ronments. It is also interesting to think about the species related to CrO_8^{3-} by one-electron reduction or oxidation. The b_1 orbital in which the lone electron resides is Cr-O antibonding and slightly O-O bonding. Thus CrO_8^{2-} should have a stronger metal-oxygen bond. To our knowledge this species is unknown. The NbO_8^{3-} ion in $KMgNbO_8 \cdot 7H_2O$ has been the subject of a crystallographic study.[62] It has a D_{2d} structure similar to that of CrO_8^{3-}, with Nb-O distances between 1.99 and 2.07 Å.

Acknowledgment. Our work was generously supported by the Advanced Research Projects Agency through the Materials Science Center at Cornell University and by the National Science Foundation. The stay of N. R. at Cornell was made possible by a fellowship from the Deutsche Forschungsgemeinschaft. We are grateful to E. L. Muetterties for his encouragement of this study.

Registry No. $(C_2H_4)_3Ni$, 50696-82-7; $(C_2H_4)_2Ni$, 52392-74-2; $(C_2H_4)_4Ni$, 52393-03-0; $(C_2H_4)_6Cr$, 52393-04-1; CrO_8^{3-}, 12526-97-5.

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[62] G. Mathern and R. Weiss, *Acta Crystallogr., Sect. B*, 27, 1598 (1971).

Contribution from the Departments of Chemistry, Cornell University, Ithaca, New York 14850, and Queen Mary College, University of London, London E1 4NS, Great Britain

Pentacoordinate Nitrosyls

ROALD HOFFMANN,* MAYNARD M. L. CHEN, MIHAI ELIAN, ANGELO R. ROSSI, and D. MICHAEL P. MINGOS

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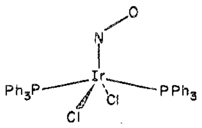
A molecular orbital model of pentacoordinate nitrosyls is constructed, based not on an NO^+-NO^- dichotomy but on a coherent MNO bonding scheme derived from the interaction of an ML_4 fragment of varying geometry with an NO. For $\{MNO\}^8$ species the model leads to the following conclusions: the better the σ- or π-donating capability of the basal ligands in a square pyramid, the more likely is the nitrosyl to bend. In compounds of the type $ML_2L'_2NO$, L trans to L, the nitrosyl group should bend in the plane containing the poorer donors. In a compound of the type $ML_2DA(NO)$, D = π donor trans to A = π acceptor, if the NO group bends in the DMA plane, then it should bend toward the acceptor. Limitations and a possible reversal of the usual view that a linear nitrosyl coordinates as NO^+ and a bent one as NO^- are presented. A nitrosyl ligand is less likely to bend in the equatorial position of a trigonal bipyramid than in the apical site of a square pyramid. If a nitrosyl in the equatorial position of a trigonal bipyramid bends, then it would prefer to do so in the axial plane rather than the equatorial one. Nitrosyl groups in axial positions in a trigonal bipyramid and basal sites in a square pyramid should be linearly coordinated. In ML_4NO species, if L are strong π-acceptor substituents, a trigonal bipyramid with an equatorial nitrosyl will be preferred. If the ligands are strong π donors, a range of geometries is possible, from a strongly bent square pyramid to a less bent trigonal bipyramid. A bent nitrosyl will move its nitrogen off the coordination axis in the direction of π coordination. Observed crystal structures are generally in accord with these theoretical inferences.

The aim of this paper is to present a coherent and comprehensive theoretical model of the electronic structure of pentacoordinate nitrosyls. Crystallographic and chemical studies have established an interesting range of coordination geometries for the NO ligand. For the pentacoordinate species of interest to us the predominant geometries are the square pyramid with a strongly bent apical nitrosyl ligand and trigonal bipyramid with a linear equatorial nitrosyl.[1] Representative of these are $IrCl_2(NO)(PPh_3)_2$ (**1**)[2] and $Mn(NO)(CO)_4$ (**2**).[3] Other structural types do occur, for instance a square pyramid with a linear basal nitrosyl in $Ru(Cl)(NO)_2(PPh_3)_2^+$ [4] or one with a linear apical NO in $Fe(NO)(S_2CN(CH_3)_2)_2$.[5] Moreover the demarcation line between square pyramid and trigonal bipyramid is not rigidly drawn, and several of the key compounds (*e.g.*, **1**, with a PIrP angle of 170° and a ClIrCl angle of 157°) are intermediate in structure. Nevertheless, it is useful to focus first on the geometrical extremes and then study their interconversions.



