment; the ^{15}N nucleus was found to be deshielded by over 700 ppm in square-pyramidal complexes of cobalt (Table VIII). The nitrogen shieldings in these compounds are the lowest yet observed for transition metal nitrosyl compounds, and it is likely that the strong deshielding correlates with very low-energy excitations in the electronic spectrum. Indeed, [Co(NO)(salen)] is known to exhibit temperature-independent paramagnetism, which is consistent with a very small ligand field splitting (*150*).

A small number of clusters containing bridging nitrosyl ligands (*151*) have been studied by ^{15}N NMR spectroscopy, and in these compounds the nitrogen is also found to be deshielded relative to linear nitrosyl groups (see Table VIII).

^{15}N NMR spectroscopy was used to characterize the complex that was initially believed to be $[RhCl(NO)_2(PR_3)_2]$ {R = Cy, ^{i}Pr} (*113*) and discussed in Section III,C in connection with crystallographic disorder problems. The ^{15}N NMR resonances of both derivatives have very similar chemical shifts to those found for $[RhCl(NO_2)(NO)(PPh_3)_2]$ (Table VII), which demonstrates that the complexes obtained by reaction of NO(g) with $[RhCl(SO_2)(PR_3)_2]$ {R = ^{i}Pr, Cy} are correctly formulated as nitrosyl-nitro compounds.

Recently, the ^{15}N NMR spectrum of $[Fe_4S_3(NO)_7]^-$ (*11, 152*) was reported. The spectrum is shown in Fig. 10 and exhibits three signals consistent with linear nitrosyl ligands, two of which show a mutual coupling of 4.3 Hz. These have been assigned to the axial and equatorial nitrosyl ligands attached to the basal iron atoms.

In the rhodium nitrosyl complexes that have been studied to date, the $^{1}J(^{103}Rh\text{-}^{15}N)$ coupling constants decrease significantly when the NO group bends, in agreement with the theoretical considerations. In $[RhCl(NO)(PPh_3)_2]^+$, which contains a linear nitrosyl ligand, the value is 52 Hz (*116*), which is somewhat higher than expected by analogy with $^{1}J(^{103}Rh\text{-}^{13}C)$ in rhodium carbonyl complexes (*153*). For $[RhCl(CO)(NO)(PPh_3)_2]^+$, in which the nitrosyl group is bent, the observed

TABLE VIII

^{15}N NMR MEASUREMENTS ON TRANSITION METAL NITROSYL COMPOUNDS

	$\delta(^{15}N)$ (ppm)[a]	J (Hz)
$[NO]BF_4$ (SO_2)[b]	−7.5	
$[Me_2SONO]^+$ (SO_2)[b]	+612.6	
Linear nitrosyl complexes:		
$[Fe(CN)_5(NO)]^{2-}$ (H_2O)[c]	−13.5	
$[Co(CO)_3(NO)]$ ($CHCl_3$)[c]	14.0	
$[CoCl_2(NO)(PMePh_2)_2]$[n]	261.3	
$[M(\eta\text{-}C_5H_5)(CO)_2(NO)]$ ($CHCl_3$)[d]		
M = Cr	49.0	
M = Mo	37.6	
M = W	16.5	
$[RuCl_3(NO)(PMePh_2)_2]$ (CD_2Cl_2)[e]	−30.9	$^2J(^{31}P\text{-}^{15}N) = 3.8$
$[RuCl_3(NO)(PPh_3)_2]$[m]	−36.7	
$[RuCl(SO_4)(NO)(PPh_3)_2]$[m]	38.3	
$[RuCl(NO)(PPh_3)_2]$ (CH_2Cl_2)[n]	27.0	$^2J(^{31}P\text{-}^{15}N)$
$[RuCl(NO)(SO_2)(PPh_3)_2]$ (CH_2Cl_2)[n]	22.9	$^2J(^{31}P\text{-}^{15}N)$
$[RhCl(NO)(P^iPr_3)_2]^+$ (CD_2Cl_2)[e,f]	24.0	$^1J(^{103}Rh\text{-}^{15}N) = 52$
$[Rh(NO)(PPh_3)_3]^+$ (CH_2Cl_2)[n]	—	$^2J(^{31}P\text{-}^{15}N) = 12.7$ $^1J(^{103}Rh\text{-}^{15}N)$
$[Ni(NO)(PMePh_2)_3]^+$ (CH_2Cl_2)[n]	58.2	$^2J(^{31}P\text{-}^{15}N) = 11.4$
Bent nitrosyl complexes:		
$[Co(ketox)_2(NO)]$ ($CHCl_3$)[e,f]	740.3	
(DMSO)	717.3	
$[Co(salen)_2(NO)]$ (DMSO)[e,f]	736.9	
$[Co(benacen)(NO)]$ (DMSO)[e,f]	723.0	
$[RuCl(CO)(NO)(PPh_3)_2]$ (CH_2Cl_2)[n]	338.3	
$[RhCl(CO)(NO)(P^iPr_3)_2]^+$ (CD_2Cl_2)[e,f]	368.3	$^1J(^{103}Rh\text{-}^{15}N) = 4.6$
$[RhCl(NO_2)(NO)(PR_3)_2]$ (CH_2Cl_2)[e]		
R = ^{i}Pr	467.6	
	43.6	$^1J(^{103}Rh\text{-}^{15}N) = 27$
R = Cy	466.1	
	45.8	$^1J(^{103}Rh\text{-}^{15}N) = 28$
R = Ph	481.5	
	43.6	$^1J(^{103}Rh\text{-}^{15}N) = 29$
Dinitrosyl complexes		
$[M(\eta\text{-}C_5H_5)Cl(NO)_2]$[d]		
M = Cr	190.6	
M = Mo	185.4	
M = W	172.9	
$[Ru(NO)_2(PPh_3)_2]$ (CH_2Cl_2)[n]	52.5	$^1J(^{31}P\text{-}^{15}N) = 4.0$
$[Os(NO)_2(PPh_3)_2]$ (CH_2Cl_2)[n]	11.6	
$[Rh(NO)_2(PPh_3)_2]^+$ (CH_2Cl_2)[n]	81.1	$^1J(^{31}P\text{-}^{15}N) = 4.5$ $^1J(^{103}Rh\text{-}^{15}N) = 40.4$
$[Ir(NO)_2(PPh_3)_2]^+$ (CH_2Cl_2)[n]	23.8	$^1J(^{31}P\text{-}^{15}N) = 7.4$

TABLE VIII (*Continued*)

	$\delta(^{15}N)$ (ppm)[a]	J (Hz)
$[\mathrm{RuCl(NO)_2(PPh_3)_2}]^+$ ($\mathrm{CH_2Cl_2}$ 203K)[n]	130.0	$^1J(^{31}P\text{-}^{15}N) = 2.5$
$[\mathrm{OsCl(NO)_2(PPh_3)_2}]^+$ ($\mathrm{CH_2Cl_2}$)[n]	68.4	$^1J(^{31}P\text{-}^{15}N) = 2.5$
Bridging nitrosyls (shifts relative to NH_3)		
$[\mathrm{Ru_3(NO)(CO)_{10}}]^-$[g,h]	814	
$[\mathrm{Ru_3H(NO)(CO)_{10}}]$[h,i]	807	
$[\mathrm{Os_3(NO)(CO)_{10}}]^-$[g,h,j]	760	
$[\mathrm{FeRu_3(NO)(CO)_{12}}]^-$[k]	391	
$[\mathrm{Fe_4N(NO)(CO)_{11}}]$[l]	366	
$[\mathrm{FeRu_3N(NO)(CO)_{11}}]$[l]	369	

[a] Relative to neat liquid nitromethane, positive downfield, measured at 25° unless otherwise stated.

[b] G. A. Olah, B. G. B. Gupta, and S. C. Narang, *J. Am. Chem. Soc.* 1979, **101**, 5317.

[c] See ref. *148*.

[d] See ref. *149*.

[e] See ref. *113*.

[f] See ref. *116*.

[g] R. E. Stevens, T. J. Yanta, and W. L. Gladfelter, *J. Am. Chem. Soc.* 1981, **103**, 4981.

[h] See ref. *151*.

[i] B. F. G. Johnson, P. R. Raithby, and C. Zuccaro, *J.C.S. Dalton* 1980, p. 99.

[j] B. F. G. Johnson, J. Lewis, J. M. Mace, P. R. Raithby, R. E. Stevens, and W. L. Gladfelter, *Inorg. Chem.* 1984, **23**, 1600.

[k] D. E. Fjare and W. L. Gladfelter, *J. Am. Chem. Soc.* 1981, **103**, 1572; 1984, **106**, 4799.

[l] D. E. Fjare and W. L. Gladfelter, *Inorg. Chem.* 1981, **20**, 3533.

[m] D. H. Evans, Part II Thesis, Univ. of Oxford, 1983.

[n] D. J. Sherman and D. M. P. Mingos, unpublished observations.

coupling constant is only 4.6 Hz (*113*), and in the complexes $[\mathrm{RhCl(NO_2)(NO)(PR_3)_2}]$ (R = ^{i}Pr, Cy, and Ph) (*115*), which also contain a strongly bent nitrosyl ligand, the coupling is unresolved for the low-field resonance assigned to this group. In constrast, the signal for the nitro group is split into a doublet with a coupling constant of the order of 30 Hz.

Ruthenium forms a wide range of nitrosyl coordination compounds, from $\{RuNO\}^6$ complexes such as (**12**), through $\{RuNO\}^8$ (e.g., (**13–15**) (*154–157*)) to $\{RuNO\}^{10}$ complexes such as (**16**) (*158*). Therefore, it provides a good test of the variation of ^{15}N chemical shifts.

The ^{15}N NMR chemical shifts and coupling constants for compounds (**13**)–(**16**) are tabulated in Table IX; all the spectra were obtained from samples with 99% ^{15}N enrichment. The bent nitrosyl ligands resonate at high field whereas linear groups are found at medium field. It is instructive to compare the NMR data for $[\mathrm{RuCl(CO)(NO)(PPh_3)_2}]$ (**15**)

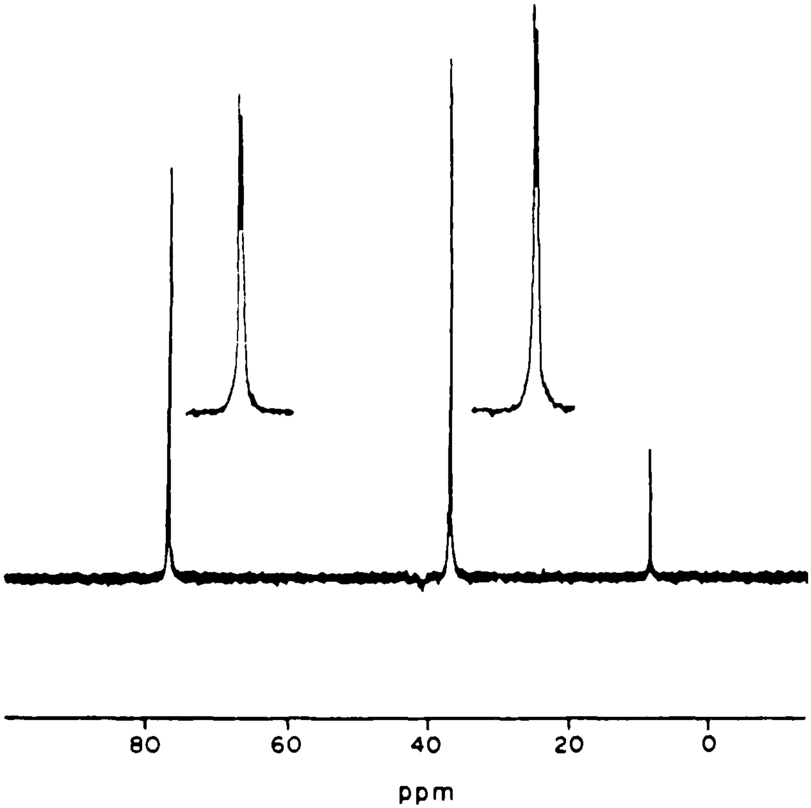
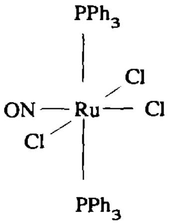
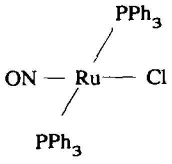


FIG. 10. Part of the ^{15}N NMR spectrum of $[Fe_4S_3(NO)_7]^-$.

with that for $[RuCl(NO)(SO_2)(PPh_3)_2]$ (14) since both complexes have been characterized by single-crystal X-ray analysis. The RuNO bond angle in the former is about 120° whereas, in the isoelectronic sulphur dioxide complex the SO_2 ligand adopts the rare η^2-coordination mode, which is also found in $[Rh(NO)(SO_2)(PPh_3)_2]$ (*159*), and the nitrosyl geometry is linear. The ^{15}N NMR data are in agreement with these crystal structure determinations, suggesting that the nitrosyl ligand, at least, retains its coordination mode in solution. In the case of (14), there is no evidence for or against the possibility that the SO_2 ligand adopts a simple terminal bonding mode in solution, as found in the solid-state structure of $[Co(NO)(SO_2)(PPh_3)_2]$ (*160*). It is interesting to speculate that ^{33}S NMR spectroscopy ($I = \frac{3}{2}$) may prove to be as useful as ^{15}N NMR has in nitrosyl chemistry in distinguishing the alternative coordination modes of the SO_2 ligand. The nitrogen–phosphorus coupling constants support the theoretical and experimental conclusions



(12)



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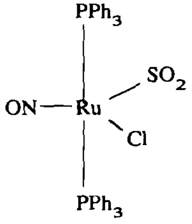

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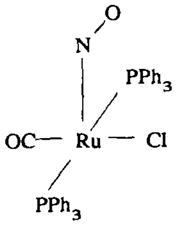

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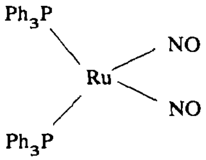


(16)

that in bent nitrosyl complexes the ^{15}N coupling to other nuclei in the molecule may be small or unresolvable whereas linear complexes exhibit $^{2}J(^{31}P{-}^{15}N)$ coupling constants of the order of 1.5–5 Hz. In the case of $[RuCl(NO)(CO)(PPh_3)_2]$ (**15**), the coupling constant must be smaller than the experimental linewidth, which is 0.7 Hz.

