The Coordination Chemistry of Nitric Oxide
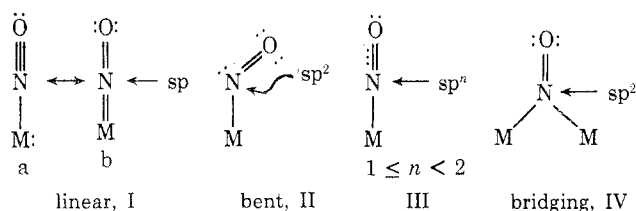
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Complexes of nitric oxide have been known for centuries, yet never has interest in transition metal nitrosyls been as keen as at present. In part a natural adjunct to the growth of interest in organometallic chemistry, especially metal carbonyls and complexes of π acids, the marked surge of research in this area has been stimulated by several important developments during the past decade.

Prior to 1960 the interactions of nitric oxide with transition metal ions were studied principally as a way of synthesizing nitrosyl complexes, and the bonding of NO to transition metal ions was envisioned in one of several possible ways, Lewis structures I–IV, of which the first three correspond to ter-

minal nitrosyls.[1-3] Structures I and II are commonly called the *linear* and *bent,* or NO^+ and NO^-, modes of nitric oxide coordination, respectively. The latter designation arises from the formalism used in coordination chemistry in which the electron pair in the metal–ligand σ bond is associated entirely with the ligand for the purpose of assigning ligand charge and metal oxidation state.[4]

In the assignment of formal oxidation state the existence of metal–ligand π bonding is ignored, but since π bonding is vital to the linear mode of NO coordination (structure Ib), the NO^+ designation has been extensively criticized as not representative of physical reality regarding charge distributions, bond strengths, and the like. It is worth remembering, however, that formalisms in general are merely useful constructs. In nitrosyl and organometallic chemistry, the available formalisms (the oxidation state formalism and the electroneutral approach[1,5]) are not intended as substitutes for detailed bonding descriptions.
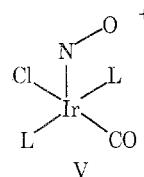
Coordination by NO^+ is directly analogous to metal–carbonyl bonding (CO and NO^+ are isoelectronic) with its synergistic coupling of σ and π bonding.

Coordination by NO^-, on the other hand, was proposed by Sidgwick[1] as analogous to that by halide ion and structurally similar to organic nitroso compounds. While several possibilities for NO coordination had thus been recognized, the prevailing view prior to 1960 was that in all but a few systems the linear mode of coordination was followed, as in the historically important nitroprusside ion $Fe(NO)(CN)_5^{2-}$ [1,2] and the nitrosyl carbonyls $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$.[6] In none of the other systems, such as $Co(NO)(NH_3)_5^{2+}$,[7] was *definitive* evidence available establishing any other structural arrangement for metal–NO bonding.

A significant turning point in nitrosyl chemistry was achieved in 1967 with the report by Ibers and Hodgson[8] of the first structurally documented bent nitrosyl complex, V. This structure unequivocally es-

tablished the structural duality of coordinated NO, and in doing so confirmed the bent mode of metal–nitrosyl bonding (II) suggested years earlier.[1] Moreover, since V had been prepared from the reaction of NO^+ with $IrCl(CO)(PPh_3)_2$ in which the metal complex served as an electron-pair donor, it was seen that NO^+ possessed amphoteric character and could function as either an electron-pair acceptor[8] or an electron-pair donor with concomitant π back-bonding (I).

The interconvertibility of the linear and bent modes of nitric oxide coordination was postulated in 1969 by Collman and coworkers[9] in the context of the catalytic activity of certain metal nitrosyls. Since the linear and bent modes of bonding (I and II) differ by

(1) N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc., Ser. A,* 144, 521 (1934); N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. I, Clarendon Press, Oxford, 1950, p 685.

(2) T. Moeller, *J. Chem. Educ.,* 23, 542 (1946); T. Moeller, "Inoganic Chemistry," Wiley, New York, N.Y., 1952, p 598.

(3) (a) J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.,* 7, 32 (1958); (b) W. P. Griffith, J. Lewis, and G. Wilkinson, *ibid.,* 7, 38 (1958).

(4) J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N.Y., 1972, Chapter 8.

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N.Y., 1972, Chapter 22.

(6) R. L. Mond and A. E. Wallis, *J. Chem. Soc.,* 121, 22 (1922); A. A. Blanchard, *Chem. Rev.,* 26, 409 (1940); J. S. Anderson and W. Hieber, *Z. Anorg. Allg. Chem.,* 208, 238 (1932).

(7) (a) J. Sand and O. Genssler, *Ber. Deutsch. Chem. Ges.,* 36, 2083 (1903); (b) A. Werner and P. Karrer, *Helv. Chim. Acta,* 1, 54 (1918).

(8) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.,* 7, 2345 (1968); D. J. Hodson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.,* 90, 4486 (1968).

(9) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.,* 91, 5659 (1969).

an electron pair on the nitrosyl ligand, interconversion would alternately withdraw and donate an electron pair to the metal center. On bending of the nitrosyl, an electron pair would be withdrawn from the metal, creating a vacant coordination site and thus fulfilling a key criterion of catalytic activity.[10] This proposal gave great impetus to further studies on transition metal nitrosyls, especially in relation to homogeneous catalysis.[10,11]

The advances in the chemistry of coordinated nitric oxide were accompanied by mounting concern over the role of NO as a major air pollutant. Each year 10^6 tons of nitrogen oxides (NO and NO_2) are produced in fossil fuel combustion processes, mainly as NO, according to eq 1.[12] Environmental control of NO_x has pursued two lines of investigation involving, first, the modification of combustion conditions to minimize the formation of nitrogen oxides and, second, the development of catalysts for the facile conversion of NO into less harmful chemical entities.

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \longrightarrow NO \qquad (1)$$

$$\Delta H_f^\circ = 21.6 \text{ kcal/mol}; \Delta G_f^\circ = 20.72$$
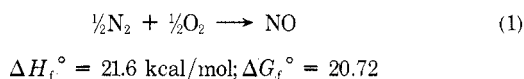
Despite its thermodynamic instability, NO is kinetically inert with respect to decomposition and reduction, and requires the presence of a catalyst for many of its reactions. These catalysts are invariably metals or metal oxides such as CuO, Rh_2O_3, Co_3O_4, Pt, and $La_{1-x}Pb_xMnO_3$,[13-15] which may or may not be supported. The need to know how NO interacts with the metal centers of a catalyst surface has also served as a stimulus to studies during the past decade on the reactions of NO with metal complexes in solution.

The activity in the chemistry of metal–nitric oxide complexes has been accompanied by a number of excellent reviews.[16-22] Several of these are comprehensive, while others are specialized in the areas of nitrosyl structures,[21] NO bonding,[19] organometallic nitrosyls,[17] synthetic methods,[22] and the reactions of coordinated NO^+.[20] The purpose of this Account is to present a perspective on the coordination chemistry of nitric oxide with emphasis on the relationship of structure to chemical reactivity and on the reactions of NO promoted or catalyzed by metal complexes.