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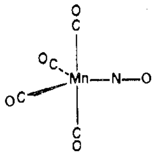

2

Our primary goal is an understanding of the electronic structure of these nitrosyl complexes. Given the wealth of structural data on these compounds, it is natural to focus initially on geometrical questions, exemplified by the following: Why do the nitrosyls bend, when they do? In compound **1** why is the bending in the sterically more hindered PIrP plane? If we can understand these matters, we can turn to predictive questions of the type: What pattern of ligand substitution can induce a nitrosyl ligand in a trigonal

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* To whom correspondence should be addressed at Cornell University.

(1) A recent comprehensive review of nitrosyl stereochemistry is given by B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Phys. Chem., Ser. One*, 11, 33 (1973). Earlier reviews are by B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966), and W. P. Griffith, *Advan. Organometal. Chem.*, 7, 211 (1966).

(2) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1035 (1971). The compound was synthesized by C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969), and by M. Angoletta and G. Caglio, *Gazz. Chim. Ital.*, 93, 1591 (1963).

(3) B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, 8, 1288 (1969). The compound was synthesized by P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83, 2593 (1961).

(4) C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, 92, 4760 (1970); C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1088 (1972).

(5) G. R. Davies, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 81 (1968); G. R. Davies, J. A. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970).

bipyramid to bend? The geometrical concerns are not our only ones. We would also like to understand how the reactivity of a nitrosyl is modified by coordination, and we would like to provide an account of the various physical properties, such as the photoelectron and infrared spectra of the compounds.

Valuable contributions to our understanding of the electronic structure of the nitrosyls have been made in several theoretical studies.[2,6-14] In the course of our discussion we will draw on these, as well as the work on pentacoordination[15] and metal-ligand fragments[16] done in our group.

It is common to consider the linear nitrosyls as complexes of NO^+ and the bent molecules as complexes of NO^-. That dichotomy may have heuristic value but will not be directly used in our studies. Since we are working in a molecular orbital representation, what will matter to us is the number, symmetry type, and relative energy of the orbitals contributed on one hand by the metal and its associated ligands and on the other hand by the nitrosyl group. The system brings a certain number of electrons into the interacted level scheme. What matters with respect to geometry is the bonding propensity (as a function of angle, as a function of substituent) of the levels occupied, not the source of the electrons which fall into that level scheme. Thus, if we simplify the nitrosyl to a doubly occupied N lone pair and an extra electron, a total of three electrons, then the electron count in the valence levels (3d on metal + four ligand donor orbitals + nitrosyl) is 18 for both **1** and **2**. Why one is linear and the other bent must be explicated from the details of the level structure.

The theoretical procedure we follow is twofold, combining symmetry arguments with extended Huckel calculations. The latter, whose details are given in the Appendix, were carried out on $Mn(NO)(CO)_4$ and two models for **1**, $Ir(NO)Cl_4^{2-}$ and $Ir(NO)Cl_2(PH_3)_2$. In further studies σ and π donors and acceptors were modeled by introducing pseudosubstituents, atoms with variable electronegativity and variable donor-acceptor capability.

We begin with the square-pyramid geometry of a hypothetical $ML_4(NO)$ where the nitrosyl is apical and the basal ligands L at this point are assumed to possess no π-bonding capability. A study of linear *vs.* bent NO is best approached by the construction of an interaction diagram between the ML_4 fragment and the nitrosyl. The basis orbitals are shown in Figure 1. At left are the familiar orbitals of a square-planar complex. A pyramidal distortion from D_{4h} to C_{4v} changes the composition of the levels little but does produce the energy trends indicated. The e level (*xz* and *yz*) moves up, as it becomes slightly metal-basal ligand antibonding. The z^2 level moves down, its antibonding somewhat relieved upon bending. The nitrosyl group is here reduced to its essentials—the donor orbital, a lone pair on N, somewhat delocalized, and that pair of superlative acceptor orbitals, the π^* levels. The energy of those π^* orbitals relative to the metal z^2 level will be seen later to be a crucial matter, but let us initially assume that z^2 is below π^*.

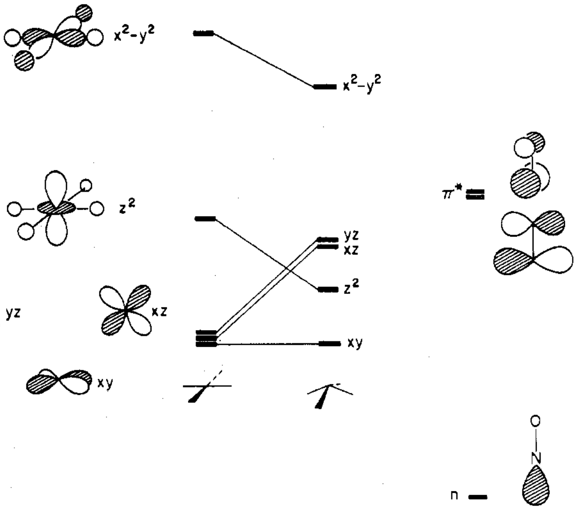

Figure 1. Left: energy levels and wave functions of a square-planar complex. Center: energy trends upon distortion from D_{4h} to C_{4v} schematically illustrated. Right: important orbitals of a nitrosyl ligand. The vertical energy scale is schematic.