The only example of a $\{RuNO\}^{10}$ complex measured is the dinitrosyl $[Ru(NO)_2(PPh_3)_2]$ (**16**). The chemical shift and coupling constants for this compound agree with those expected for linear nitrosyl groups, which it has been shown experimentally to have. Not surprisingly, the

TABLE IX

^{15}N NMR DATA FOR SOME RUTHENIUM NITROSYL COMPLEXES

	$\delta(^{31}P)$/ppm	$\delta(^{15}N)$/ppm	$^{2}J(^{31}P{-}^{15}N)$/Hz
$RuCl_3(NO)(PPh_3)_2$ (**12**)[a]	—	−36.7	—
$RuCl(SO_4)(NO)(PPh_3)_2$[a]	—	38.3	—
$RuCl(NO)(PPh_3)_2$ (**13**)[b]	31.10	27.0	1.4
$RuCl(NO)(SO_2)(PPh_3)_2$ (**14**)[b]	27.23	22.9	5.4
$RuCl(NO)(CO)(PPh_3)_2$ (**15**)[b]	20.21	338.3	< 0.7
$Ru(NO)_2(PPh_3)_2$ (**16**)[b]	51.98	52.5	4.0

[a] Data from D. H. Evans, Part II Thesis, Univ. of Oxford, 1983.
[b] Data from D. J. Sherman, D.Phil. Thesis, Univ. of Oxford, 1988.

small inequivalence in the nitrosyl ligands observed in two independent crystallographic determinations (RuNO 178°, 175° and 171°, 168°) (*158, 161*) is not detected in solution and is probably caused by packing forces in the solid state.

7. *^{15}N NMR Studies of Nitrosyls in the Solid State*

The application of ^{15}N NMR spectroscopy for the unequivocal determination of nitrosyl geometry in the solid state was realized when the ^{15}N NMR spectrum of (**16**) was measured, using ^{1}H cross-polarization (CP) and magic-angle spinning (MAS) in the solid state. ^{15}N spectra of solids (usually with enrichment) have become more accessible due to methods such as ^{1}H (CP), high-power ^{1}H dipolar decoupling, and MAS; and ^{15}N solid-state NMR spectroscopy has been used with success in studies of large biomolecules such as enzymes and nucleic acids (*162, 163*). Recently, ^{15}N NMR has also emerged as a promising technique in surface studies but has so far only been used for studying organic molecules absorbed on inorganic surfaces such as silica (*164*).

Isotropic chemical shifts, obtained from solution studies, are useful indicators of the electronic environment around the nucleus, but they provide only a fraction of the available information. The shielding tensor components, which can be extracted from spinning sidebands in solid-state spectra, also contain useful information on bonding and structure, because they are sensitive to bond type. Techniques other than nitrogen NMR, such as spin-rotation (*165*) or relaxation (*166*) measurements, can be used to determine the nitrogen shielding tensor.

The CP-MAS spectra of 100% ^{15}N-labeled [$Ru(NO)_2(PPh_3)_2$] (**16**) are shown in Figs. 11 and 12. The first spectrum contains the spinning

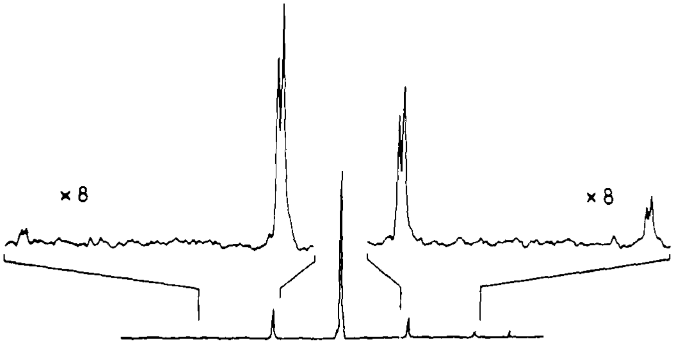


FIG. 11. CP-MAS ^{15}NMR solid-state NMR spectrum of [$Ru(NO)_2(PPh_3)_2$].

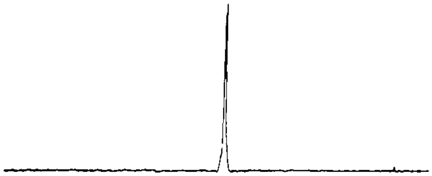


FIG. 12. CP-MAS ^{15}N NMR solid-state NMR spectrum of $[Ru(NO)_2(PPh_3)_2]$ with TOSS.

sidebands from which the components of the shift-tensor can be derived, and these are given in Table X (*167*). Two observations may be noted from this data. The shielding tensors for both nitrosyl ligands are axially symmetric since $\sigma_{22} = \sigma_{33}$, as is found in the solid-state ^{13}C NMR spectra of mononuclear metal carbonyl complexes (Table XI). Also, σ_{11} should be approximately constant for axially symmetric environments, as noted in Table XI and found in the shielding tensors of some small linear molecules containing nitrogen (Table XII). The second spectrum has had the sidebands totally suppressed (*168*) to identify the isotropic signals, which are at 40.0 and 37.0 ppm. These and the shift tensors are consistent with the presence of two linear nitrosyl ligands in slightly different environments, as observed in the crystal structure. The mean of the isotropic shifts, 38.5 ppm, is shifted by about 14 ppm (increased shielding) relative to the shift observed in solution in benzene, which can be attributed to solvation effects and is

TABLE X

^{15}N NMR SHIFT TENSOR COMPONENTS FOR $[Ru(NO)_2(PPh_3)_2]$ MEASURED BY CP-MAS SPECTROSCOPY[a,b]

σ_{zz} (ppm)	σ_{xx}	σ_{yy}	σ_0[c]	δ[d]	Δ[e]	$\delta^{15}N$[f]	η[g]
176	508	508	397	−221	0	37	−331
189	505	505	400	−211	0	40	−316

[a] Data from J. Mason, D. M. P. Mingos, D. J. Sherman, J. Schafer, and E. O. Stejskal, *J.C.S. Chem. Commun.* 1985, p. 444.

[b] The tensor components σ_{ii} are in ppm (high frequency is positive). The uncertainty in line positions is 0.5 ppm, and in the tensor components it is about 2 ppm (relative) and 20 ppm (absolute). The tensor components are ordered by the inequalities $\sigma_{zz} - \sigma_0 > \sigma_{xx} - \sigma_0 > \sigma_{yy} - \sigma_0$. The shifts are relative to $(NH_4)_2SO_4$.

[c] The isotropic shift, defined by $\sigma_0 = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}/3)$.

[d] $\delta = \sigma_{zz} - \sigma_0$.

[e] The anisotropy factor, given by $\Delta = (\sigma_{yy} - \sigma_{xx})/\delta$.

[f] The chemical shift relative to $MeNO_2$(l), high-frequency positive.

[g] The anisotropy, defined by $\eta = 3\ \delta/2$.

TABLE XI

^{13}C SHIELDING TENSORS IN METAL CARBONYL COMPLEXES[a,b]

	σ_{11}[c]	σ_{22}[d]	σ_{33}[d]	η
CO	275		−131	406
$Cr(CO)_6$	255		−168	423
$Mo(CO)_6$	260		−158	417
$W(CO)_6$	256		−139	395
$Fe(CO)_5$	255		−170	425
$Fe_2(\eta\text{-}C_5H_5)_2(CO)_4$ terminal	270		−169	444
bridging	6	−124	−143	138
$Fe_3(CO)_{12}$	191	−131	−140	327
$Ru_3(CO)_{12}$	248	−134	−163	397
$Os_3(CO)_{12}$	240		−107	347
$Ir_4(CO)_{12}$	238		−92	322

[a] Values of absolute shielding obtained by referring the chemical shifts to an absolute scale derived from CO by microwave spectroscopy.

[b] Data from J. W. Gleeson and R. W. Vaughan, *J. Chem. Phys.* 1983, **78,** 5384; T. M. Duncan, J. T. Yates, and R. W. Vaughan, *J. Chem. Phys.* 1980, **73,** 975.

[c] For axial symmetry, the paramagnetic contribution to σ_{11} is zero, and so σ_{11} equals the diamagnetic contribution, which is approximately independent of chemical environment.

[d] For axial symmetry $\sigma_{22} = \sigma_{33}$.

comparable to those reported for organic molecules. (*169*) The spectra demonstrate the sensitivity of the CP-MAS technique as a probe of nitrosyl geometry in the solid state and establish ^{15}N solid-state NMR spectroscopy as an alternative to single-crystal X-ray crystallography for distinguishing bent and linear coordination modes of the nitrosyl ligand in the solid state, especially when the crystallographic study is beset by disorder problems. They also illustrate the ability of the technique to identify very similar but inequivalent nitrogen sites in the solid state. The problems associated with the technique stem from the low number of research groups that have the requisite probes for observing ^{15}N on CP-MAS machines and from the considerable acquisition times required even when cross-polarization and isotopic-labeling techniques are employed. These problems have limited our use of solid-state nitrogen NMR to a small number of nitrosyl compounds, but the utility and sensitivity of the technique for transition metal complexes has been established.

Eisenberg synthesised the complex $[RuCl(NO)_2(PPh_3)_2](BF_4)$ (**17**) in 1972 by addition of $[NO]BF_4$ to the square-planar mononitrosyl

TABLE XII

^{15}N SHIELDING TENSORS[a,b]

	σ_{11}	σ_{22}	σ_{33}	η
N_2O[c] Terminal nitrogen	349	−18	−18	367
Central nitrogen	364	−144	−144	508
MeCN[d]	346	−142	−142	488
HCN[e]	348	−215	−215	563
N_2[e]	335	−319	−319	654
$[NO_3]^-$[d]	9	−188	−214	210
Pyridine[d]	395	−168	−387	672
Nitrobenzene[d]	30	−32	−399	398

[a] All values are in ppm relative to NH_3(l).

[b] Data from P. K. Bhattacharyya and B. P. Dailey, *J. Chem. Phys.* 1975, **59,** 5820; S. Kaplan, A. Pines, R. G. Griffen, and J. S. Waugh, *Chem. Phys. Lett.* 1974, **25,** 78; R. M. Garvey and F. C. DeLucia, *J. Mol. Spectrosc.* 1974, **50,** 529; M. G. Gibby, R. G. Griffin, A. Pines, and J. S. Waugh, *Chem. Phys. Lett.* 1972, **17,** 80; D. Schweitzer and H. W. Speiss, *J. Magn. Reson.* 1974, **15,** 529; 1974, **16,** 243; S. I. Chan, M. R. Baker, and N. F. Ramsey, *Phys. Rev. A* 1964, **136,** 1224; L. M. Ishol and T. A. Scott, *J. Magn. Reson.* 1977, **27,** 23.

[c] Measured by liquid crystal methods.

[d] Measured by CP-MAS ^{15}N NMR spectroscopy.

[e] Measured by spin-rotation microwave spectroscopy in the gas phase.

$[RuCl(NO)(PPh_3)_2]$. X-ray structural analysis (*170, 171*) showed (**17**) to have a 5-coordinate square-pyramidal geometry and confirmed the presence of both linear and bent nitrosyl groups.

The solid-state spectrum of 100% ^{15}N-labeled $[RuCl(NO)_2(PPh_3)_2]BF_4$ (**17**) is shown in Figs. 13 (with) and 14 (without) total suppression of spinning sidebands (TOSS). The spectra clearly demonstrate that the complex in the solid state does contain both linear and bent nitrosyl ligands, with isotropic shifts of 26 and 303 ppm, respectively, and that the molecule is not fluxional in the solid at ambient temperatures. The spectral assignments were based on the fact that a large deshielding was expected for the bent ligand and on the very large shielding anisotropy extracted from the shielding tensor (Table XIII). This anisotropy, +832 ppm, represents a larger absolute value than the largest previously recorded for nitrogen, −603 ppm in the N_2 molecule (*172*) and 672 ppm in pyridine (*173*). The most extreme component corresponds to deshielding, by excitations of $n(N)$-π^* transitions, which are particularly strong for the low-lying $\pi^*(NO)$ orbitals.

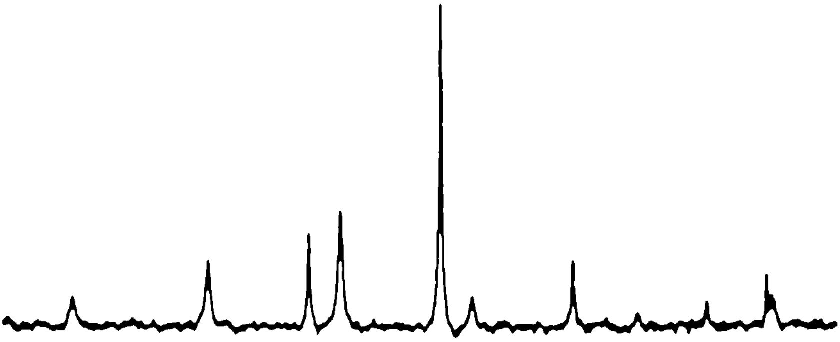


FIG. 13. CP-MAS ^{15}N solid-state NMR spectrum of $[RuCl(NO)_2(PPh_3)_2]$.

The shielding tensor for the linear nitrosyl ligand is axially symmetric with a fairly large anisotropy (−442 ppm), which is comparable to the middle nitrogen in N_2O (−508 ppm) (*174*), and similar to those observed for the linear nitrosyl ligands in $[Ru(NO)_2(PPh_3)_2]$ (**16**).

8. Dynamic Processes

The structure of (**17**) in solution is of interest because of Collman *et al*'s proposal that the nitrosyl ligands undergo a rapid intramolecular fluxional process, (**17a**) ↔ (**17b**) (*175*). The evidence for this interconversion derives from the fact that the IR spectrum of the solid product, isolated from the addition of $[^{15}NO]BF_4$ to a solution of the mononitrosyl $[RuCl(^{14}NO)(PPh_3)_2]$, showed that $^{14,15}N$ scrambling had occurred. A trigonal-bipyramidal form (**18**) was proposed as the transition state in this process though exchange between coordinated and free NO^+ is

FIG. 14. CP-MAS ^{15}N solid-state NMR spectrum of $[RuCl(NO)_2(PPh_3)_2]BF_4$ with TOSS.

TABLE XIII

^{15}N NMR SHIFT TENSOR COMPONENTS FOR $[RuCl(NO)_2(PPh_3)_2]BF_4$ MEASURED BY CP-MAS SPECTROSCOPY[a,b]

σ_{zz}	σ_{xx}	σ_{yy}	σ_0	δ	Δ	$\delta^{15}N$	η
91	533	533	386	−295	0	26	−442
1218	318	453	663	+555	0.24	303	+832

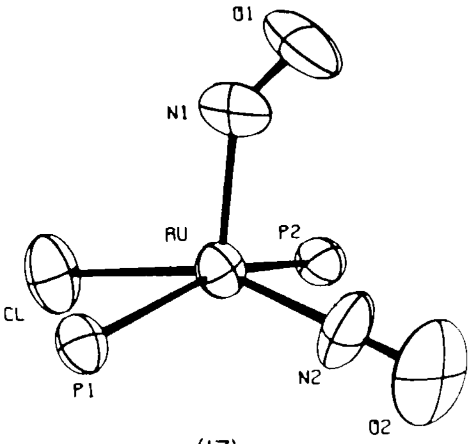
[a] Data from J. Mason *et al.*, *J.C.S. Chem. Commun.* 1985, p. 444.