(10) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968); J. P. Collman and W. R. Roper, *Advan. Organometal Chem.*, 7, 53 (1968).

(11) For a number of excellent reviews, see *Advan. Chem. Ser.*, 70 (1968). Also see: (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966), and subsequent papers by Wilkinson and co-workers; (b) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).

(12) W. Bartok, A. R. Crawford, and A. Skopp, *Chem. Eng. Progr.*, 67, 64 (1971).

(13) (a) E. R. S. Winter, *J. Catal.*, 22, 158 (1971); (b) C. S. Howard and F. Daniels, *J. Phys. Chem.*, 62, 215 (1958).

(14) (a) M. Shelef, K. Otto, and H. Gandhi, *Atmos. Environ.*, 3, 107 (1969); (b) K. Otto and M. Shelef, *J. Phys. Chem.* 76, 37 (1972), and references therein; (c) M. Shelef and K. Otto, *J. Catal.*, 10, 408 (1968); (d) M. Shelef and H. S. Gandhi, *Ind. Eng. Chem., Prod. Res. Develop.*, 11, 2 (1972).

(15) (a) R. L. Klimisch and G. J. Barnes, *Environ. Sci. Technol.*, 6, 543 (1972); (b) R. J. H. Voorhoeve, J. P. Remeika, and D. W. Johnson, Jr., *Science*, 180, 62 (1973).

(16) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966).

(17) W. P. Griffith, *Advan. Organometal. Chem.*, 7, 211 (1968).

(18) N. G. Connelly, *Inorg. Chim. Acta Rev.*, 6, 48 (1972).

(19) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 13, 339 (1974).

(20) J. Masek, *Inorg. Chim. Acta Rev.*, 3, 99 (1969).

(21) B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Phys. Chem., Ser. One*, 11, 33 (1972).
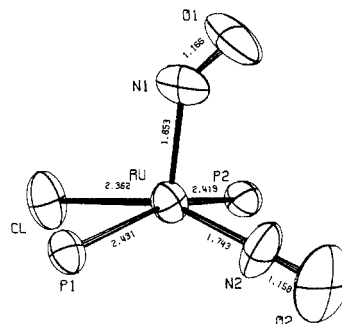
(22) K. G. Caulton, *Coord. Chem. Rev.*, in press.

Figure 1. The inner coordination geometry of Ru-$(NO)_2Cl(PPh_3)_2^+$.

The Structures of Nitrosyls

In order to understand the reactivity of coordinated nitric oxide, one must first consider the molecular and electronic structures of transition metal nitrosyls and the interrelationship of nitrosyl bonding mode and coordination geometry. We focus on five-coordinate nitrosyls because they provide a most fertile ground for inquiry. The two principal geometries in five-coordination are the square pyramid (SP) and the trigonal bipyramid (TBP), and for sterically unencumbered systems the energetic difference between these geometries is not thought to be great.[23] Examination of the representative structures presented in Table I reveals that, for the platinum group systems, if the complex has an SP geometry with an apical nitrosyl then the NO ligand bonds in a bent manner, whereas if the complex has a TBP geometry the nitrosyl coordinates linearly. In all of these cases the complexes are isoelectronic, as described below.

Representative of the first of these structural types is the complex $Ru(NO)_2Cl(PPh_3)_2^+$, VI,[24] which was

VI
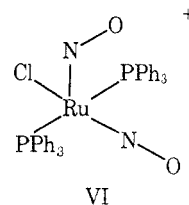
synthesized by reaction of ethanolic solutions of NO^+-PF_6^- with the Stiddard and Townsend complex Ru-$(NO)Cl(PPh_3)_2$.[25] This reaction was carried out in order to prepare a dinitrosyl system possessing both linear and bent modes of nitric oxide coordination. The structure of VI is shown in Figure 1. As, hoped, the complex is SP with an angularly coordinated NO^- in the apical position and a linearly bonded NO^+ in the basal plane.[24] A comparison of the bonding parameters for the two metal–nitrosyl units shows that the M–N distance for a linear nitrosyl is shorter than that for a bent NO (see Figure 1) because of greater metal nitrosyl π bonding in the former unit. The nitrosyl stretching frequencies ν_{NO} of 1845 and 1687 cm^{-1} for the linear and bent nitrosyls,

(23) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966).

(24) (a) C. G. Pierpont, D. G. VanDeveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, 92, 4760 (1970); (b) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1088 (1972).

(25) M. H. B. Stiddard and R. E. Townsend, *Chem. Commun.*, 1372 (1969).

Table I
Representative Five-Coordinate Group VIII Nitrosyl Complexes

Complex[a]	No. of electrons	Coordination geometry[b]	M–N–O angle, deg	M–N distance, Å	ν_{NO}	Ref
Fe(NO)(mnt)$_2^-$	20	Distorted SP–ap NO[c]	180 (0)	1.61 (1)	1867	d
Fe(NO)(Me$_2$dtc)$_2$	21	SP–apNO	170.4 (6)	1.720 (5)	1690	e
Fe(NO)(mnt)$_2^{2-}$	21	SP–apNO	165 (2)	1.58 (2)	1645	d
Ru(NO)$_2$ClL$_2^+$	22	SP–apNO baNO	138 (2) 178 (2)	1.85 (2) 1.74 (2)	1687 1845	24
RuH(NO)L$_3$	22	TBP–axNO	176 (1)	1.79 (1)	1645	27
Ru(NO)(diphos)$_2^+$	22	TBP–eqNO	174 (1)	1.74 (1)	1673	26
Os(NO)$_2$(OH)L$_2^+$	22	SP–apNO baNO	127 (2) *ca.* 180	1.98 (5) 1.71 (4)	1632 1842	f
Os(NO)(CO)$_2$L$_2^+$	22	TBP–eqNO	177 (1)	1.89 (1)	1750	g
Co(NO)(Me$_2$dtc)$_2$	22	SP–axNO	135 (1)	1.75 (1)	1630	h
Co(NO)(diars)$_2^{2+}$	22	TBP–eqNO	179	1.68	1852	41
Co(NO)Cl$_2$L$'_2$	22	Distorted TBP– eqNO[i]	165 (1)	1.70 (1)	1735, 1630	44
Rh(NO)Cl$_2$L$_2$	22	SP–apNO	125 (1)	1.91 (1)	1620	j
Ir(NO)Cl$_2$L$_2$	22	SP–apNO	123 (2)	1.94 (2)	1560	k
Ir(NO)Cl(CO)L$_2^+$	22	SP–apNO	124.1 (9)	1.97 (1)	1680	8
IrH(NO)L$_3^+$	22	TBP–axNO	175 (3)	1.68 (3)	1715	l