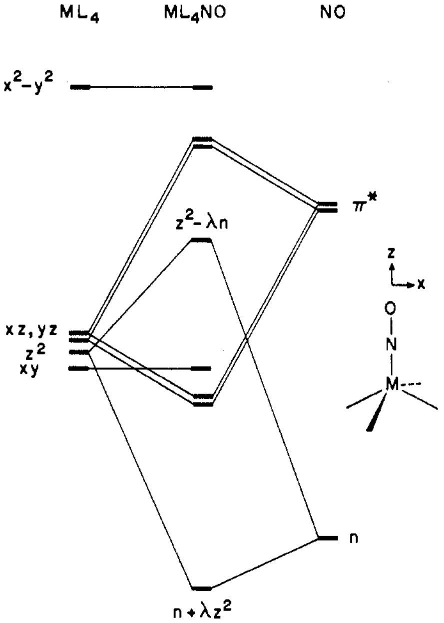

Figure 2. Interaction diagram for a linear nitrosyl in the apical position of a square pyramid.

Consider next the formation of the linear nitrosyl complex. Two strong interactions occur—the σ mixing between n and z^2 and the π interaction between degenerate π^* and metal *xz* and *yz*. This is shown schematically in Figure 2. At this point we can specify the occupation of the various levels. Irrespective of where the electrons originally came from or how we assigned them, there are a total of ten electrons (for compounds similar to **1** or **2**) in the above scheme. If we adopt the notation scheme used by Enemark and Feltham,[11-13] denoting the MNO fragment by $\{MNO\}^r$, where r is the num-

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(6) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).

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

(8) (a) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971); (b) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **12**, 199 (1973).

(9) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966); H. B. Gray, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, **84**, 3405 (1962).

(10) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **11**, 437 (1972).

(11) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, in press.

(12) R. D. Feltham and J. H. Enemark, *Theor. Chim. Acta*, in press.

(13) J. H. Enemark and R. D. Feltham, *J. Amer. Chem. Soc.*, **96**, 5003, 5004 (1974).

(14) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Amer. Chem. Soc.*, **96**, 2795 (1974).

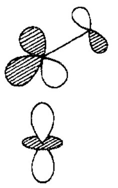
(15) A. Rossi and R. Hoffmann, to be submitted for publication; R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).

(16) M. Elian and R. Hoffmann, to be published.

ber of electrons associated with the metal d orbitals and the π^* orbitals of the nitrosyl, then both **1** and **2** are $\{MNO\}^8$ complexes. To make the correspondence with our interaction diagram one must omit from our electron count the pair of electrons in the nitrosyl n donor orbital.

We can proceed to assigning an energetic role to the various interactions. The n-z^2 interaction is a four-electron, closed-shell, destabilizing interaction.[17] If a geometric distortion is available to decrease that interaction, such a distortion will be utilized. The xz, yz-π^* interaction is stabilizing and will be maximized.

Now suppose the MNO angle is lowered from 180°, the NO group moving in the xz plane. Then z^2 will decrease its interaction with n, which is no longer collinear with the M-N bond. At the same time z^2 will begin a favorable stabilizing interaction with one of the NO π^* levels, π^*_{xz}. The latter interaction was symmetry forbidden in the linear coordination. These points are shown in **3**. In the course of the same bending the metal xz orbital goes up in energy—its π bonding with π^*_{xz} decreasing, while antibonding with n, absent in the linear geometry, it is now turned on. This is illustrated in **4**.



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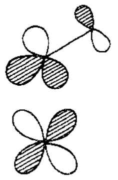


4

We have just constructed the essential features of a Walsh diagram for bending of a nitrosyl group in $ML_4(NO)$. The result is not novel, matching the conclusions reached by Mingos.[7] The actual diagram in Figure 3 for the model $IrCl_4(NO)^{2-}$ corroborates our qualitative conclusions. Whether a nitrosyl group is bent or not depends on two opposing factors: the slope of the z^2 level, which favors bending, and the slope of xz level, which favors linearity. There are several immediate corollaries of this picture. Unless otherwise stated these apply to $\{MNO\}^8$ systems.