[b] See Table X for definitions of terms.

an alternative mechanism. Indeed, we have found that addition of $^{15}NO^+$ to (**17**) leads to rapid incorporation of the nitrogen label into both the linear and the bent nitrosyl sites in the complex, indicating that exchange with free NO^+ is occurring at room temperature.

The ^{15}N NMR spectrum of 100% ^{15}N-labeled $[RuCl(NO)_2(PPh_3)_2]BF_4$ at room temperature consists of a triplet at about 130 ppm with $^2J(^{31}P\text{-}^{15}N) = 2.5$ Hz, indicating rapid equivalencing of the nitrosyl ligands or the presence of a symmetrical complex. On cooling a sample of (**17**) to 183 K, little line-broadening is observed, putting an upper limit for the free energy of activation for the process (**17a**) ↔ (**17b**) at 35 kJ mol^{-1}. The observation of $^{31}P\text{-}^{15}N$ scalar coupling confirms that the following dissociative process is very slow on the NMR time scale:

$$[RuCl(NO)_2(PPh_3)_2]^+ \rightleftharpoons [RuCl(NO)(PPh_3)_2] + NO^+$$



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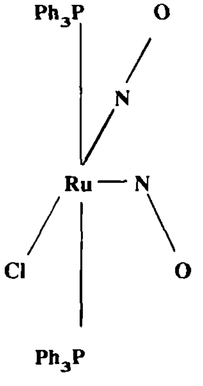

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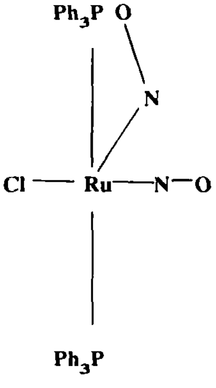
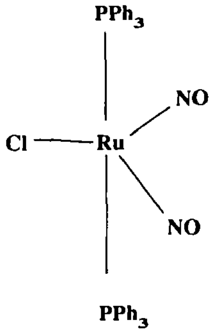


(17b)

Therefore, it cannot account for the rapid fluxional process that averages the two nitrosyl environments and leads to the isotope scrambling observed experimentally.

The chemical shift of (**17**) in solution is both solvent and temperature dependent, and its value of about 130 ppm represents an increase in shielding of 34.5 ppm compared with the average of the isotropic shifts in the solid, 164.5 ppm. For the 4-coordinate complex $[Ru(NO)_2(PPh_3)_2]$ (**16**), the change in ^{15}N chemical shift on going from the solid to benzene solution is a decrease in shielding of 14 ppm, which is comparable in magnitude and direction with known solvent effects for nitrogen. The increase in averaged shielding on dissolution of (**6**) suggests that an alternative structure such as (18), with two essentially linear nitrosyl groups, is present in the solution in measurable quantities and is not merely a transition state on the reaction coordinate between (**17a**)



(18)

and (**17b**). The two species (**17**) and (**18**) cannot be independently observed because they are in a very rapidly established equilibrium that is not frozen out by cooling to the practical limit of the machine's range.

To examine the species present in solution a faster technique was required that could also distinguish between the coordination modes of the nitrosyl ligands. Solution IR studies were the obvious choice and the FT-IR spectrum of $[RuCl(NO)_2(PPh_3)_2]^+$ showed IR bands attributed to nitrosyl ligands at 1826, 1778, 1742(sh), and 1723 cm^{-1}. The first and last bands are assigned to the linear and bent ligands in (**17**), respectively, and the other two bands can be attributed to the presence of a significant amount of the isomer (**18**).

The observation of an equilibrium isotope effect in the solution ^{15}N NMR spectrum of (**17**) has been analyzed in terms of a rapidly equilibrating system containing square-pyramidal and trigonal-bipyramidal forms of the complex. The $^{14,15}N$ equilibrium isotope effect is observable in this system because of the large differences in nitrosyl stretching frequencies and, more importantly, in the chemical shifts for the linear and bent forms of the ligand. This situation is general for dinitrosyl complexes, and in these compounds equilibrium isotope effects should be observable if equilibria of the type (**17a**) ↔ (**17b**) are occurring.

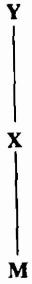
The simulation can be used to calculate the proportion of the trigonal-bipyramidal isomer (**18**) in solution at room temperature. The value obtained is 27%, comparing favorably with the impression gained from the IR spectral data.

IV. Bonding in Nitrosyl Complexes

A. INTRODUCTION

A great deal of effort has gone into determining the factors that influence the geometries of diatomic and related polyatomic molecules when coordinated to transition metal centers. A bending distortion changes the coordination mode from linear (**19**) to bent (**20**) and, further, through a kinked conformation (**21**) to side-on η^2-coordination (**22**). The process culminates in oxidative addition in which the X—Y bond is broken (**23**).

In addition to studying the more general problem of the activation of small molecules by transition metal compounds, a number of researchers have made a detailed study of the nitrosyl ligand using molecular



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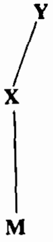

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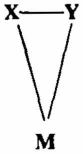

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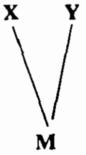


(23)

orbital techniques (*176–180*). Figure 15 illustrates the orbitals of a homonuclear diatomic ligand that are responsible for bonding to a transition metal center. These are the ($1_{\pi g}$) (π^*) and the ($3\sigma_g$) (n) orbitals. Since the π^* orbitals of these molecules are similar in energy

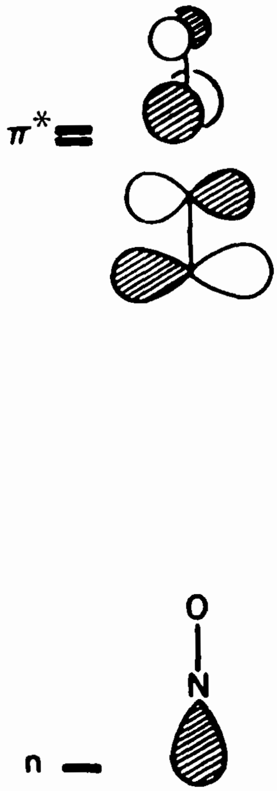


FIG. 15. The orbitals of a homonuclear diatomic responsible for bonding to transition metal fragments.

to the metal *d* orbitals, and since their mutual overlap is sizeable, any assignment of electrons in the complex to one fragment or the other is arbitrary, a situation that is especially acute for nitrosyl and dioxygen ligands. For example, the complex $[Rh(NO)(PPh_3)_3]$ can be considered formally as Rh(−I) and NO^+ or Rh(+I) and NO^-, but the extensive delocalization between the metal and nitrosyl group means that the actual electron distribution diverges significantly from both of these extreme descriptions. This dichotomy has been partially overcome by using the $\{MXY\}^n$ notation, introduced by Feltham and Enemark (*8*), in which *n* is the number of electrons on the metal and in the π^* orbitals of the diatomic ligand. This system avoids any partition of the electrons to one fragment or another. Thus, the preceding rhodium example is described as {RhNO} (*10*).

B. FIVE- AND SIX-COORDINATE COMPLEXES

Hoffmann, Mingos, and co-workers have performed extended Hückel calculations on the $\{MNO\}^8$ complexes $[Mn(NO)(CO)_4]$, $[Ir(NO)Cl_4]^{2-}$, and $[IrCl_2(NO)(PH_3)_2]$ (*179*). From the Walsh diagram shown in Fig. 16 it can be seen that the bending process (**19**) → (**20**) is governed by two interactions. As the nitrosyl bends, the $d_z{}^2$ orbital interacts favorably with $\pi_{xz}{}^*$ and decreases its antibonding interaction with the nitrogen lone pair n_N (**24**). In the course of the same bending motion, the metal d_{xz} orbital decreases its bonding interaction with $\pi_{xz}{}^*$ and increases its antibonding character with n_N (**25**).

Similar calculations on the octahedral complex $[Co(NH_3)_5(NO)]^{2+}$ result in the Walsh diagram shown in Fig. 17 (*178*), which arrives at essentially the same conclusions. Whether a nitrosyl group bends is determined by the relative slopes of these two levels. The stabilization of the $d_z{}^2$ orbital is governed by the energy of the π^* levels in the free ligand. Across the first period, the energy of these π^* orbitals in homonuclear diatomic molecules rapidly lowers, and in agreement with this, it is found that mononuclear CO and N_2 complexes are invariably linear whereas those of the strong π-acceptor O_2 are always bent or η^2. Nitric oxide, lying between these two extremes, might be expected to show intermediate coordination properties. A number of other nitrogen ligands, such as diazenido and methyleneamido, also show this linear ↔ bent isomerism, and there are also examples of bent groups in complexes of the hydrazido(2−) ligand such as $[Re(\eta\text{-}C_5H_5)(CO)_2\{N_2H(p\text{-}C_6H_4OMe)\}]$ (ReNN 138.1°) (*181*) and in mononuclear imido compounds such as $[Mo(NPh)_2(S_2CNEt_2)_2]$ (MoNC 139.4°) (*182*).

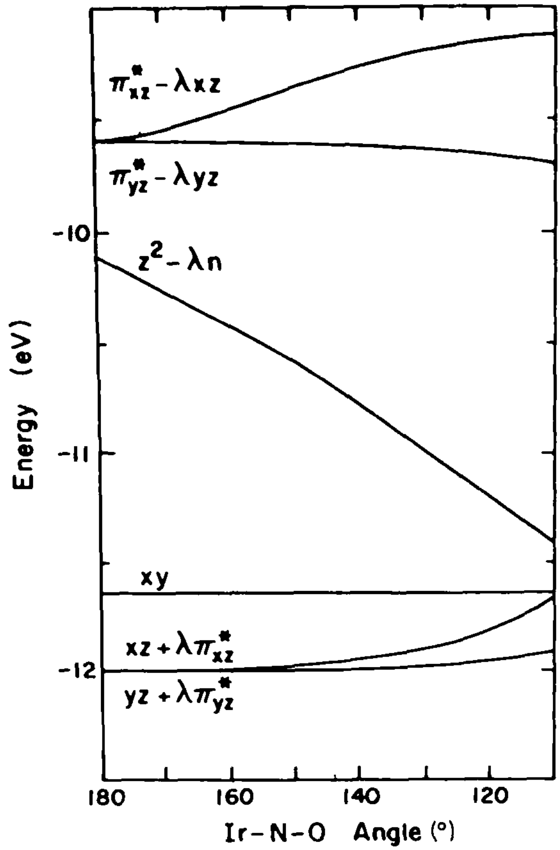
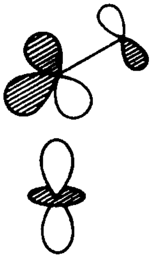


FIG. 16. Walsh diagram for the bending of the NO group in the hypothetical complex [$ML_4(NO)$].

In addition to modifying the geometry of the coordinated ligand by changing the energy of its π^* orbitals, it can be affected by changing the energy of the metal $d_z{}^2$ and d_{xz} orbitals. These are determined by the basal and apical substitution and by the position of the metal in the periodic table. Thus strong π-donors raise the energy of the metal orbitals, increasing the importance of the stabilizing interaction of $d_z{}^2$, which favors bending, while decreasing the destabilizing interaction of d_{xz}, which prevents bending. The driving force to bend is therefore enhanced. The relationship between the position of the central metal in the periodic table and the nitrosyl geometry is much harder to evaluate.

Calculations also predict that the nitrosyl group will bend in



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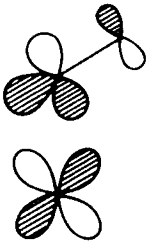

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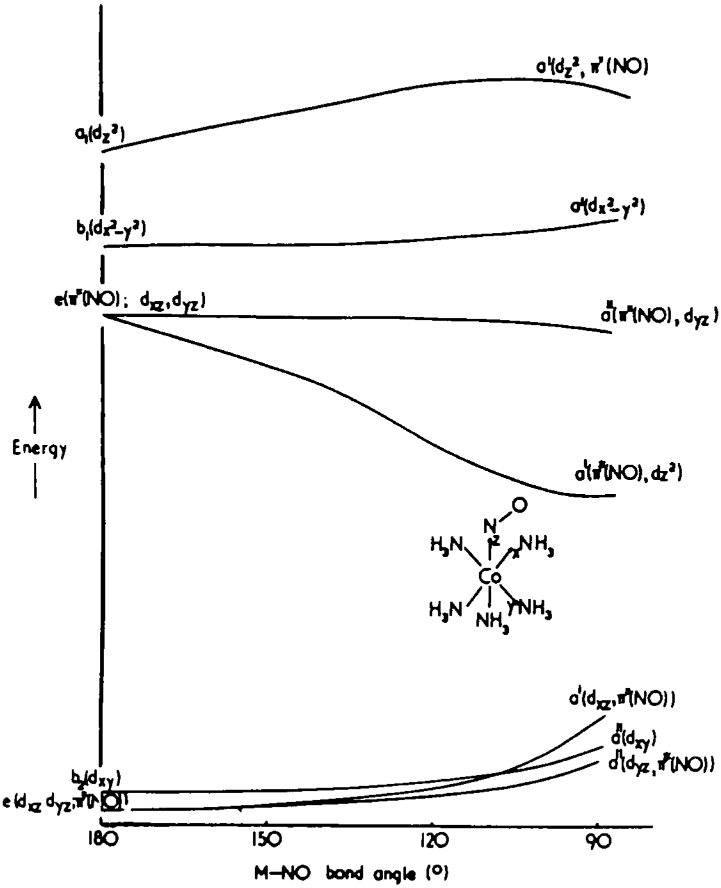
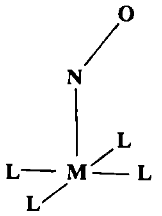


FIG. 17. Walsh diagram for bending of the nitrosyl group in $[Co(NO)(NH_3)_5]^{2+}$.

the plane containing the poorer π-donors, as observed in $[IrCl_2(NO)(PPh_3)_2]$ (*61*), and toward the acceptor ligands, as in $[IrCl(CO)(NO)(PPh_3)_2]^+$ (*183*) and $[RuCl(NO)_2(PPh_3)_2]^+$ (*170*).