a L = PPh$_3$; mnt = maleonitriledithiolate; Me$_2$dtc = *N,N*-dimethyldithiocarbamate; L' = PMePh$_2$. *b* ap = apical; ax = axial; ba = basal; eq = equatorial; SP = square pyramidal; TBP = trigonal bipyramidal. *c* Trans S–Fe–S bond angles are 162.4 (1) and 147.9 (1)°. *d* D. G. Van-Derveer, *et al*, American Crystallography Association Meeting Abstracts, Vol. 1, P4 (1973). *e* (At −80°) G. R. Davies, *et al., J. Chem. Soc.*, 1275 (1970). *f* J. M. Waters and K. R. Whittle, *Chem. Commun.*, 518 (1971). *g* G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 119 (1972). *h* J. H. Enemark and R. D. Feltham, *J. Chem. Soc., Dalton Trans.*, 718 (1972). *i* Trans angles are P–Co–P = 168 (1) and Cl–Co–Cl = 108.4 (3)°. *j* S. Z. Goldberg, C. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, submitted for publication. *k* D. M. P. Mingos and J. A. Ibers, *ibid.*, 10, 1035 (1971). *l* D. M. P. Mingos and J. A. Ibers, *ibid.*, 10, 1479 (1971).
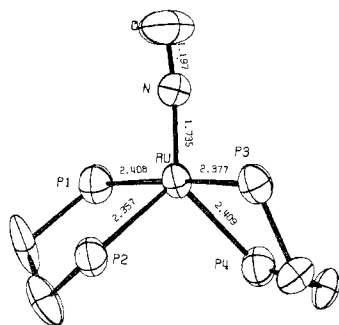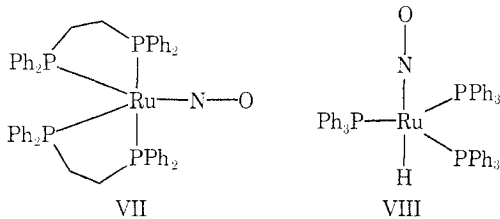

Figure 2. The inner coordination geometry of Ru(NO)(diphos)$_2^+$.

respectively, are also consistent with the notions of metal–nitrosyl bonding embodied in structures I and II.

Representative examples of the TBP linear NO structures are Ru(NO)(diphos)$_2^+$ (VII)[26] and RuH-(NO)(PPh$_3$)$_3$ (VIII).[27] Complex VII was originally

prepared by Townsend[28] and, because of a ν_{NO} value of 1673 cm^{-1}, was assumed to have a SP structure

similar to V and VI. However, the structure as shown in Figure 2 turns out to be TBP with a linearly coordinated nitrosyl in the equatorial position and bidentate diphos ligands spanning equatorial and axial positions.

Complex VIII is the triphenylphosphine member of the series RuH(NO)L$_3$, L = tertiary phosphine, synthesized by Wilson and Osborn.[29] All of these systems have ν_{NO} in the range 1620–1645 cm^{-1}, and all except the methyldiphenylphosphine member of the series are effective as hydrogenation and isomerization catalysts of terminal olefins. At least two of the systems also exhibit fluxional behavior.[29] As predicted from solution studies, the structure of VIII is TBP with an axial nitrosyl linearly coordinated.[27] Because of the low steric requirements of the hydride, the complex shows an expected distortion toward pseudotetrahedral geometry.

Complexes VI–VIII and the related Os and Ir complexes of Table I thus exhibit only three different structural arrangements and support the empirical conclusion that in five-coordinate nitrosyls the coordination geometry and the mode of nitric oxide coordination are intimately related.

The Bonding and Bending of Nitrosyls

To develop notions of bonding and bending in nitrosyls requisite for understanding this relationship, one must go beyond the simple picture conveyed by structures I–III to molecular orbital theory. Our approach to this problem was inspired mainly by Walsh's study[30] of triatomic molecules such as linear

(26) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 12, 199 (1973).
(27) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1094 (1972).
(28) R. E. Townsend, personal communication.
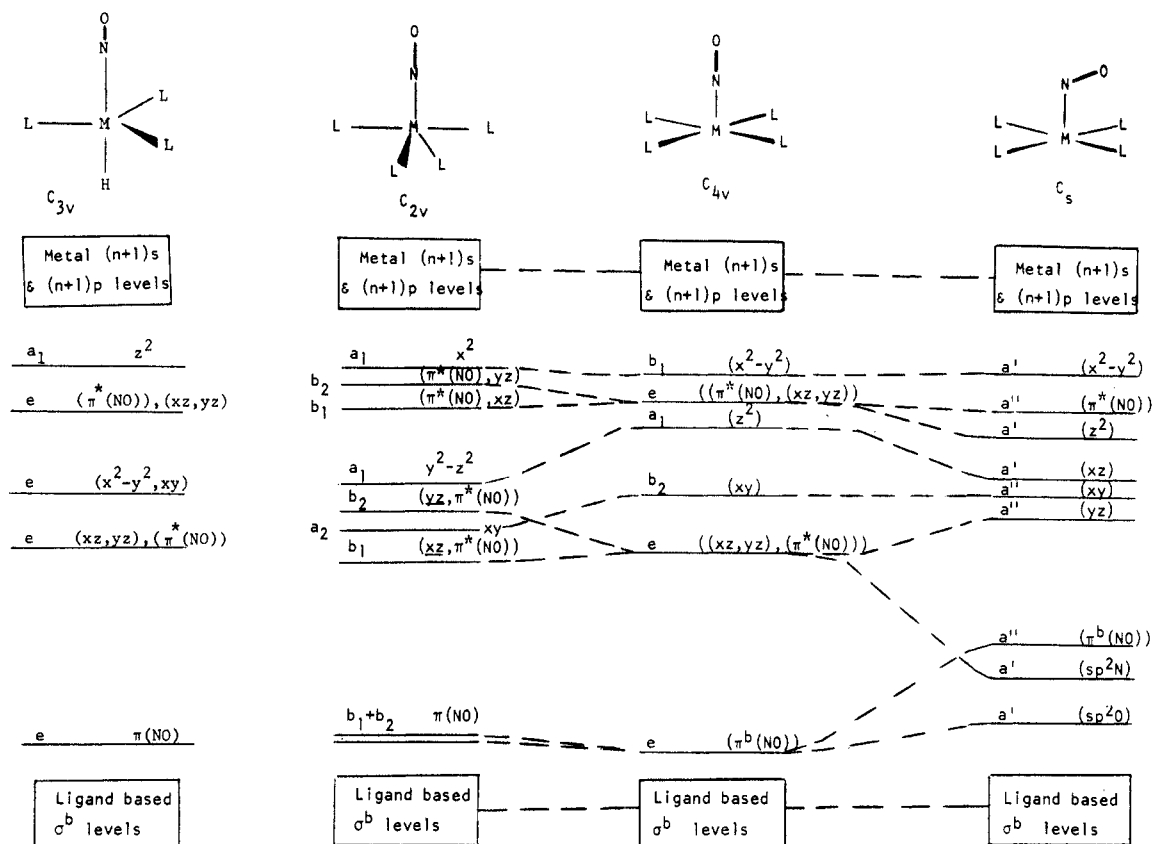(29) S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 93, 3068 (1971).

Figure 3. Molecular orbital energy level orderings for five-coordinate nitrosyls and their correlations.

NO_2^+ and bent NO_2^- in which energy levels between the limiting geometries were correlated. While Walsh's analysis dealt solely with the B–A–B bond angle in AB_2 systems,[30] a similar treatment of metal nitrosyls has to contend with more degrees of freedom than the M–N–O angle, the most important being the coordination geometry about the metal.[31]

To simplify the correlations, only one structural parameter was allowed to vary at a time with all others held constant. The results, which are shown in Figure 3, are based on qualitative MO energy level orderings for the three observed structure types, SP bent apical NO (C_s symmetry), TBP linear equatorial NO (C_{2v}) and TBP linear axial NO (C_{3v}), plus that for a square-pyramidal linear apical NO structure of C_{4v} symmetry. The energy levels of the C_{4v} structure are correlated with those of the SP bent NO complex as the M–N–O unit bends[31] and with those of the TBP-equatorial NO complex as the ligand-field geometry varies.[26]

In considering the two SP structures, one sees that the π bonding e level ((xz,yz), π^*(NO)) splits in C_s symmetry with the a' member connecting to a stable nitrosyl localized level not present in C_{4v} and the a'' member correlating with the metal yz level. Consequently, the d_{z^2} level in C_{4v}, which is strongly σ^* with respect to the metal–nitrosyl bond, correlates with the largely nonbonding xz level in C_s. The first correlation results in a change in orbital character from a metal-based π function to one localized on the nitrosyl which helps explain the oxidative addition of

NO^+ to d^8 complexes to yield bent nitrosyl or NO^- systems.[32]

The key correlation between the energy levels of the C_{4v} and C_{2v} structures is that between the σ^* d_{z^2} orbital in C_{4v} and the less strongly antibonding a_1 level in C_{2v} designated as $y^2 - z^2$. (The unconventional label $y^2 - z^2$ arises because of the change in principal symmetry axis in going from the ideal TBP to the C_{2v} TBP-equatorial NO structure.) Correlations involving the C_{3v} structure are not shown because of the need to designate a specific rearrangement mechanism and the difficulties attendant in deriving orbital energies for the intermediate structures.

The major conclusions of the correlation diagrams of Figure 3 become evident when electrons are placed into the level orderings. For five-coordinate nitrosyl complexes of the platinum metals, each system contains 22 electrons counted *assuming NO^+* in the following way: ten electrons in the ligand σ^b functions, four electrons in the π^b(NO) set, and a d^8 metal configuration. In C_{4v} symmetry this number of electrons would require occupation of the σ^* d_{z^2} level, and the structure thus becomes unstable relative to the alternative geometries. By bending the nitrosyl (C_s structure), the system avoids placing electrons into a strongly antibonding orbital but at the cost of metal–nitrosyl π bonding. On the other hand, variation of the ligand field to TBP allows the maintenance of a strong metal–nitrosyl π interaction but reduces the

(30) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).
(31) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971).

(32) In this regard, we note that the delocalized π bonding e level in C_{4v} is traditionally assigned to the metal (xz,yz) set, leading to the NO^+ formulation of the nitrosyl regardless of the per cent nitrosyl π^* character calculated for the molecular orbitals of this level.
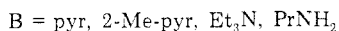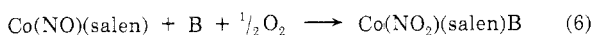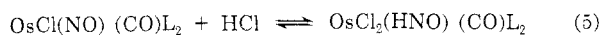
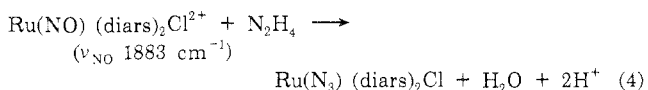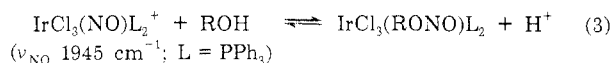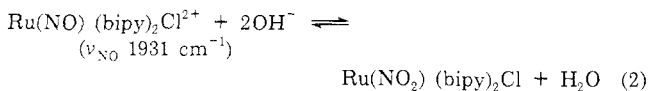effectiveness of σ bonding in the entire structure.[33] Hence, five-coordinate 22-electron nitrosyl complexes have several stable structural alternatives. The factors which lead to a particular arrangement, while not fully delineated, relate to the steric and electronic effects of other ligands in the system and the nature of the central metal. A second and related conclusion is that, unless sterically constrained, the structures of C_s, C_{2v}, and C_{3v} symmetry may not represent deep energetic minima and that interconversion between them may be facile.

For complexes constrained by steric and electronic effects to be SP, an additional conclusion can be drawn. Whereas 22-electron systems are required to have a bent nitrosyl structure, 20-electron systems should have linear M–N–O units in order to maximize both σ and π interactions, and 21-electron systems should be slightly bent. While the available evidence presented in Table I tends to support this conclusion, there is a paucity of structural data on such systems.

Correlation diagrams similar to Figure 3 have been presented by other investigators, and this approach has been used in dealing with four-coordinate nitrosyl complexes and dinitrosyl systems.[19,34,35] The major differences between the published correlations for the five-coordinate NO complexes involve the position of the nitrosyl localized level in the C_s structure and its consequent correlations. Current efforts in this area are being devoted to developing a simple, usable theory which will have predictive capabilities.[19,35]

Interrelating Reactivity and Structure

The chemical reactivity of coordinated NO depends on the mode of bonding. Thus, linearly coordinated nitrosyls with ν_{NO} greater than *ca.* 1850 cm^{-1} undergo nucleophilic attack at the nitrosyl N atom as shown by reactions 2–4,[36–38] while bent nitrosyls undergo electrophilic attack as in reactions 5 and 6.[39,40]

$$Ru(NO)\,(bipy)_2Cl^{2+} + 2OH^- \rightleftharpoons$$
$$(\nu_{NO}\ 1931\ cm^{-1})$$
$$Ru(NO_2)\,(bipy)_2Cl + H_2O \quad (2)$$

$$IrCl_3(NO)L_2^+ + ROH \rightleftharpoons IrCl_3(RONO)L_2 + H^+ \quad (3)$$
$$(\nu_{NO}\ 1945\ cm^{-1};\ L = PPh_3)$$

$$Ru(NO)\,(diars)_2Cl^{2+} + N_2H_4 \longrightarrow$$
$$(\nu_{NO}\ 1883\ cm^{-1})$$
$$Ru(N_3)\,(diars)_2Cl + H_2O + 2H^+ \quad (4)$$

$$OsCl(NO)\,(CO)L_2 + HCl \rightleftharpoons OsCl_2(HNO)\,(CO)L_2 \quad (5)$$

$$Co(NO)(salen) + B + {}^1/_2O_2 \longrightarrow Co(NO_2)(salen)B \quad (6)$$

$$B = pyr,\ 2\text{-Me-pyr},\ Et_3N,\ PrNH_2$$

(33) If only σ bonding is assumed for the M–L interactions in 22-electron $M(NO)L_4$ systems, then the trigonal-bipyramidal linear NO structure will have two orbitals occupied which are weakly σ^* with respect to bonds in the equatorial plane, whereas the square-planar bent NO structure will have no M–L σ^* orbitals occupied.