The orbital ordering assumed ($\pi_{xz} > d_z{}^2$) results in an increased population of NO (π^*) and a consequent weakening of the N—O bond on bending. In addition, there is an effective transfer of electron density from the metal to the nitrosyl group. However, if z^2 lies above $\pi_{xz}{}^*$, then, though bending is still favored, the electron transfer is in the opposite direction, and the N—O bond becomes stronger.

These arguments apply to C_{4v}-$[ML_4(NO)]$ complexes and the octahedral complexes derived from them by adding a ligand L in the trans-apical coordination site. For the trigonal bipyramid with an equatorial nitrosyl ligand, Hoffmann *et al.* (*179*) found that since, for comparable ligands, the $d_z{}^2$ orbital lies at much lower energy than in the square pyramid, the driving force to bend is much lower. Similar conclusions are reached for square-pyramidal complexes with a basal nitrosyl ligand and for trigonal-bipyramidal structures with axial NO groups. Thus adoption of the trigonal-bipyramidal structure leads to a preference for a linear nitrosyl geometry. This structure is preferred for $[ML_4(NO)]$ when L are strong π-acceptor ligands, and potential energy surfaces for the interconversion of (**26**) to (**27**) have been calculated,



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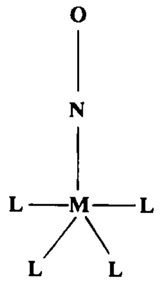

(27)

which confirms this qualitative analysis for $Mn(NO)(CO)_4$ and $[Ir(NO)Cl_4]^{2-}$ (*179*). From these calculations, a linear geometry is predicted for the former but a strongly bent nitrosyl group is expected for $[Ir(NO)Cl_4]^{2-}$.

For complexes with various values of $\{MNO\}^n$, calculations show that the bent structure would be relatively stable for $\{MNO\}^8$ or $\{MNO\}^7$ complexes, in which the z^2-derived orbital is filled or half-filled whereas the linear geometry is favored by $\{MNO\}^n$ (n = 1–6). This is borne out by the structures summarized in Table XIV.

TABLE XIV

EXPERIMENTAL M-N-O ANGLES IN SOME METAL NITROSYL COMPLEXES

Compound	n[a]	M-N-O (deg)
$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Me(NO)}]$	4	178[b]
$[\mathrm{MoTPP(MeOH)(NO)}]$	5	180[c]
$[\mathrm{Cr(CN)_5(NO)}]^{2-}$		176[d]
$[\mathrm{ReBr_4(EtOH)(NO)}]^{-}$		169[e]
$[\mathrm{Fe\{S_2C_2(CN)_2\}_2(NO)}]^{-}$	6	180[f]
$[\mathrm{Fe(CN)_5(NO)}]^{2-}$		166[g]
$[\mathrm{Cr}(\eta\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2(NO)}]$		178.7[h]
$[\mathrm{Ru(S_2CNEt_2)_3(NO)}]$		170[i]
$[\mathrm{RuCl_3(NO)(PPh_3)_2}]$		180[j]
$[\mathrm{Fe(S_2CNEt_2)_2(NO)}]$	7	152–170[k]
$[\mathrm{FeTPP(NO)}]$		149[l]
$[\mathrm{Fe(SCN)(NO)(das)_2}]^{+}$		158.6[m]
axial-$[\mathrm{IrCl(NO)(CO)(PPh_3)_2}]^{+}$	8	124[n]
$[\mathrm{CoTPP(NO)}]$		135[o]
$[\mathrm{Co(S_2CNMe_2)_2(NO)}]$		135[p]
$[\mathrm{IrH(NO)(PPh_3)_3}]^{+}$		175[q]
equatorial-$[\mathrm{Ru(NO)(diphos)_2}]^{+}$		174[r]
equatorial-$[\mathrm{Mn(NO)(CO)_4}]$		180[s]

[a] {MNO} classification.

[b] See ref. *64*.

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[g] A. H. Lanfranconi, A. J. Alvarez, and E. E. Castellano, *Acta Crystallogr., Sect. B* 1973, **B29,** 1733.

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[i] A. Domenicano, A. Vacioga, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *J.C.S. Chem. Commun.* 1966, p. 476.

[j] B. L. Haymore and J. A. Ibers, *Inorg. Chem.* 1975, **14,** 3060.

[k] See ref. *67*.

[l] W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.* 1975, **97,** 17.

[m] J. H. Enemark, R. D. Feltham, B. T. Huie, P. L. Johnson, and K. B. Swedo, *J. Am. Chem. Soc.* 1977, **99,** 3285.

TABLE XIV (*Continued*)

[n] See ref. *183*.

[o] W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.* 1973, **95**, 8281.

[p] J. H. Enemark and R. D. Feltham, *J.C.S. Dalton* 1972, p. 718.

[q] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.* 1971, **10**, 1479.

[r] G. Bombieri, E. Forsellini, R. Graziani, and G. Zotti, *Transition Met. Chem.* 1977, **2**, 264.

[s] B. A. Frenz, J. H. Enemark, and R. D. Feltham, *Inorg. Chem.* 1969, **8**, 1288.

C. THE VALENCE-BOND APPROACH

The molecular orbital methods discussed in the previous section have highlighted the electronic factors responsible for the bending of the nitrosyl ligand, but the arguments do little to help predict when such bending will occur or estimate the equilibrium concentrations of the two possible isomers (**26**) and (**27**) in solution. A valence-bond approach, coupled with the inert-gas rule, provides a simple way of estimating the relative stabilities of the linear and bent structures. The valence-bond equivalent of the stabilization of the $a_1(d_{z}{}^2 + \pi_{xz}{}^*)$ orbital is the localization of an orbital on nitrogen, which is essentially a lone pair, as shown in Fig. 18.

Using valence-bond theory, we can draw a neutral C_{4v}-[ML$_4$(NO)] complex in the canonical forms (**28**)–(**32**). The linear structures (**28**–**30**) obey the 18-electron rule, but the bent structures (**31** and **32**), due to the localization shown in Fig. 18, are formally 16-electron com-

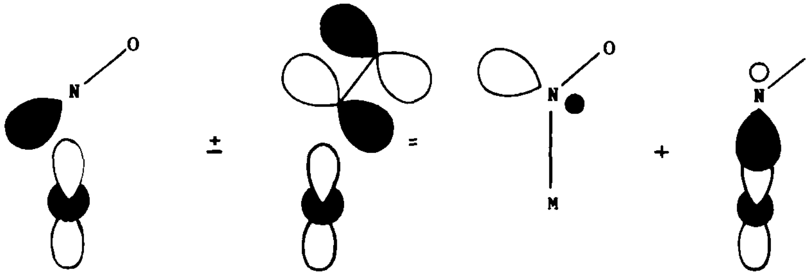
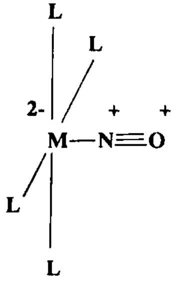


FIG. 18. Mixing of orbitals on bending of the NO ligand in the hypothetical complex [ML$_4$(NO)]. The resulting orbitals are a strongly M-N antibonding orbital and a nitrogen lone pair.



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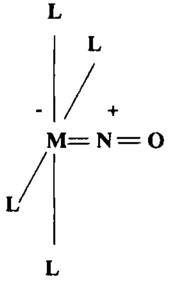

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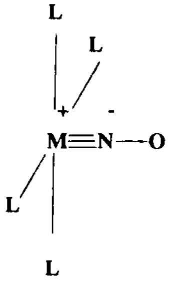

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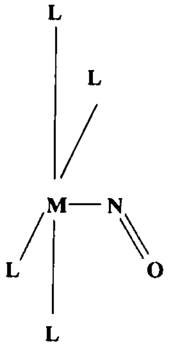

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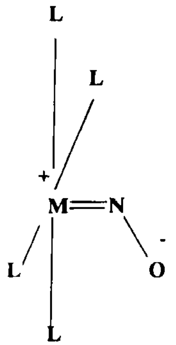


(32)

pounds. A variety of factors lead to a complex conforming to the 18-electron rule, including the promotion energy of the metal, ligand electronegativity, and metal–ligand overlap. Nevertheless, it is clear that those metals and ligands that commonly form 18-electron compounds will stabilize the canonical forms (**28–30**). In addition, the canonical forms indicate that the N—O bond order, to which the ν_{NO} stretching frequency is related, is not a function of whether the nitrosyl is bent or linear but rather a function of the metal and ligands that stabilize one particular canonical form. Thus, strong π-acceptor ligands such as CO stabilize canonical forms similar to (**28**) whereas π-donor ligands stabilize the canonical forms such as (**30**) and may even induce the nitrosyl group to bend. Table XV gives a classification of ligands according to those most likely to obey the 18-electron rule. It can be seen that the canonical forms (**31** and **32**) are stabilized only by dithiocarbamate and mixed phosphine-halide complexes such as $[Co(S_2CNMe_2)_2(NO)]$ and

TABLE XV

CLASSIFICATION OF LIGANDS ACCORDING TO THEIR LIKELIHOOD OF OBEYING THE 18-ELECTRON RULE

	Ligand Type						
Row	Carbonyls	Carbonyl phosphines	Phosphine hydrides	Arsines and phosphines	Carbonyl and phosphine halides	Phosphine halides and pseudohalides	Dithiocarbamates
First Row	$Mn(NO)(CO)_4$ $Co(NO)(CO)_3$	$Mn(NO)(CO)_2(PPh_3)_2$ $Co(NO)(CO)(PPh_3)_2$		$Co(NO)das_2^{2+}$ $Ni(NO)P^+$ $Mn(NO)_2(P\{OMe\}_2Ph)_3^+$		$CoCl_2(NO)(PMePh_2)_2$ $MnCl(NO)_2(P\{OMe\}_2Ph)_2$ $Ni(NCS)(NO)(PPh_3)_2$ $Co(NCS)(NO)das_2^+$ $FeCl(NO)_2(PPh_3)$	$Fe(NO)(S_2CNMe_2)_2$ $Co(NO)(S_2CNMe_2)_2$
			linear complexes				
Second Row			$RuH(NO)(PPh_3)_3$	$Ru(NO)dppe_2^+$ $Ru(NO)_2(PPh_3)_2$	$RuI(CO)(NO)(PPh_3)_2$ $RuCl(CO)(NO)(PPh_3)_2$	$RhBr_2(NO)(P\{OPh\}_3)_2$ $RhCl_2(NO)(PPh_3)_2$ $RuCl(NO)_2(PPh_3)_2^+$	
Third Row		$Os(NO)(CO)_2(PPh_3)_2^+$ $Ir(NO)(CO)(PPh_3)_2$	$IrH(NO)(PPh_3)_3^+$	$Ir(NO)(PPh_3)_3$ $Os(NO)_2(PPh_3)_2$ $Ir(NO)_2(PPh_3)_2^+$	$IrCl(CO)(NO)(PPh_3)_2^-$ $IrI(CO)(NO)(PPh_3)_2^-$	$IrCl_2(NO)(PPh_3)_2$	
						bent complexes	

$P = \{Ph_2PCH_2CH_2\}_3P$

TABLE XVI

EXPERIMENTAL M-N-O BOND ANGLES FOR SOME 4-COORDINATE METAL NITROSYL COMPLEXES

Complex	n[a]	M-N-O (deg)
$[Cr(N\{SiMe_3\}_2)_3(NO)]$	4	180[b]
$[\{Ru(NO)(PPh_2Me)(\mu_2\text{-}PPh_2)\}_2]$	8	174[c]
$[\{Ir(NO)(PPh_3)(\mu^2\text{-}CF_3CCCF_3)\}_2]$		157, 171[d]
$[\{IrCl(NO)(PPh_3)\}_2(\mu_2\text{-}O)]$		176[e]
$[Co(NO)(CO)_3]$	10	180[f]
$[Co(NO)(CO)_2(PPh_3)]$		178[g]
$[Rh(NO)(PPh_3)_3]$		157[h]
$[Ir(NO)(PPh_3)_3]$		180[i]
$[Ni(NCS)(NO)(PPh_3)_2]$		162[j]
$[Ni(N_3)(NO)(PPh_3)_2]$		153[k]
$[Ni(NO)(CP_3)]^+$		180[l]

[a] M-N-O classification.

[b] D. C. Bradley, M. B. Hursthouse, C. W. Newing, and A. J. Welch, *J.C.S. Chem. Commun.* 1972, p. 567.

[c] J. Reed, A. J. Schultz, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.* 1974, **13**, 3001.

[d] J. Clemens, M. Green, M.-C. Kuo, C. J. Fritchie, J. T. Magus, and F. G. A. Stone, *J.C.S. Chem. Commun.* 1967, p. 583.

[e] P.-T. Cheng and S. C. Nyburg, *Inorg. Chem.* 1975, **14**, 327.

[f] L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.* 1937, **33**, 1233.

[g] D. L. Ward, C. N. Caughlan, G. E. Voecks, and P. W. Jennings, *Acta Crystallogr., Sect. B* 1972, **B28**, 1949.

[h] J. A. Kaduk and J. A. Ibers, *Isr. J. Chem.* 1977, **15**, 143.

[i] V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc., A* 1971, p. 2420.

[j] K. J. Haller and J. H. Enemark, *Inorg. Chem.* 1978, **17**, 3552.

[k] J. H. Enemark, *Inorg. Chem.* 1971, **10**, 1952.

[l] D. Berglund and D. W. Meek, *Inorg. Chem.* 1972, **11**, 1493.

$[IrCl_2(NO)(PPh_3)_2]$. Naturally, with complicated ligand combinations it is more difficult to evaluate the total effect of the ligands, but chemists have gained a qualitative understanding of when to expect stable 16-electron complexes that can be applied readily to nitrosyl complexes.

D. FOUR-COORDINATE COMPLEXES

Similar deductions to those made above for 5- and 6-coordinate complexes can be made for 4-coordinate structures, though no calculations have been reported. Mingos (*178*) suggested that the bending process in $\{MNO\}^{10}$ complexes would be favorable for the square-planar geometry but not for the tetrahedral. Hoffmann *et al.* (*179*) felt that since the d_{z^2}, d_{xy}, $d_{x^2-y^2}$, and π^* orbitals lie at very similar energies, the orbital occupation and the behavior on bending could not be determined *a priori*.

The limited structural evidence for 4-coordinate d^{10} structures (see Table XVI) suggests that the canonical forms with a bent nitrosyl only make an appreciable contribution for $[Ni(N_3)(NO)(PPh_3)_2]$ and $[Rh(NO)(PPh_3)_3]$.

The valence-bond approach gains from its relative simplicity and comes to many of the same conclusions as the molecular orbital analysis.