(34) D. M. P Mingos, *Inorg. Chem.*, **12**, 1209 (1973).

(35) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974).

(36) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971); **10**, 2150 (1971).

(37) C. A. Reed and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 1243 (1972).

(38) P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

Linearly coordinated nitrosyls having lower ν_{NO} values, indicative of significant contributions from resonance structure Ib and decreased electrophilicity of the nitrosyl N atom, are inert to nucleophilic attack.

The conversion of NO$^+$ to NO$^-$ has been demonstrated by adding coordinating anion to the coordinatively saturated TBP-equatorial NO complex Co(NO)(diars)$_2$$^{2+}$ (diars = o-phenylenebis(dimethylarsine)), thereby necessitating the transfer of an electron pair from the metal to the nitrosyl, giving the bent nitrosyl product Co^{III}(NO)(diars)$_2$X$^+$ (X = Cl$^-$, Br$^-$, NCS$^-$).[41] In the platinum group systems, a less easily rationalized conversion involves the reaction of CO with IrCl(NO)L$_2$$^+$ to give V.[42]

The reversible interconversion of linear and bent nitrosyls in stereochemically nonrigid molecules has attracted considerable attention, but to date the best evidence for such interconversion remains indirect. For example, when Ru(NO)$_2$ClL$_2$$^+$ (VI) is synthesized by the reaction of Ru(^{15}NO)ClL$_2$ with ^{14}NO$^+$BF$_4$$^-$,[43] the label is completely scrambled, implying rapid equilibration through the proposed mechanism 7.[24b] For the fluxional nitrosyl hydride

$$ (7) $$
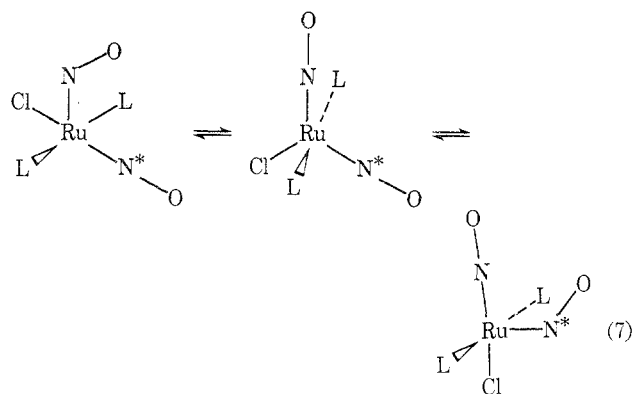
systems RuH(NO)L$_3$,[29] rapid interconversion between the TBP-axial NO structure of VIII and one in which two of the phosphines remain equivalent suggests the possible intermediacy of a SP-apical NO structure which would necessitate nitrosyl bending. Finally, Collman and coworkers have described a "paradox" in explaining two different nitrosyl stretching frequencies observed in complexes Co(NO)Cl$_2$L$_2$, where L is tertiary phosphine.[44] These complexes appear to undergo intramolecular redox reactions involving nitrosyl bending in solution and on solid surfaces, although a structure determination of a typical member of the series, Co(NO)Cl$_2$(P-MePh$_2$)$_2$, reveals only one isomer in the bulk crystal.[44]

The significance of the interconversion of linear and bent NO's lies in the transfer of the electron pair between the metal and the nitrosyl, allowing the

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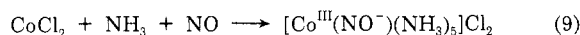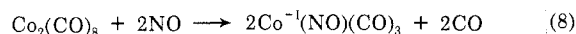(42) C. A. Reed and W. R. Roper, *Chem. Commun.*, 1459 (1969).

(43) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, **93**, 1788 (1971).

(44) C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, **12**, 1304 (1973).

metal center to achieve coordinative unsaturation in a unique way.[9] Since this is a prime criterion in catalytic activity,[10] it has been suggested that NO can activate a metal center more so than the corresponding carbonyl which exhibits no tendency to bend.[9] Catalytically active group VIII nitrosyls include $MH(NO)L_3$ (M = Ru, Os),[29] $Rh(NO)(PPh_3)_3$,[9] and $Fe(NO)_2(CO)_2$[45] in reactions such as hydrogenation, isomerization, and diolefin dimerization, but as yet no definitive link between catalytic activity of nitrosyls and NO bending has been established. Further study in this vein is clearly warranted.
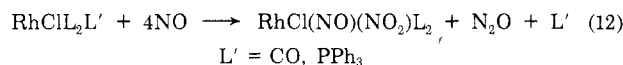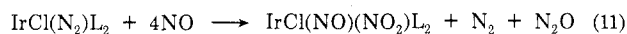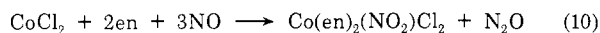
Reactions of Nitric Oxide Promoted by Metal Complexes

The simplest interaction of NO with transition metal ions is that leading to the formation of nitrosyls in which the NO ligand coordinates in either the linear or bent manner, as illustrated by reactions 8 and 9.[6,7] In analyzing the more complex reactions

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co^{-I}(NO)(CO)_3 + 2CO \quad (8)$$

$$CoCl_2 + NH_3 + NO \longrightarrow [Co^{III}(NO^-)(NH_3)_5]Cl_2 \quad (9)$$

below, the initial formation of a nitrosyl species will be assumed.

Examples of nitric oxide disproportionation promoted by metal complexes in solution are now well established and are exemplified by reactions 10–13

$$CoCl_2 + 2en + 3NO \longrightarrow Co(en)_2(NO_2)Cl_2 + N_2O \quad (10)$$

$$IrCl(N_2)L_2 + 4NO \longrightarrow IrCl(NO)(NO_2)L_2 + N_2 + N_2O \quad (11)$$

$$RhClL_2L' + 4NO \longrightarrow RhCl(NO)(NO_2)L_2 + N_2O + L' \quad (12)$$

$$L' = CO, PPh_3$$

$$IrBr(NO)_2L_2 + 2NO \longrightarrow IrBr(NO)(NO_2)L_2 + N_2O \quad (13)$$

(L = PPh_3),[46-48] in which the product NO_2 remains coordinated to the metal center. Reaction 10[46] is the most easily comprehensible since it is unencumbered with additional steps or complicating side reactions. In (10), the initial formation of the bent nitrosyl species, $[Co(NO)(en)_2Cl]Cl$,[49] is followed first by electrophilic attack of free NO on the coordinated NO^- and subsequently by reaction with a second NO molecule leading to products.[46] It is uncertain whether initial NO attack is through the nitrogen or oxygen end of the molecule (the dipole moment of NO is only 0.16 D), but the fact that the product nitro complex and the reactant Co(III)NO^- species in (10) have the same stereochemistry is proposed as supporting the notion that the Co–N bond remains intact throughout the reaction sequence and that the free NO molecule attacks the bent nitrosyl with its oxygen end.[46]

Reactions 11–13 may also proceed by electrophilic attack on a bent nitrosyl, but initial NO substitution is needed in (11)[47] and (12)[48] to yield the common reactive system $M(NO)_2XL_2$ (IX) which is suggested by the occurrence of reaction 13.[47] Since IX has two more valence-shell electrons than $Ru(NO)_2Cl(PPh_3)_2^+$ (VI), it must have at least one bent

Scheme I

IXa

IXb
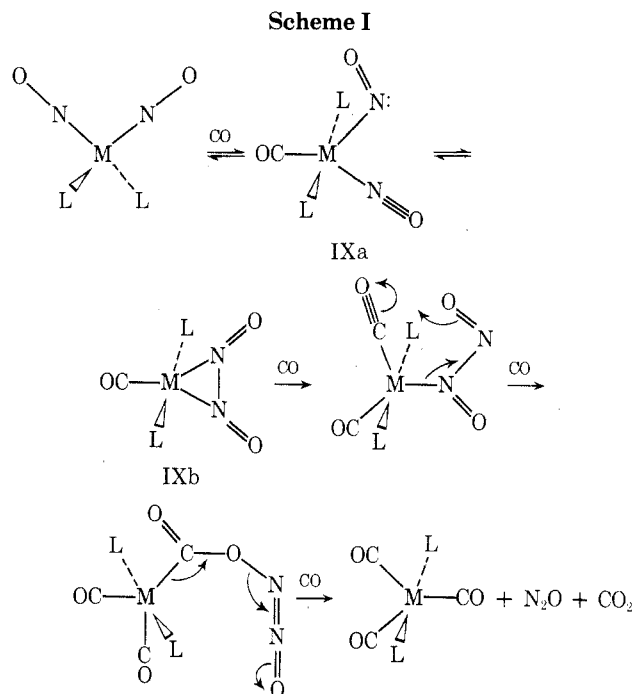
nitrosyl which can serve as the reactive site in the NO disproportionation reaction. Alternatively, Ibers and Haymore[47] have proposed that, in systems such as IX, the two nitrosyls function as a cis dinitrogen dioxide ligand. An equilibrium between $M(N_2O_2)$ and $M(NO^+)(NO^-)$ can then be envisioned to connect these two formulations (i.e., XIa $\rightleftharpoons$ XIb) and explain the observed reaction chemistry.

In 1973 Johnson and Bhaduri[50] showed that the dinitrosyl complex $Ir(NO)_2L_2^+$ reacts with CO reducing the nitrosyl ligands to N_2O and forming CO_2 via reaction 14. This reduction of coordinated NO has re-

$$Ir(NO)_2L_2^+ + 4CO \longrightarrow Ir(CO)_3L_2^+ + N_2O + CO_2 \quad (14)$$
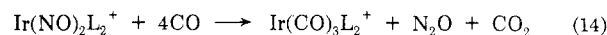
cently been extended to other dinitrosyl systems.[47] In rationalizing reaction 14, Johnson and Bhaduri[50] proposed a mechanism involving a nitrene intermediate, but since the initial addition of CO to $Ir(NO)_2L_2^+$ results in a complex isoelectronic with IX, an alternative mechanism based on $M(NO^+)(NO^-)$ or $M(N_2O_2)$ becomes plausible, as in Scheme I.[50a] By reacting the product complex with NO, the reactant dinitrosyl can be regenerated and a continuous catalytic cycle becomes possible.[50]

Reactants of Nitric Oxide Catalyzed by Metal Complexes

The use of homogeneous catalysts to effect conversion of NO into less noxious products is a recent and environmentally significant development in the coordination chemistry of nitric oxide. Inspired by the report of reaction 12 in which a Rh(I) complex is apparently oxidized to Rh(III) by NO[48] (the nitrosyl ligand in the product appears to coordinate as NO^-)

(45) J. P. Candlin and W. H. Hanes, *J. Chem. Soc. C*, 1856 (1968).
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(50a) Johnson, Bhaduri, and coworkers have recently revised their mechanistic proposal [*J. Chem. Soc., Chem. Commun.*, 809 (1974)] to coincide with that of Ibers and Haymore[47] involving a M–(N_2O_2) intermediate based on certain isotope labeling experiments. However, careful analysis of their data renders proof of this mechanism inconclusive at this time.

Table II
Reduction of NO by CO Catalyzed by Solutions of $[Rh(CO)_2Cl_2]^-$

Run	Catalyst solution[a]	Time, hr	ΔP_{NO}[b]	ΔP_{CO}	P_{CO_2}	P_{N_2O}
I	$RhCl_3 \cdot xH_2O$	20.5	110	66	52	39
II	$Ph_4As[Rh(CO)_2(Cl)_2]/4ml$ of HCl	23	314	149	138	128
III	$[Rh(CO)_2(\mu\text{-}Cl)]_2/4$ ml of HCl	23	316	149	138	120
IV	Recharge of run II	23	304	143	145	125
V	$Ph_4As[Rh(CO)_2Cl_2]$	23	47	33	9	14
VI	$Ph_4As[Rh(CO)_2Cl_2]/\sim 40$ mmol of HCl gas	21.5	46	16	9	5
VII	$Ph_4As[Rh(CO)_2Cl_2]/3$ ml of H_2O	23	243	100	98	91
VIII	$Ph_4As[Rh(CO)_2Cl_2]/1.8$ ml of H_2O and 1.4 g of LiCl	23	167	79	80	71
IX	$Ph_4As[Rh(CO)_2Cl_2]/6.3$ ml of 70% $HClO_4$	24	262	129	139	117

[a] All solutions contained 1 mM Rh in 100 ml of ethanol. Amounts of other components are specified. Initial ratio of NO:CO was 4:3 unless otherwise stated. CO was added first. HCl refers to a 37% aqueous solution. [b] Partial pressures are in mmHg and were calculated from calibration plots using vpc with estimated errors of ±2% of reported values. ΔP_{NO} and ΔP_{CO} are the changes in partial pressure of reactant gases from $t = 0$ to the time indicated for each run; P_{CO_2} and P_{N_2O} are the partial pressures of the product gases at the end of the time period.

and the well-known reduction of $RhCl_3$ by CO according to eq 15,[51] we decided to investigate catalysis

$$RhCl_3 + 3CO + H_2O \longrightarrow$$
$$[RhCl_2(CO)_2]^- + CO_2 + 2H^+ + Cl^- \quad (15)$$
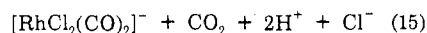
of the reduction of NO by CO using ethanolic solutions of $RhCl_3 \cdot xH_2O$. In this mixed-gas study, the reaction vessel was charged to an initial pressure of *ca.* 620 mm in a 4:3 NO:CO ratio and the reaction progress was monitored by gas chromatographic analysis of the gas mixture and by system pressure decrease. As shown in run I of Table II, catalysis of reaction 16 was indeed observed.[52] However, the

$$2NO + CO \longrightarrow N_2O + CO_2 \quad (16)$$
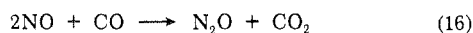
reaction was characterized by an 8–10-hr induction period during which the solution changed in color from dark red to olive green and only slow product evolution occurred.