V. Reactions of Transition Metal Nitrosyl Complexes

A. INTRODUCTION

In this section the reactivity of metal nitrosyl complexes is discussed and related to the NO coordination mode. A considerable difference between the chemistry of nitric oxide and carbon monoxide complexes has already been noted. The reactivity of nitric oxide coordinated to transition metal centers, and of nitrosyl clusters, were thoroughly reviewed in 1979 by McCleverty (*7*) and in 1985 by Gladfelter (*11*), respectively; therefore only a summary is presented here. Nucleophilic reactions of linear nitrosyl groups will not be considered.

The catalysis of oxidation processes by transition metal nitrosyl and nitro-complexes has aroused considerable interest, and reactions involving the transfer of oxygen atoms either to or from the nitrosyl ligands represent an important area of nitric oxide chemistry and of the nitrogen oxides generally. Another reason for studying such chemistry lies in the understanding that can be gained of the potentially important heterogeneous chemistry of nitric oxide; an aspect that will become evident in the following discussion is the number of parallels that can be drawn between heterogeneous reactions of NO gas and the chemistry of nitrosyl complexes in solution.

A range of metals and metal oxides catalyze the reduction of NO. The most successful reducing agent is synthesis gas since the catalytic process is relatively fast (*184*), unlike the catalyzed decomposition of NO to N_2 and O_2. The observed nitrogen-containing products depend on the catalytic system used: Pd- and Pt-based catalysts convert NO to NH_3 (*184*) whereas iridium and ruthenium systems minimize ammonia production and convert nitric oxide to dinitrogen.

Infrared spectroscopic studies (*185–188*) indicate that nitric oxide is adsorbed onto metal surfaces, not only as the familiar nitrosyl ligand but also as $[N_2O_2]^{2-}$ (hyponitrite) units. On metal oxide surfaces, chelating nitrite has also been detected, and such species are believed to be intermediates in oxygen-exchange reactions between $N^{18}O$ and bulk oxide in NiO or Fe_2O_3. The rate of this process is measurable under conditions (e.g., room temperature) in which gas-phase dissociation is minimal. Spectroscopic studies also suggest that nitric oxide reacts

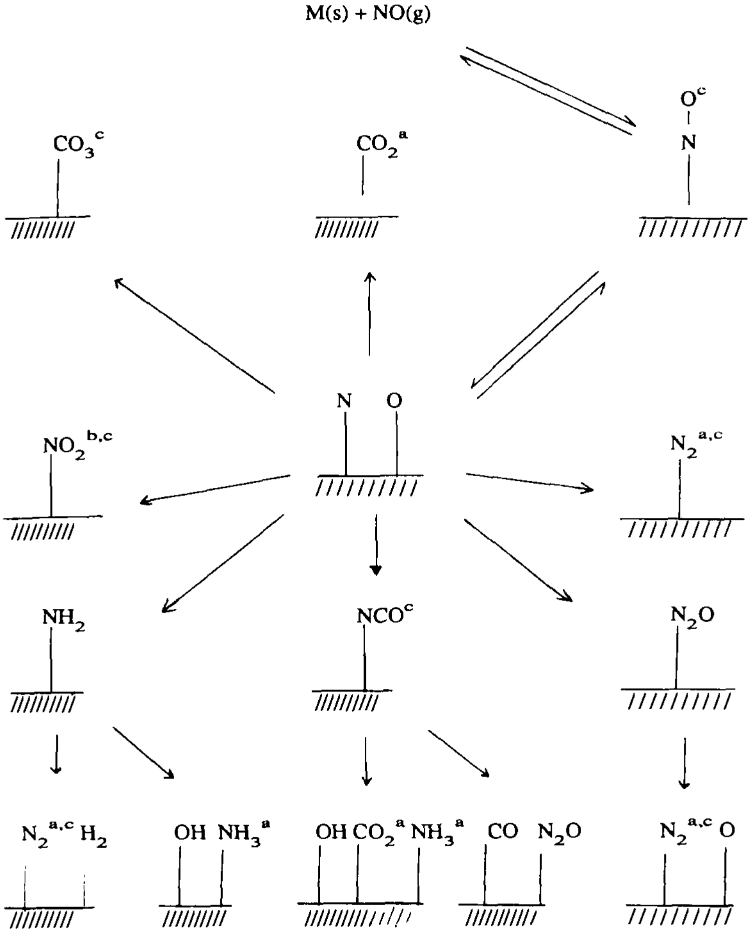


FIG. 19. Possible processes occurring on the surface of metals or metal oxides in the reduction of nitric oxide with synthesis gas, where (a) denotes products readily desorbed and observed as products, (b) denotes species believed to occur in oxide-exchange reactions, and (c) denotes intermediates observed by infrared spectroscopy.

with CO on metal surfaces to give an array of coordinated species such as isocyanate, carbonate, nitrite, nitrate, and N_2, and labeling studies have determined that the oxygen of surface isocyanate is derived from nitric oxide, not from carbon monoxide. The low proportion of N_2O found in these reactions (except with silver and gold catalysts) reflects the ability of platinum-metal compounds to decompose N_2O to oxide and N_2. The proposed reactions occurring on the surfaces of heterogeneous catalysts are summarized in Fig. 19.

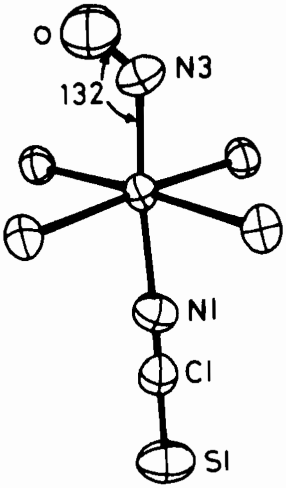
B. REACTIONS INVOLVING OXYGEN TRANSFER TO NITROSYL LIGANDS

A number of transition metal nitrosyl complexes are readily oxidized by molecular oxygen in the presence of Lewis bases to give nitro or nitrato compounds (e.g., [Co(salen)(NO)]. Kinetic studies (*189*) on this reaction suggest there is an initial rapid coordination of the base to give an intermediate such as [Co(salen)(NO)L] (**33**), which is likely to contain a strongly bent nitrosyl ligand by analogy with $[CoX(NO)(diars)_2]^+$ {X = Br, NCS} (**34**) (*190*). The bent nitrosyl complex (**33**) can then react with oxygen by an electron transfer process to give the mononuclear peroxy compound (**35**). The proposed mechanism, illustrated in Fig. 20, leads to a binuclear peroxo complex (**36**). Homolytic fission of the peroxide bond of (**36**) then yields the nitro complex. Evidence for the intermediacy of the peroxo species (**36**) comes from the reaction of [NiCl(NO)(diphos)] with O_2 on irradiation. An intermediate was detected by ESR spectroscopy consistent with a dimeric d^9 Ni(I) peroxocomplex, formulated as $[\{NiCl(diphos)\}_2\text{-}\{\mu^2\text{-}N(=O)OON(=O)\}]$ (*191*).

The complex [Co(dmgh)(NO)] would be expected to react in the same fashion as the compounds just discussed, but under comparable conditions (e.g., in the presence of Lewis bases) it gives a mixture of nitrato and nitro products (*192*). The factors that influence the proportion of nitro and nitrato products have not been established by mechanistic studies, but a possible pathway involves the isomerization of the peroxy intermediate (**35**) to the nitrato species (**37**), as indicated in Fig. 20, or by further oxidation of the nitro product. Recent studies (*193*) have shown that the nitro complex is a reactive intermediate in the formation of $[RuCl(NO_3)(bpy)_2]^+$. Tertiary phosphine complexes of the platinum metals also tend to give nitrato products (*194*):

$$[Ir(NO)_2(PPh_3)_2]^+ \longrightarrow [Ir(NO_3)(NO)(PPh_3)_2]^+$$

$$[Pt(NO_2)(NO)(PPh_3)_2] \longrightarrow [Pt(NO_2)(NO_3)(PPh_3)_2]$$



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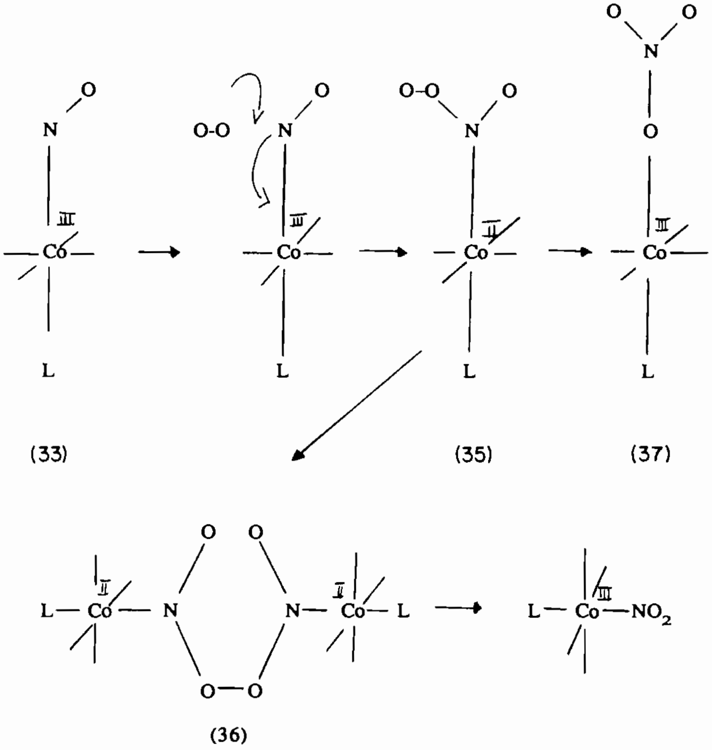


FIG. 20. The proposed mechanism for the reaction of 5-coordinate cobalt nitrosyl complexes with oxygen.

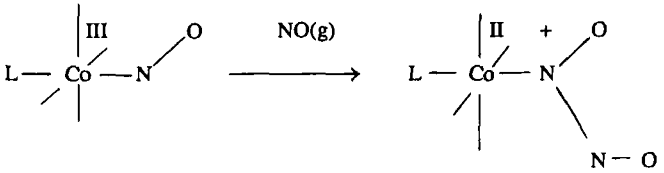
In a number of cases, other ligands such as CO are preferentially oxidized (*195, 196*):

$$[RuCl(NO)(CO)(PPh_3)_2] \longrightarrow [RuCl(NO)(O_2)(PPh_3)_2]$$

$$[OsCl(NO)(CO)(PPh_3)_2] \longrightarrow [OsCl(CO_3)(NO)(PPh_3)_2]$$

In some elegant work by Feltham, which vividly illustrates the O-atom transfer reaction, it was shown that *cis*-$[Fe(S_2CNMe_2)_2(NO_2)(NO)]$ undergoes oxygen-atom scrambling by an intramolecular attack of nitrite oxygen on the nitrosyl group (*197*). A similar process can be visualized for the deoxygenation of nitrite and nitrate ligands by carbon monoxide, which provides an important synthetic route to nitrosyl complexes. Coordinated nitrite can also transfer oxygen to phosphine (*198*) or to alkenes (*15, 199*), but a discussion of these reactions is beyond the scope of this review.

Nitrosyl complexes are also oxidized by NO gas itself, and complexes that are reactive to O_2 also undergo this reaction; thus, $[Co(dmgh)_2(NO)(MeOH)]$ reacts in the presence of pyridine to give $[Co(dmgh)_2(NO_2)py]$ (*200*). It has been suggested that the reaction occurs in a similar fashion to the first steps of oxidation with molecular oxygen, that is, via the intermediate (**38**), which can react further with free NO to give N_2O and coordinated NO_2[6].



(38)

Very little mechanistic evidence has been presented concerning this reaction; but Gans (*201*), studying the interaction of NO with Co(II) ammines, isolated the brick-red dimeric hyponitrite complex $[Co_2(NH_3)_{10}(\mu_2\text{-}N_2O_2)]^{4+}$ in low yield. Gans suggested that the reaction with NO first gave $[Co(NH_3)_5(NO)]^{2+}$, which went on to yield $[Co(N_2O_2)(NH_3)_5]^{2+}$ [see (**38**)]. This intermediate reacts further with free $[Co(NH_3)_6]^{2+}$ to give the binuclear hyponitrite product.

A variety of other complexes react with nitric oxide to give oxygen transfer products. The reaction of $[RhCl(PPh_3)_3]$ with NO, free from NO_2, gives N_2O and the nitrosyl nitro compounds $[RhCl(NO_2)(NO)(PPh_3)_2]$ (*69*), and low-valent carbonyl compounds yield an array of nitrosyl-nitrite polymers and oligomers on reaction with nitric oxide (*202*). Such species, formed as products or as intermediates in these reactions, may serve as models for the complex chemisorption observed for nitric oxide on metal surfaces.