With the finding that this induction period could be dramatically shortened either by reaction with CO prior to exposure to the mixed gases or by addition of aqueous HCl to the solution, it became apparent that initial reduction of $RhCl_3$ *in situ* according to reaction 15 was prerequisite to catalytic activity. Investigation of the catalytic properties of $[RhCl_2(CO)_2]^-$ confirmed this idea and established unequivocally that this species is the true catalyst in the $RhCl_3$ system.[53]

The results of our studies on the homogeneous $[RhCl_2(CO)_2]^-$ catalyst system are summarized in Table II. In contrast to run I, formation of the green catalytic intermediate from this anion (runs II and III) is complete within 2 hr. During the ensuing 6 hr conversion continues at a nearly uniform rate to consume 50% of the reactant gases, corresponding to the production of *ca.* 15 mmol of products per mmol of Rh, within the first 8 hr of exposure to the mixed gases. A marked decrease in the rate of product evolution is then observed with regeneration of the $[RhCl_2(CO)_2]^-$ anion which can be recovered in virtu-
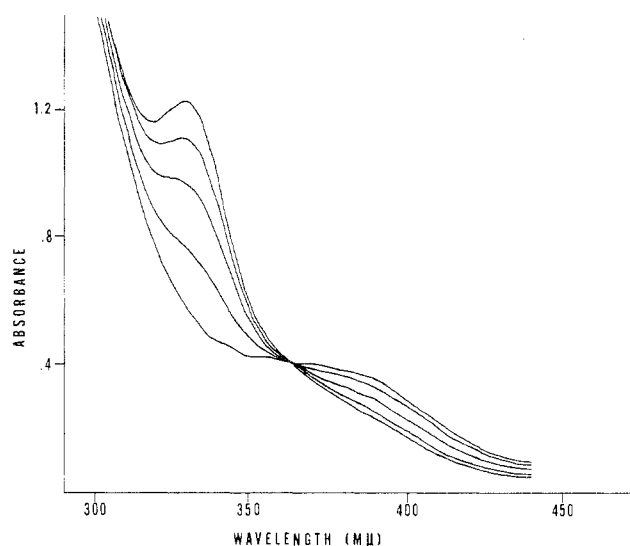

Figure 4. Ultraviolet absorption spectrum of a 0.628 mM catalyst solution of $(AsPh_4)[RhCl_2(CO)_2]$ in EtOH–HCl over 2 hr. The solution was stirred under CO–NO and sealed in a flow cell. The maximum at 332.5 nm (ϵ 3.05 × 10^3 l./(mol cm)) is characteristic of $[RhCl_2(CO)_2]^-$.

ally quantitative yield as its $AsPh_4^+$ salt. Alternatively, the system can be recharged with NO–CO (run IV), and the results of runs II and III repeated. The existence of an equilibrium between $[RhCl_2(CO)_2]^-$ and a presumed green catalytic intermediate was established from the isosbestic point at 360 nm obtained monitoring the uv spectrum of a dilute solution of the carbonyl anion charged under a CO–NO atmosphere as shown in Figure 4.

Since initial reaction of $[RhCl_2(CO)_2]^-$ under the mixed gases obviously involves NO substitution or adduct formation, we have investigated the reaction of $[RhCl_2(CO)_2]^-$ with NO alone and find that rapid stoichiometric evolution of CO_2 and N_2O occurs with the formation of a dark red solution which catalyzes the continued slow reduction of NO. This latter observation is consistent with the report by Stanko and coworkers[54] discussed below on the $RhCl_3$ catalyzed disproportionation of NO. Re-formation of $[RhCl_2(CO)_2]^-$ under CO is accompanied by N_2O and
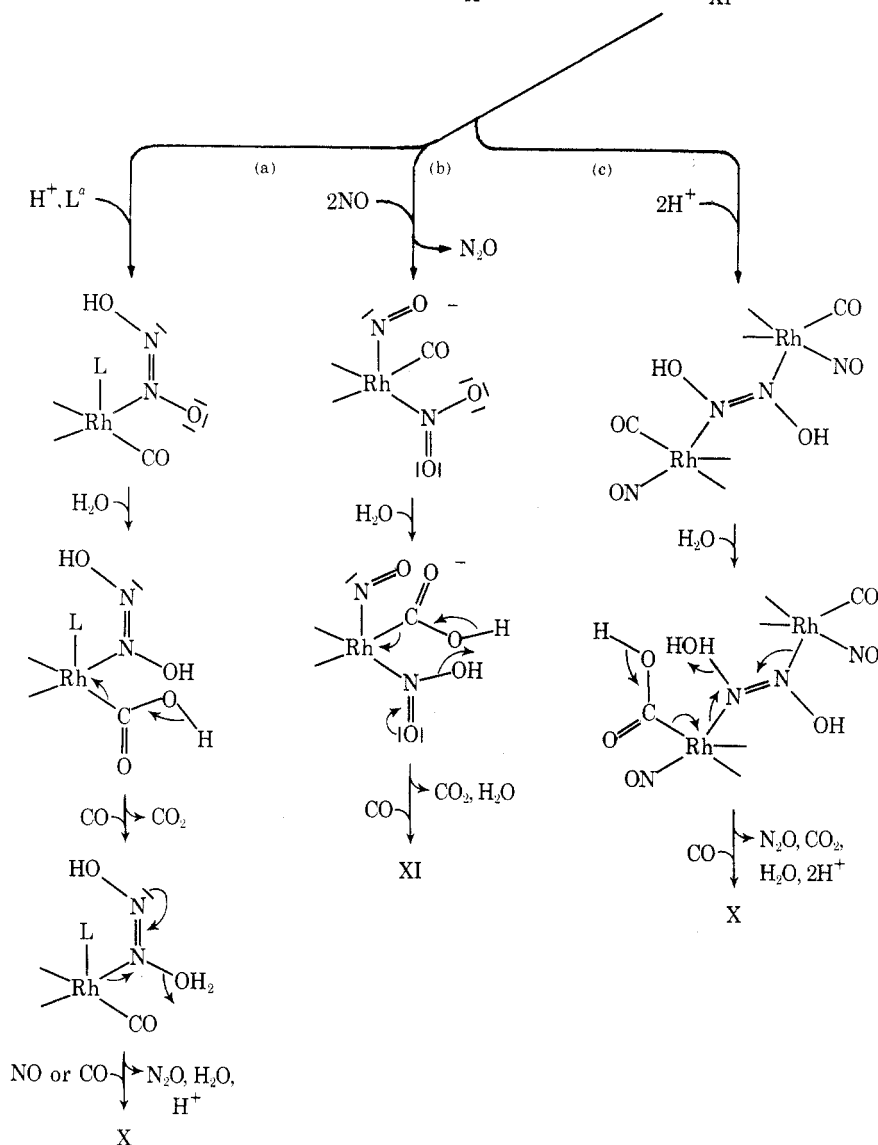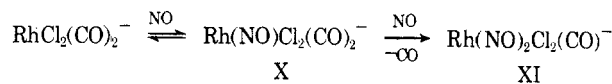
(51) B. R. James, G. L. Rempel, and F. T. T. Ng, *J. Chem. Soc. A*, 2454 (1969), and references therein; J. A. Stanko, G. Petrov, and C. K. Thomas, *Chem. Commun.*, 1100 (1969).
(52) J. Reed, Jr., and R. Eisenberg, *Science*, 184, 568 (1974).
(53) C. D. Meyer and R. Eisenberg, *J. Amer. Chem. Soc.*, submitted for publication.
(54) J. A. Stanko, C. A. Tollinche, and T. H. Risby, *Can. J. Chem.*, in press; J. A. Stanko, personal communication.