C. REACTIONS INVOLVING OXYGEN TRANSFER FROM NITROSYL LIGANDS TO EARLY TRANSITION METALS

Although no simple nitrosyl complexes of Group IIIA and IVA metals have been structurally characterized, and only a small number of nitrosyls of Group VA metals have been isolated, a great deal of work has been reported on the reduction of small inorganic molecules, especially N_2O and NO, by organometallic complexes of early transition metals. It has become apparent that complexes of NO and N_2O with these metals are unstable with respect to disproportionation, a reaction in which the ligand acts as a source of oxygen atoms. Initial work (*203*), centering on cyclopentadienyl complexes of titanium with NO, proved inconclusive, yielding uncharacterized polymeric titanium-containing products. Subsequently, it was found that N_2O was also an efficient oxidizing agent for cyclopentadienyl titanium compounds (*204*) and yielded nonpolymeric products:

$$[\mathrm{Ti}(\eta\text{-}C_5H_5)_2(\mu_2\text{-}O)] \xrightarrow{N_2O} [\{\mathrm{Ti}(\eta\text{-}C_5H_5)\}_2(\eta^2\text{-}O)]$$

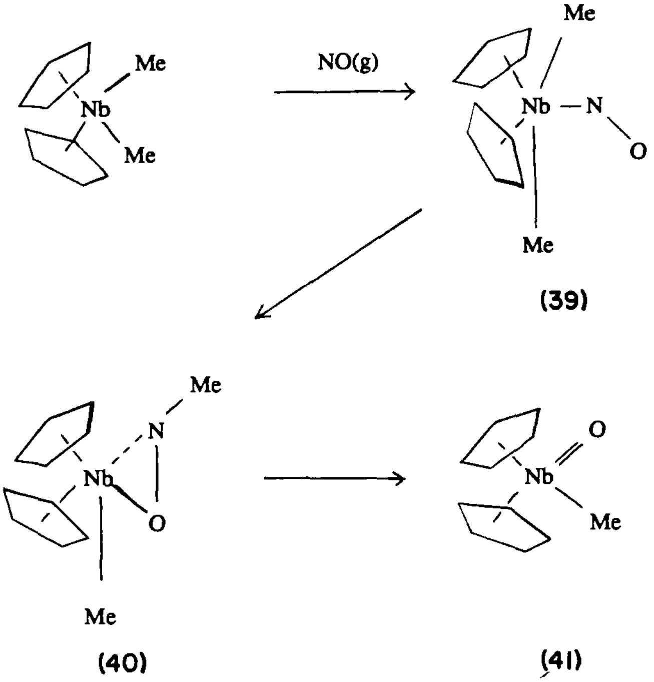
No detailed mechanistic study of these reactions has been made, and there is little evidence to support the intermediacy of nitrosyl or dinitrogen oxide complexes. Since this report, much interest has been shown in the efficient synthesis of oxide-bridged clusters and dimers of IIIA–VIA metals using nitrogen oxides as the oxidizing agents. The following reactions provide typical examples (*205–207*):

$$[\mathrm{V}(\eta\text{-}C_5H_5)_2] \xrightarrow{N_2O} [\mathrm{V}_5(\eta\text{-}C_5H_5)_5(\mu_3\text{-}O)_6]$$

$$[\mathrm{Cr}(\eta\text{-}C_5H_5)_2] \xrightarrow{N_2O} [\mathrm{Cr}_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}O)_4]$$

$$[\mathrm{Sm}(\eta\text{-}C_5Me_5)_2] \xrightarrow{NO} [\mathrm{Sm}_2(\eta\text{-}C_5Me_5)_4(\mu_2\text{-}O)]$$

In addition to the formation of bridging oxide compounds, NO reacts with paramagnetic alkyl complexes of the early transition metals to give terminal oxo complexes. Such reactions have been observed for $[\mathrm{ReOMe_4}]$ (*208*), $[\mathrm{ReMe_6}]$ (*209*), $[\mathrm{Nb}(\eta\text{-}C_5H_5)_2\mathrm{Me_2}]$ (*210*), $[\mathrm{V}(CH_2SiMe_3)_4]$ (*210*), and a number of other compounds. A possible mechanism is outlined in Fig. 21 for the reaction of $[\mathrm{Nb}(\eta\text{-}C_5H_5)_2\mathrm{Me_2}]$ with



(39)

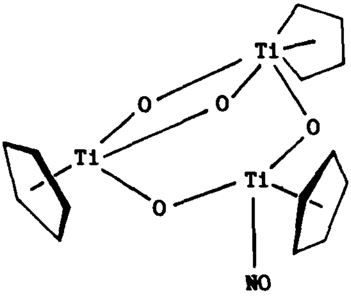
(40)

(41)

FIG. 21. Proposed mechanism for the reaction of $[Nb(\eta\text{-}C_5H_5)_2Me_2]$ with NO(g).

NO on the basis of NMR and IR spectroscopy. At low temperatures, an unstable complex with ν_{NO} at 1670 cm^{-1}, assigned to the bent nitrosyl of (**39**), was observed. By monitoring the ^1H NMR spectrum at room temperature, researchers observed a signal they assigned to the N-methyl group of (**40**), and η^2-nitrosomethane complexes have been isolated and structurally characterized (*211*). This complex then decomposes, either by a binuclear mechanism or by unimolecular elimination of methylnitrene, to give azomethane and the resulting oxocomplex (**41**).

The reaction of $[Ti(\eta\text{-}C_5H_5)_2(CH_2Ph)]$ (*210*) with nitric oxide is worth consideration at this point. In keeping with the tendency of titanium to form Ti—O—Ti rather than Ti=O bonds, the paramagnetic intermediate $[Ti_3(\eta\text{-}C_5H_5)_3O_4]$ (**42**) is postulated in both this reaction and the reaction of $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$ with CO/H_2 (*212*). In the absence of NO, the paramagnetic intermediate dimerizes to give the royal-blue cluster $[Ti_6(\eta\text{-}C_5H_5)_6(\mu\text{-}O)_8]$. In this case, the oxidizing agent may be H_2O, which is formed with CH_4 in the reaction of CO with hydrogen, since



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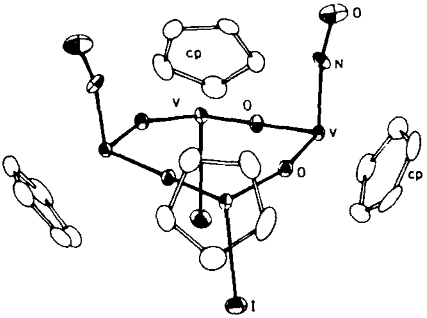


(43)

the analogous cluster is formed in the oxidation of [Ti(η-C_5Me_5)$_2$(CH_2Ph)] with water (*213*). With NO present, a compound of stoichiometry [Ti_3(η-C_5H_5)$_3$$O_4$(NO)] has been isolated and on the basis of ^1H NMR and IR spectroscopy the structure (**42**) has been proposed. A similar compound [V_4(η-C_5H_5)$_4$$I_2(NO)_2$($\mu$-O)$_4$] (**43**) has recently been synthesized by reaction of [V(η-C_5H_5)$_2$I(NO)] with wet thf (*214*). The reaction of [V(η-C_5Me_5)$_2$$Cl_2$] with NO gives both [V($\eta$-$C_5Me_5$)$OCl_2$] and [$V_4$($\eta$-$C_5Me_5$)$_4$$Cl_4$($\mu$-O)$_4$], presumably by the known dimer [V_2(η-C_5Me_5)$_2$$Cl_2$($\mu$-O)] (*215*).

D. Insertion of Nitric Oxide into Metal-Carbon Bonds

With diamagnetic alkyl complexes of the early transition metals, a very different reaction to that described in the previous section is observed. These compounds readily react with NO to give complexes of *N*-alkyl-*N*-nitrosohydroxylamine (anha) by the mechanism proposed in Fig. 22.

This reaction has been shown to be quite general and has been applied to a variety of metal alkyls, as shown by the following examples (*216–220*):

$$[\mathrm{Ti}(\eta\text{-}C_5H_5)\mathrm{Me}_3] \longrightarrow [\mathrm{Ti}(\eta\text{-}C_5H_5)\mathrm{Me}(\mathrm{anha})_2]$$

$$[\mathrm{Zr}(\eta\text{-}C_5H_5)_2\mathrm{Ph}_2] \longrightarrow [\mathrm{Zr}(\eta\text{-}C_5H_5)_2\mathrm{Ph}(\mathrm{anha})]$$

$$[\mathrm{MMe}_2\mathrm{Cl}_3] \longrightarrow [\mathrm{MCl}_3(\mathrm{anha})_2] \quad \{\mathrm{M} = \mathrm{Nb}, \mathrm{Ta}\}$$

$$[\mathrm{MMe}_6] \longrightarrow [\mathrm{MMe}_4(\mathrm{anha})_2] \quad \{\mathrm{M} = \mathrm{Mo}, \mathrm{W}\}$$

It has also been applied to cluster alkyls such as the following (*219*):

$$[\mathrm{Re}_3\mathrm{Cl}_3(\mathrm{CH}_2\mathrm{SiMe}_3)_6] \longrightarrow [\mathrm{Re}_3\mathrm{Cl}_3(\mathrm{CH}_2\mathrm{SiMe}_3)_5(\mathrm{anha})]$$

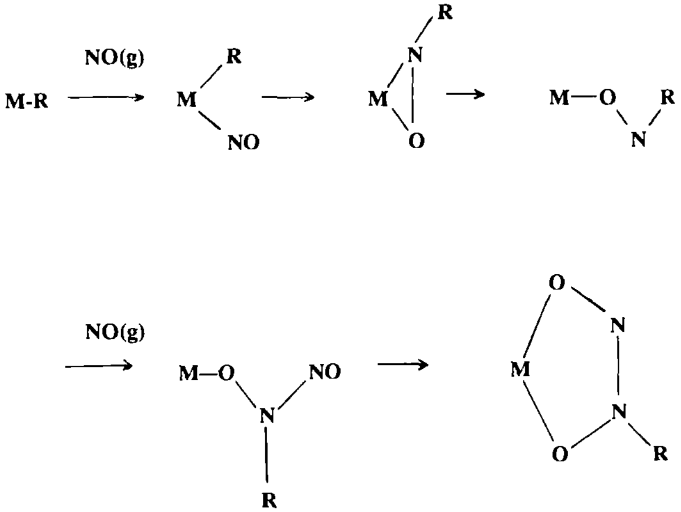


FIG. 22. Proposed mechanism for the reaction of diamagnetic metal alkyl complexes with NO(g).

In support of the mechanism in Fig. 22, complexes containing anha ligands have been synthesized by reaction of nitrosobenzene complexes with NO^+ such as *(220)*:

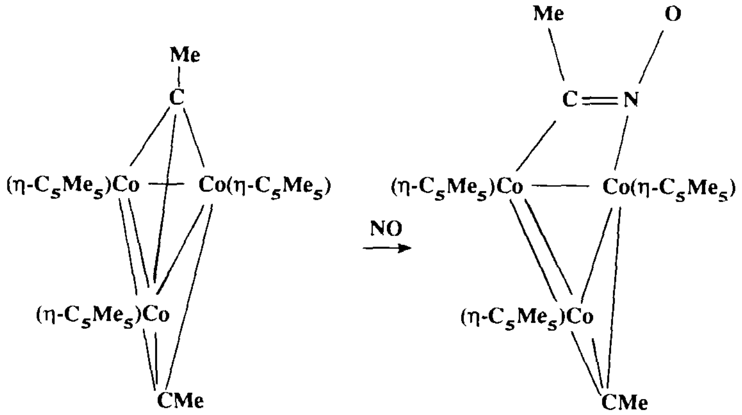
$$[Pt(PhNO)(PPh_3)_2] \xrightarrow{NO^+} [Pt(anha)(PPh_3)_2]^+$$

Such insertion reactions of NO were thought to be rare, but in recent years a number of examples have been reported. Reaction of $[Cr(\eta\text{-}C_5H_5)Me(NO)_2]$ with NO^+ gives the complex $[Cr(\eta\text{-}C_5H_5)(NO)_2\{N(OH)Me\}]$ *(221)*, whereas it does not undergo insertion when treated with other Lewis bases such as PMe_3. The reaction is probably better thought of as electrophilic attack by the incoming nitrosonium ion on the methyl group. A number of other nitrosyl alkyl complexes have been shown to undergo NO insertion on treatment with bases, such as *(222, 223)*:

$$[Co(\eta\text{-}C_5H_5)Me(NO)] \xrightarrow{Me_3P} [Co(\eta\text{-}C_5H_5)\{N(=O)Me\}PMe_3]$$

$$[Fe(\eta\text{-}C_5H_5)Me_2(NO)] \longrightarrow [Fe(\eta\text{-}C_5H_5)Me\{N(=O)Me\}PMe_3]$$

The first example of insertion of NO into a cluster metal–alkyl bond has recently been reported in compound (**44**) *(224)*.



(44)

Although the experimental evidence is scanty at present, it strongly suggests that the nitrosyl ligand is much less susceptible to insertion into metal–alkyl bonds than coordinated carbon monoxide. This assertion is supported by the processes illustrated in Fig. 23 (*225*). In this and other reactions, the electron pair is accommodated by other ligands. In [Mo(η-C_5H_5)$_2$Me(NO)] (**5**), one C_5H_5 ligand is η^3 (*64*), and no evidence of bending of the nitrosyl group or of NO insertion has been reported for this compound. For [V(η-C_5H_5)$_2$I(NO)], there is evidence for linear ↔ bent isomerism (*50*), whereas [V(η-C_5Me_5)$_2$I(NO)] appears to have only a linear NO group and displaced rings (*226*).

The reaction of [Ru(η-C_5H_5)Cl_2(NO)] with [Al(CH_2R)$_3$] leads to complexes containing C—N bonds. The products isolated in the further reaction of these with PMe_3 depend on the nature of R. When R=H,

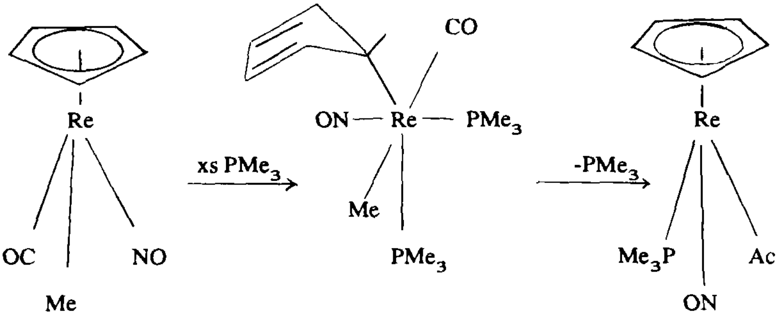
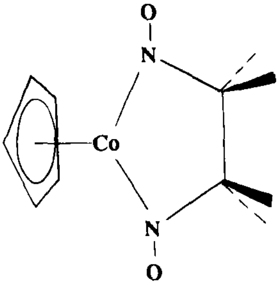


FIG. 23. The reaction of [Re(η-C_5H_5)Me(NO)(CO)] with PMe_3 resulting in insertion of the methyl into the carbonyl group.

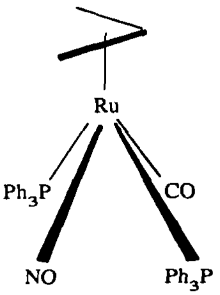
$[Ru(\eta\text{-}C_5H_5)(CN)(PMe_3)_2]$ results, but with R=Me, the product is the amidato complex $[Ru(\eta\text{-}C_5H_5)(NHCOMe)(PMe_3)_2]$ (*227*).

There are a number of interesting stoichiometric reactions of transition metal nitrosyl complexes with organic substrates to give products containing C—N bonds. Bergman *et al.* reinvestigated the reaction of the dimer $[\{Co(\eta\text{-}C_5H_5)(NO)\}_2]$ with alkenes and found that under an atmosphere of NO they gave the complexes (**45**) (*14, 228*). It would appear that cleavage of the dimer occurs with NO to give the formally 20-electron complex $[Co(\eta\text{-}C_5H_5)(NO)_2]$, though nothing is known of its structure. Subsequent attack by alkene on this complex gives the observed product. Reduction of (**45**) with lithium aluminum hydride gives high yields of the vicinal-diamino derivatives of the alkene.



(45)

A number of metal nitrosyl complexes react with activated alkyl halides to yield, ultimately, organic nitrogen-containing products. The most widely studied reagent is $[Ru(NO)_2(PPh_3)_2]$ (*229*), though other compounds such as $[CoCl(NO)(CO)_2]^-$ (*230*) and $[Fe(NO)(CO)_3]^-$ (*231*) have been used. These reactions have been discussed in depth elsewhere (*6*). Another reaction of some industrial importance is the catalytic reaction of NO gas with alkenes. Over Ag_2O or PbO the product from propene is acrylonitrile. In a study of this type of reaction (*232*),



(46)

[{NiBr(η-C_3H_5)}$_2$] was found to react with nitric oxide to give the complex [NiBr(NO)(η^4-$CH_2{=}CHCH{=}NOH$)], which liberates the organic ligand on heating or on treatment with a tertiary phosphine. An analogous reaction is observed with [Ru(η-C_5H_5)(NO)(PPh_3)$_2$] and CO (*233*). The carbonyl adduct (**46**) formed initially has been isolated and characterized spectroscopically and has been shown to liberate acrolein oxime on warming.

E. OXYGEN TRANSFER FROM NITROSYL GROUPS TO OTHER COORDINATED LIGANDS

One of the reactions of nitric oxide that has received some attention is the oxygen transfer reaction:

$$NO + CO \longrightarrow N_2O + CO_2 \qquad \Delta G^\circ = -328\ \text{kJ mol}^{-1}$$

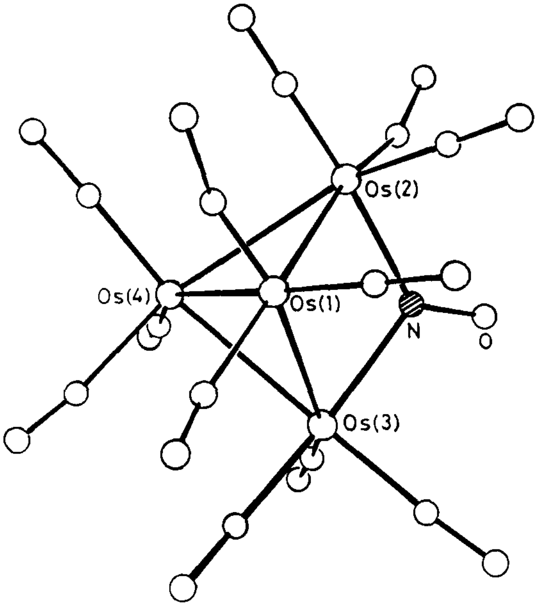
A number of platinum-metal complexes are found to catalyze this process under mild conditions, which was first studied by Johnson and Bhaduri (*234*). They showed that [Ir(NO)$_2$(PPh_3)$_2$]$^+$ reacts stoichiometrically with carbon monoxide to give [Ir(CO)$_3$(PPh_3)$_2$]$^+$ and gaseous CO_2 and N_2O. The carbonyl can in turn be reconverted to the nitrosyl complex with NO gas, thus providing a catalytic pathway. Subsequently, other complexes were shown to react similarly: for example, [IrCl(NO_2)(NO)(PPh_3)$_2$] and [Rh(NO)$_2$(PPh_3)$_2$]$^+$ (*235*). The isoelectronic Ru and Os compounds react extremely slowly under pressure or on irradiation, and the Fe and Co counterparts fail to react in this fashion at all (*236*). $RhCl_3 \cdot nH_2O$ in ethanol was also found to catalyze this conversion, and it is believed that the active catalytic species here is [$RhCl_2(CO)_2$]$^-$ (*237*). Very recent work has also shown that alkaline solutions of [$Rh_2Cl_2(CO)_4$] catalyze the CO reduction of NO and N_2O to dinitrogen (*238*).

A mechanism for the oxygen-transfer reaction involving nitrido intermediates has been propounded, and such complexes have been suggested as intermediates in a number of other reactions of metal nitrosyl and related compounds. Thus, when [Ir(CO)(NO)(PPh_3)$_2$] is photolyzed in the presence of PPh_3 (*239*), or when azido complexes react with carbon monoxide (*240*), isocyanate compounds are isolated. They are probably formed by oxygen abstraction by CO or PR_3, followed by insertion into a metal–CO bond by the resultant nitrido ligand; such reactions are also believed to play an important part in the heterogeneous chemistry of NO-CO mixtures (see Fig. 19). Interestingly, isocyanate compounds have been reported as products in the reaction of [$\mathrm{Pt(NO_2)(NO)(PPh_3)_2}$] with CO (*241*) and of [$\mathrm{V(\eta\text{-}C_5H_5)_2CO}$] with NO (*242*). Conversion of a coordinated nitrosyl group to a nitrido ligand is a well-known reaction in transition metal cluster chemistry (*243–245*):

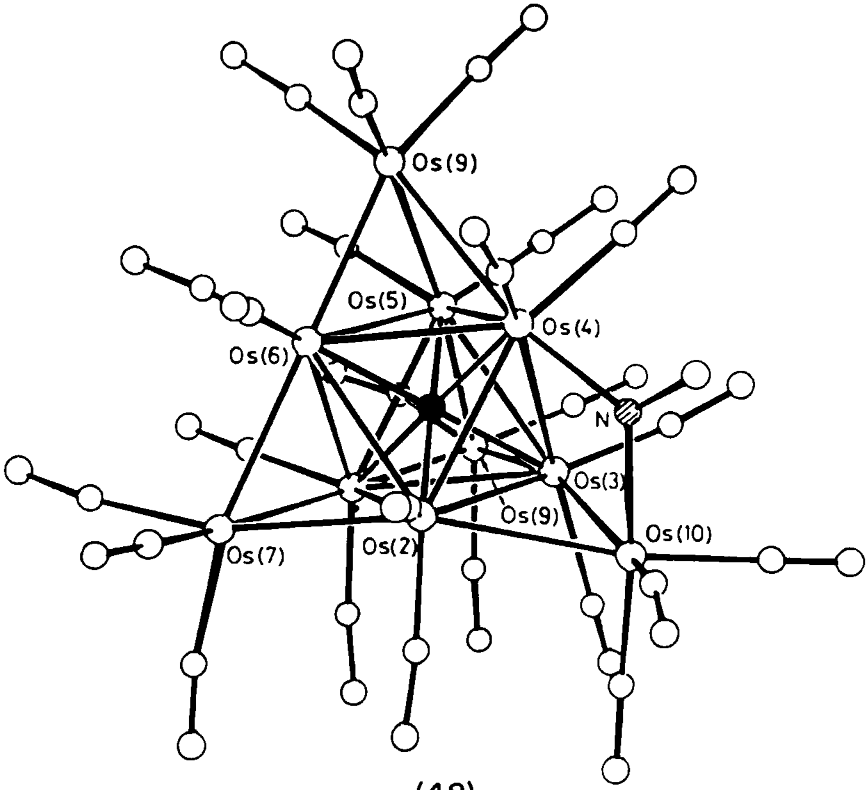
$$[\mathrm{FeRu_3(\mu\text{-}NO)(CO)_{12}}]^- \xrightarrow{\text{CO or H}^+} [\mathrm{FeRu_3(\mu_4\text{-}N)(CO)_{12}}]^-$$

$$[\mathrm{Os_4H_3(CO)_{12}(\mu_2\text{-}NO)}] \longrightarrow [\mathrm{Os_4H(\mu_4\text{-}N)(CO)_{12}}]$$

The mechanism for the nitrosyl → nitrido conversion could involve a butterfly cluster bridged across the open edge by NO, as found in the clusters [$\mathrm{Os_4H_3(CO)_{12}(NO)}$] (**47**) (*246*) and [$\mathrm{Os_{10}C(CO)_{22}(NO)}$]$^-$ (**48**) (*247*), or it could proceed by cleavage of the N—O bond to give an intermediate oxo, nitrido cluster, similar to the compound [$\mathrm{Mo_3(\eta\text{-}C_5H_5)_3O(\mu_3\text{-}N)(CO)_4}$] (**49**) (*248*). A similar compound [$\mathrm{Mo_2Fe(\eta\text{-}C_5H_5)_2(\mu_3\text{-}O)(CO)_8}$] has been isolated in the photochemically initiated reaction between [$\mathrm{Fe(CO)_5}$] and [$\mathrm{Mo_2(\eta\text{-}C_5H_5)_2(CO)_6}$] (*249*), and here it has been shown that the oxo ligand is derived from molecular oxygen, rather than from NO or CO. Gladfelter has also detected a number of isocyanate cluster compounds in the reactions of nitrosyl clusters with carbon monoxide; for example, photolysis of [$\mathrm{Ru_3(\mu\text{-}NO)(CO)_{10}}$]$^-$

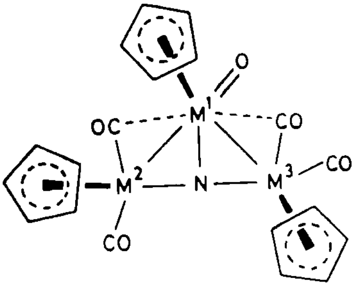


(47)



(48)

with CO gives $[Ru_3(NCO)(CO)_{11}]^-$ (*250*), consistent with the intermediacy of the nitrido cluster $[Ru_3(\mu_3\text{-}N)(CO)_{10}]^-$. Johnson *et al.* (*251*) have recently reported that reduction of $[Ru_3(\mu\text{-}NO)_2(CO)_{10}]$ with carbon monoxide gives the nitrido-nitrosyl (**50**) and nitrido-isocyanate clusters (**51**).



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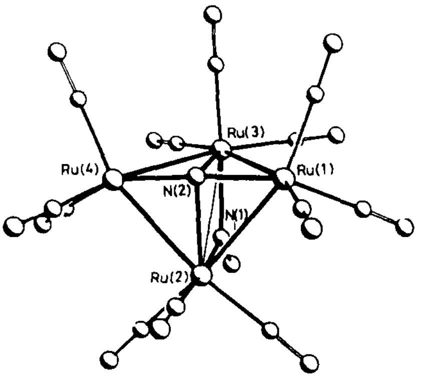
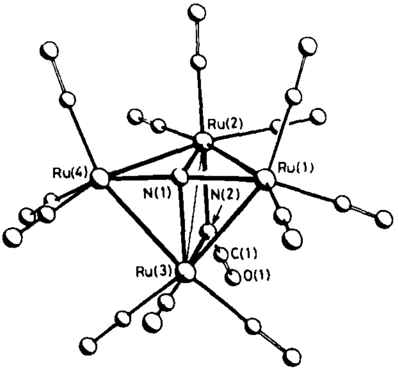


(50)



(51)

Gladfelter has recently described the reaction of $[M_4(CO)_{12}]$ {M=Co, Rh, and Ir} with $PPN[NO_2]$ (*45*). The cobalt and rhodium complexes give the known nitrido clusters $[M_6(\mu\text{-}N)(CO)_{15}]^-$ whereas the iridium cluster gives $[Ir_4(NCO)(CO)_{11}]^-$. Interestingly, reaction of $[Ir_6(NO)(CO)_{15}]^-$ with $PPN[NO_2]$ gives $[Ir_6(CO)_{15}]^{2-}$ with the evolution of N_2O and CO_2. The mechanism of this reaction is of interest because though at first sight it is similar to the oxygen-transfer reactions of mononuclear nitrosyl complexes, it may proceed by a nitrido-nitrosyl cluster similar to (**50**).

In the reaction of mononuclear dinitrosyl complexes with CO, no isocyanates have been detected, casting doubt on any mechanism involving nitrido intermediates. The mechanism has been extensively investigated and discussed elsewhere (*6*), though without many concrete conclusions, and only a general outline is shown here (Fig. 24). The key intermediates are the complexes (**52**) and (**53**), containing the *N*,*N*-nitric oxide dimer ligand or the *O*,*O*-bonded hyponitrite ligand, respectively. The essential steps in the mechanism are the formation of a 20-electron dinitrosyl complex (considering the NO ligands to be 3-electron donors), its rearrangement to (**52**) or (**53**) and the transfer of oxygen to CO. No derivatives of the 20-electron dinitrosyl intermediate or of (**53**) have been isolated, but the former have been considered as intermediates in other reactions, such as the reaction of alkenes and nitric oxide with $[\{Co(\eta\text{-}C_5H_5)(NO)\}_2]$ described in the preceding section. Hyponitrite complexes are also well known in reactions of metal-nitrosyl complexes. Reaction of the Pt(0) complex $[Pt(PPh_3)_3]$ with nitric oxide gives a product with the stoichiometry $[Pt(NO)_2(PPh_3)_2]$ (*252*), which was shown by X-ray crystallography to be the platinum hyponitrite complex (**54**).

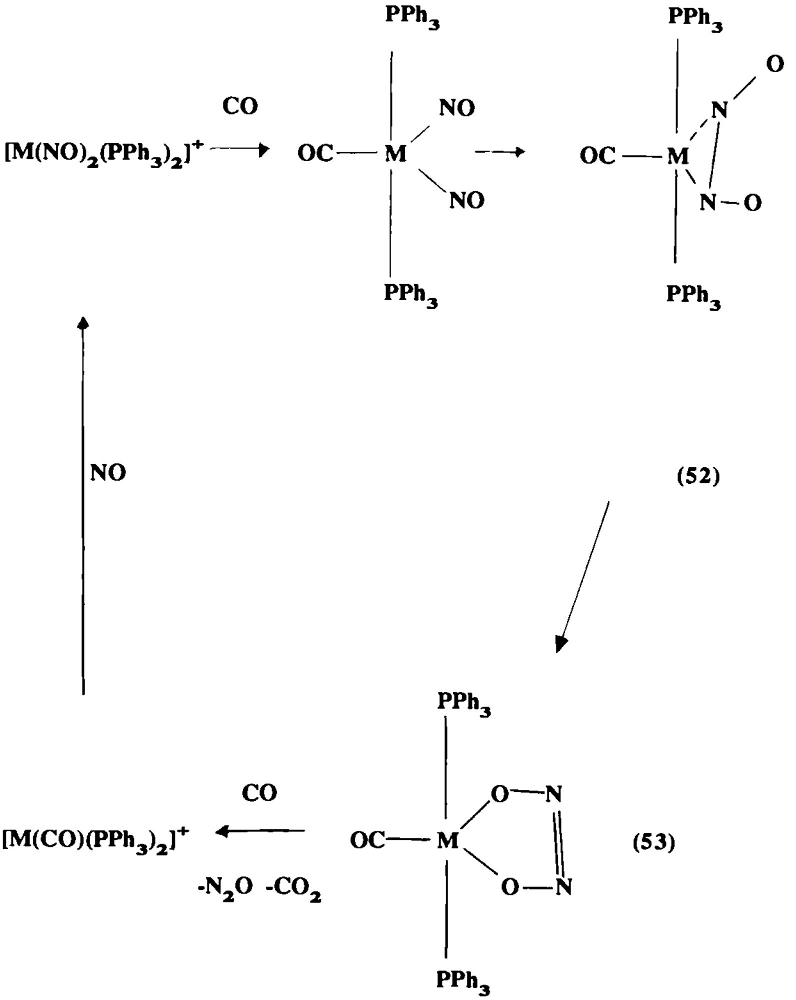
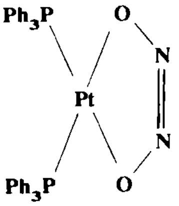


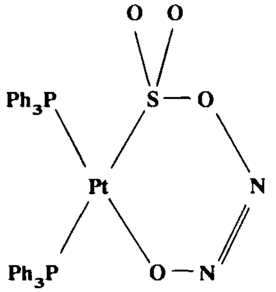
FIG. 24. Proposed mechanism for the nitrosyl-catalyzed reaction of nitric oxide with carbon monoxide.