Scheme II

$$RhCl_2(CO)_2^- \overset{NO}{\rightleftharpoons} \underset{X}{Rh(NO)Cl_2(CO)_2^-} \overset{NO}{\underset{-CO}{\longrightarrow}} \underset{XI}{Rh(NO)_2Cl_2(CO)^-}$$

^{a} L = CO, NO, or ROH.

CO_2 evolution, and the reversibility of this reaction sequence, as suggested by Johnson and Bhaduri,[50] is fundamental to the observation of a continuous redox cycle in which both the carbonyl and nitrosyl species are precursors to the same catalytic intermediate formed in the presence of mixed gases.

The importance of water and acid in the catalytic process has been investigated (runs V–IX), and both are required for maximum activity. The requirement for water suggests intimate involvement in the catalytic cycle. In view of the established requirement for water in the formation of CO_2 *via* reaction 15[51] and the formation of water in the catalyzed disproportionation of NO described below,[54] it seems likely that water is both consumed in the oxidation of CO and produced in the reduction of NO.

Several mechanistic possibilities consistent with these observations are outlined in Scheme II, in which rapid formation of a nitrosyl adduct is followed by a slow substitution reaction to form the re-active dinitrosyl carbonyl intermediate, XI. Possible mechanistic pathways which lead to product evolution are shown as a–c in which oxidation of Rh concomitant with reduction of coordinated NO leads to the formation of species containing either coordinated hyponitrite, nitrite ion, or the corresponding acids. Incorporation of water followed by reductive elimination of CO_2 and acid-catalyzed decomposition of the oxy acids completes the cycle.

In order to ascertain the importance of binuclear intermediates in the catalytic cycle, we investigated the variation in reaction rate as a function of initial metal ion concentration. Using dilute solutions (less than 6×10^{-4} M) the product evolution curves were linear over at least a 20-hr period and the rate dependence on Rh was found to be first order.[53] While the transitory formation of dimeric species as depicted in path c cannot be excluded, it is apparent that the rate-determining step involves only monomeric species.

The likely involvement of dinitrosyls in the above catalytic cycle receives support from the report by Ibers and Haymore[47] in which catalysis of reaction 16 by $Ir(NO)_2(PPh_3)^+$ and other dinitrosyl complexes is observed. However, no mechanistic studies have been made as yet on these systems.[50a] With a view to understanding the interrelationship of structure and reactivity, we have investigated the catalytic properties of various phosphine– and diolefin–rhodium complexes in Me_2SO^{55} and find promotion of the reduction of NO by CO to be a rather general phenomenon. Included in this study were $[RhL_2Cl]_2$, $RhBrL_3$, $RhClL_3$, $RhCl(CO)L_2$, $[Rh(NBD)Cl]_2$, $[Rh(COD)Cl]_2$, and $Rh(NO)L_3$ (L = PPh_3; NBD = norbornadiene; COD = 1,5-cyclooctadiene). While none of the systems is as active as $[RhCl_2(CO)_2]^-$–(EtOH)–HCl, they all exhibit rapid product formation within the first 20 hr and approach the same slow limiting rate thereafter. Initial rapid product formation could *not* be reproduced on recharging these systems.

Recently Stanko and coworkers[54] have observed the catalyzed disproportionation of NO using ethanolic solutions of $RhCl_3$ to give N_2O and ethyl nitrite. A mechanism proposed by Stanko[54] involves the formation of a Rh^{III}–$(NO^+)(NO^-)$ intermediate followed by NO^- assisted attack of ethanol on NO^+ to give ethyl nitrite and the nitrosyl hydride ligand, HNO, which upon displacement and dimerization decomposes to give N_2O and H_2O. Alternative possibilities can be formulated, and the catalyzed disproportionation and reduction reactions may actually have steps in common.

Finally, Nunes and Powell[56] reported in 1970 the Cu(I)-catalyzed reduction of NO by $SnCl_2$. The reduction products were N_2O and hydroxylamine in ratios strongly influenced by Cu(I) and Sn(II) concentrations. The kinetic results were interpreted in terms of the formation of the catalytic intermediates Cl_3Sn–$Cu(NO)Cl_2^{2-}$, Cl_3Sn–$Cu(N_2O_2)Cl_2^{2-}$, and $[Cu_2(SnCl_3)_2Cl_4(N_2O_2)]^{4-}$, with the immediate precursors of both products being two-nitrogen species.

Concluding Comments

Studies in the coordination chemistry of nitric oxide over the last few years have been numerous, and significant progress has been achieved in establishing the structural systematics of metal nitrosyls, in developing a comprehensive bonding description of them, and in elucidating and exploring the reaction chemistry of coordinated NO.

A most intriguing aspect of nitrosyl chemistry which will command attention in the future will be the more complicated reactions of nitric oxide with metal complexes which go beyond the synthesis of M–NO bonds. That complexes in solution have been used as promoting agents and true catalysts for NO disproportionation and reduction seems only a beginning. Understanding how these reactions occur and applying that knowledge to the design of new, more efficient catalyst systems will be the goals of more exhaustive studies. Other avenues of inquiry will include extension to catalytically active complexes of the first transition series, the homogeneously catalyzed reduction of NO by other gaseous species, and perhaps the simultaneous reduction of NO and SO_2 by CO.

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Molecular Fragments or Chemical Bonds?

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The atom played the central role in early chemical theories. The properties of a molecule were related to those of its constituent atoms. Early additivity schemes were expressed in terms of atomic contributions.[1] Pauling's[2] electronegativity scale is an atomic concept, based on the premise that one can assign a relative value to the ability of an atom to attract electrons to itself when in chemical combination with another.

With extraordinary perception, Lewis[3] introduced the concept of an electron pair *bond*, and in doing so focussed attention on the interactions between atoms responsible for chemical binding. Quantum mechani-

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