(54)

In addition, when *cis*-[$MoCl_2(NO)_2$(diars)] is allowed to stand in methanol, [{$MoCl_2$diars(NO)}$_2$(μ_2-N_2O_2)] is isolated (*253*), this is an example of the conversion from a d^6-dinitrosyl complex to a d^4-hyponitrite complex. A binuclear hyponitrite complex, $[Pt_2(\mu\text{-}N_2O_2)(PPh_3)_4]^{2+}$, has also been reported as the product of the reaction of (**54**) with NO^+ (*254*).

Such reactions are models for the (**52**) → (**53**) step of the preceding mechanism, and indeed, (**54**) reacts with CO to generate N_2O and CO_2 (*255*), as has been observed with other hyponitrite complexes. This is evidence that a reactive intermediate is indeed the hyponitrite complex (**53**). Reaction of $[Pt(N_2O_2)(PPh_3)_2]$ (**54**) (*254*) with SO_2 gives the sulphito complex $[Pt(SO_3)(PPh_3)_2]$; in addition, the adduct $[Pt(SN_2O_4)(PPh_3)_2]$ was isolated. This was believed to contain the six-membered ring (**55**). The same intermediate is obtained in the reaction of $[Pt(SO_2)(PPh_3)_3]$ with NO(g), and such a structure would provide a model for the oxygen-transfer stage of the mechanism in Fig. 24.



(55)

The formation of a binuclear hyponitrite intermediate in the reaction of platinum-metal dinitrosyls with CO may account for the curious kinetics observed for the reaction of $[Rh(NO)_2(PPh_3)_2]^+$ with nitric oxide–carbon monoxide mixtures (*255*). The observed rate law is

$$\text{rate} = k\cdot[\text{total Rh}]^{1/2}[\text{NO}]^{-1}$$

Therefore, some binuclear rhodium species may be formed in or before the rate-determining step.

At present it is impossible to say whether Fig. 24 represents the correct mechanism because no intermediates have been detected. A mechanism for the reaction of the hyponitrite complex (**53**) with free NO is shown in Fig. 25. This mechanism is related to the reaction of free NO with transition metal nitrosyl complexes discussed earlier though it cannot account for the stoichiometric reaction with CO.

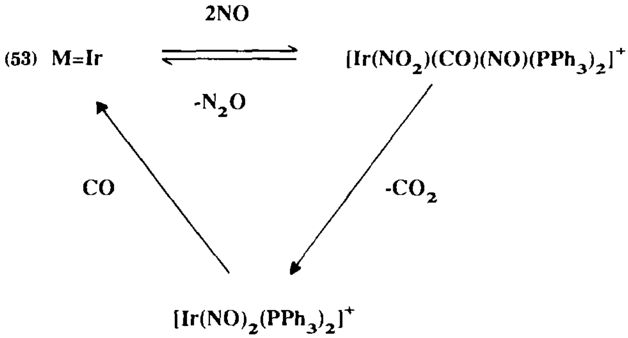
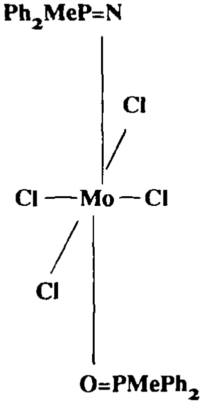


FIG. 25. Possible mechanism for the reaction of dinitrosyl complexes with carbon monoxide to give N_2O and CO_2.

Nitrosyl complexes also transfer oxygen to tertiary phosphines. Thus, $[\{FeBr(NO)_2\}_2]$ dissolves in molten PPh_3 to give $[FeBr_2(NO)(PPh_3)_2]$, $[Fe(NO)_2(PPh_3)_2]$, $Ph_3P{=}O$, and N_2 (*256*). The intermediate in this reaction may be similar to (**56**), which is obtained in



(56)

the reaction of $MoCl_5$ with NO and $PMePh_2$ (*257*). Compound (**56**) is readily hydrolyzed to yield $[MoCl_3(NH_2)(O{=}PMePh_2)_2]$.

The platinum-metal complexes that react with CO to give CO_2 and N_2O also react with tertiary phosphines (*20*):

$$R_3P + [Rh(NO)_2(PR_3)_2]^+ \longrightarrow [Rh(PR_3)_3]^+ + R_3P{=}O + N_2O$$

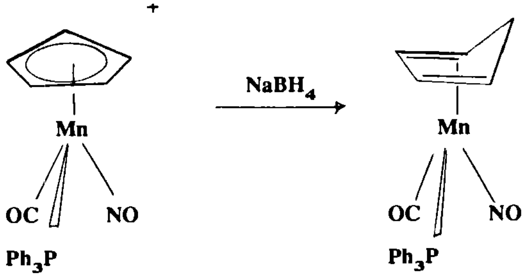
The corresponding iridium complex generally reacts in analogous fashion, but with Ph_3P it undergoes simple substitution to give $[Ir(NO)(PPh_3)_3]$. Phosphine oxidation also occurs on reaction of nitric oxide with $[NiCl_2(PEt_3)_2]$ (*258*) or $[IrH_2(PR_3)_3]^+$ (*259*).

F. Reduction of Coordinated Nitric Oxide

An important reaction of NO gas, catalyzed by transition metal surfaces, is reduction with hydrogen to give ammonia. As a consequence, a great deal of effort has been directed into studying the reduction of coordinated nitrosyl ligands.

Electrochemical reduction of the nitrosyl group is possible, which ultimately yields ammonia; thus, 4-electron reduction of an aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ gives $[Fe(CN)_5(NH_2OH)]^{3-}$ (*260*), and reaction of $[Cr(NO)(H_2O)_5]^{2+}$ or $[Ru(NO)(NH_3)_5]^{3+}$ with chromous ion gives $Cr^{2+}(aq) + NH_3$ or $[Ru(NH_3)]_6]^{2+}$, respectively (*261*). Electrochemical reduction of $[Ru(NO)(trpy)(bpy)]^{2+}$ (*262*) has been shown also to yield ammonia. Nitrido complexes can be also isolated in the reduction of $[RuCl_5(NO)]^{3-}$. With $SnCl_2$-HCl or aqueous formaldehyde, for example, $[Ru_2NCl_8(H_2O)_2]^{3-}$ is formed (*263*).

Hydride sources have been used to reduce nitrosyl complexes, but in many cases other ligands react preferentially. With $[Re(\eta\text{-}C_5H_5)(NO)(CO)_2]^+$, it is found that the carbonyl groups are reduced to formyl, hydroxymethyl, or methyl groups, depending on solvent and reducing agent (*264*), and hydride attack on the cyclopentadienylmanganese complex (**57**) occurs on the organic ligand (*265*).



(57)

With $[Cr(\eta\text{-}C_5H_5)Cl(NO)_2]$, both electron transfer and substitution by hydride are observed on reaction with $NaBH_4$ (*266*) to give a mixture of $[\{Cr(\eta\text{-}C_5H_5)(NO)_2\}_2]$ and the amido dimer $[Cr_2(\eta\text{-}C_5H_5)_2(NO)_2(\mu_2\text{-}NH_2)(\mu\text{-}NO)]$. Reduction of this complex with $Na[AlH_2(OCH_2CH_2OMe)_2]$ (*267*) gives $[Cr_2(\eta\text{-}C_5H_5)_2(NH_2)(NO)_3]$. A similar reaction occurs with *t*-butyllithium, from which the related dimer $[Cr_2(\eta\text{-}C_5H_5)_2(NO)_2(\mu_2\text{-}NO)\{\mu_2\text{-}N(OH)t\text{-}Bu\}]$ is isolated. $[\{Co(\eta\text{-}C_5H_5)(NO)\}_2]$, with ^tBuLi, gives a mixture of products including $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2]$ and $[Co_3(\eta\text{-}C_5H_4{}^tBu)_3(\mu_3\text{-}NO)_2]$ (*6*). Reaction of $[M(NO)_2(PPh_3)_2]^+$ {M=Co, Ir} with $NaBH_4/PPh_3$ is reported to yield $[M(NO)(PPh_3)_3]$ and ammonia (*20*).

Until recently, no examples of the reduction of transition metal nitrosyl compounds with molecular hydrogen were known, but two groups (*268, 269*) have reported the reduction of coordinated μ_2-NO groups in $[Ru_3H(CO)_{10}(NO)]$ by molecular hydrogen to yield μ_3-NH and μ_2-NH_2 ligands, as well as $[Ru_4H(\mu_4\text{-}N)(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$. Such a reaction is clearly related to the reduction of nitric oxide by hydrogen on metal surfaces and probably proceeds through a nitrido intermediate. Another example is (*270*)

$$H_2 + [HOs_3(CO)_{10}(NO)] \longrightarrow [H_4Os_4(\mu_3\text{-}NH)(CO)_8]$$

Evidence for a nitrido intermediate comes from the observation of isocyanate products in the hydrogenation of $[Ru_3(\mu\text{-}H)(\mu\text{-}NO)(CO)_{10}]$ (*271*).

A number of metal nitrosyl complexes are susceptible to protonation reactions, which lead to a formal reduction of the NO ligand. The bending of the nitrosyl group, concomitant with the coordination of an incoming nucleophile, leads to the formation of a much more basic nitrogen center, which can readily be protonated. A number of platinum-metal nitrosyl complexes undergo such protonation reactions when treated with "nucleophilic" acids such as HCl. The following reactions illustrate the sequential reduction of coordinated NO to ligands derived from hydroxylamine (*272–274*):

$$[OsCl(CO)(NO)(PPh_3)_2] \xrightarrow{HCl} [OsCl_2(CO)(HNO)(PPh_3)_2]$$

$$[Os(NO)_2(PPh_3)_2] \xrightarrow{2HCl} [OsCl_2(NO)(NHOH)(PPh_3)_2]$$

$$[Ru(NO)_2(PPh_3)_2] \xrightarrow{3HCl} [RuCl_3(NO)(PPh_3)_2]$$

$$[Ir(NO)(PPh_3)_3] \xrightarrow{3HCl} [IrCl_3(NH_2OH)(PPh_3)_2]$$

In the reaction of $[Ru(NO)_2(PPh_3)_2]$ with HCl, NO^- has been formally substituted, and a number of other reactions have been reported in which such a process has occurred. For example (*275–277*):

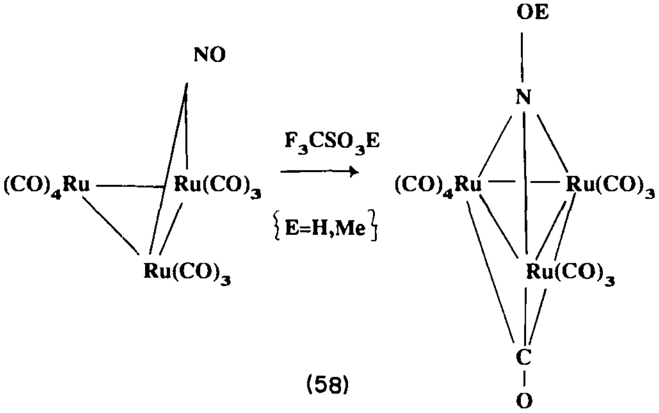
$$[Rh(NO)_2(PPh_3)_2]^+ \xrightarrow{tfa^-} [Rh(tfa)_2(NO)(PPh_3)_2]$$

$$[Ir(NO)_2(PPh_3)_2]^+ \xrightarrow{bpy} [Ir(NO)(bpy)(PPh_3)_2]^{2+}$$

$$[RuCl(NO)_2(PPh_3)_2]^+ \xrightarrow{NaI} [RuClI_2(NO)(PPh_3)_2]$$

In some cases, N_2O, which is the anhydride of HNO, has been detected as a product in these reactions.

In metal-cluster chemistry, μ_3-NO groups can be O protonated, as shown in the reaction of the triruthenium cluster (**58**) (*278*) with trifluoromethylsulphonate derivatives. In this system, there is competition between M protonation, which is relatively slow but thermodynamically favored, and O protonation.



(58)

In the managanese system $[Mn_3(\eta\text{-}C_5Me_5)_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)]$ (*279*), very similar chemistry is observed; but in addition, reduction of the nitrosyl group occurs, yielding the imido cluster $[Mn_3(\eta\text{-}C_5Me_5)_3(\mu_3\text{-}NH)(\mu_2\text{-}NO)_3]$ in low yield. Such a reaction undoubtedly proceeds by a nitrido intermediate, though the exact mechanism is, at present, unknown.

Abbreviations

R	alkyl
Me	methyl
Et	ethyl
Pr	*n*-propyl
Bu	*n*-butyl
^{i}Pr	*iso*-propyl
^{t}Bu	*tert*-butyl
Cy	cyclohexyl
Ph	phenyl
tfa	trifluoroacetyl
dtc	*N*,*N*-dialkyldithiocarbamato
tpp	tetraphenylporphyrinato

acac	acetylacetonato
salen	*N*,*N*′-ethylenebis(salicylideneiminato)
ketox	7-methylsalicylideneoximinato
benacen	*N*,*N*′-ethylenebis(benzoylacetoneiminato)
dppm	bis(diphenylphosphino)methane
dppe diphos	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dppb	1,4-bis(diphenylphosphino)butane
P_3C	1,1,1-tris(diphenylphosphinomethyl)-ethane
diars das	1,2-bis(dimethylarsino)benzene
dppbp	2,11-bis(diphenylphosphinomethyl)benz[*c*]phenanthrene
bpy	2,2′-bipyridine
en	1,2-diaminoethane
dmf	*N*,*N*-dimethylformamide
tmp	trimethylphosphate
mah	maleic anhydride
SP	square-pyramidal
CNDO	complete neglect of differential overlap
ESCA	electron spectroscopy for chemical analysis
VT	variable temperature
FT	Fourier transform
IR	infrared
IS	isomer shift
QS	quadrupole splitting
NQR	nuclear quadrupole resonance
ESR	electron spin resonance

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