1. The better the σ- or π-donating capability of the basal ligands, the more likely is the nitrosyl to bend. π-donor substituents will raise the energy of the xz (and yz) metal orbitals, as well as that of z^2. The higher z^2 lies, the stronger its stabilizing interaction, as it bends, with π^*_{xz}, the less its destabilizing interaction with n. The former dominates; thus a raising of the energy of the z^2 orbital favors bending. The higher xz, the less its destabilizing interaction with n and the greater its stabilizing interaction with π^*_{xz}. A higher position of the xz will lessen the preference of that orbital for the linear geometry. The net result of raising the energy of z^2 and xz through donor substitution is to favor bending. Conversely, basal substitution by acceptors such as carbonyls lowers the energy of z^2 and xz and tends to favor a linear nitrosyl. Our model calculations on square-pyramidal $IrCl_4(NO)^{2-}$, $IrCl_2(NO)(PH_3)_2$, and $Mn(CO)_4(NO)$ confirm this argument, making the last linear. It should be clear that the determining factor in the bending is the relative energy of the metal orbitals, z^2 and xz, relative to those of the nitrosyl n and π^*. The position of the former is predictably manipulated not only by the basal substituents but also by the position of the metal in the periodic table.

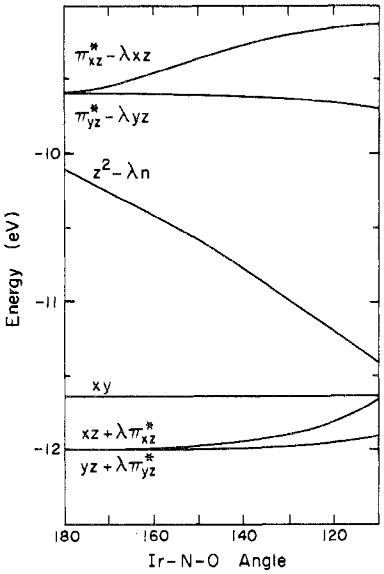


Figure 3. Calculated energy levels of $IrCl_4NO^{2-}$ as a function of the Ir-N-O angle. The labels identify the primary character of the MO, even though these orbitals are to various degrees delocalized.

The experimental evidence relevant to the influence of basal ligand donor properties on the M-N-O angle is indecisive. In part this is due to the ambivalent nature of most good ligands, which combine donor and acceptor properties, and in part to the lack of examples where donor or acceptor strength is continuously varied. One interesting series of structures is that with two dithiocarbamate ligands $Fe(NO)(S_2CNR_2)_2$ ($R = CH_3, CH_2CH_3$ [5,18]) and the related $Fe(NO)(S_2C_2(CN)_2)_2^{2-}$.[19] These are $\{FeNO\}^7$ complexes. Since there is only one electron in an orbital that favors bending of the nitrosyl, we would expect the MNO system to be less bent than in the $\{MNO\}^8$ species. The precise angle of bending is difficult to predict, because it must depend on the nature of the ligands. In those $\{MNO\}^7$ molecules which have been studied[19,20] the bending angle varies between 152 and 170°. We might mention here a single crystal esr study of $Fe(NO)(S_2CN(CH_2CH_3)_2)_2$ which confirms that the odd electron resides in a z^2 orbital.[20a] In $\{MNO\}^6$ complexes the z^2 orbital is empty. The conformational preference is set by the xz and yz orbitals, and the MNO grouping should be linear. The sole structure available, of $Fe(NO)(S_2C_2(CN)_2)_2^-$,[20b] confirms this.

An interesting set of structures are the nitrosyl complexes of the porphyrins. Nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt[21] has a Co-N-O angle of 135°, bent as would be expected for a $\{CoNO\}^8$, low-spin complex with the level ordering of Figure 3. The related nitrosyltetraphenylporphinatoiron[22] has an Fe-N-O angle of 149°.

2. In compounds of the type $ML_2L'_2(NO)$, L trans to L,

[17] L. Salem, *Proc. Roy. Soc., Ser. A*, **264**, 379 (1961); K. Muller, *Helv. Chim. Acta*, **53**, 1112 (1970).

[18] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967); L. Cambi and A. Cagnasso, *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, [6] 7, 13, 254 (1931).

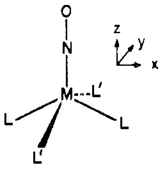
[19] (a) A. I. M. Rae, *Chem. Comm.*, 1245 (1967); J. Locke, J. A. McCleverty, E. J. Wharton, and C. J. Winscom, *ibid.*, 677 (1966). (b) A recent redetermination of the structure indicates an MNO angle between 152 and 168°: D. G. Van Derveer, A. P. Gaughan, Jr., S. L. Soled, and R. Eisenberg, Abstracts, American Crystallographic Association Meeting, 1973, Series 2, Vol. 1, p 190.

[20] (a) B. A. Goodman, J. B. Raynor and M. C. R. Symons, *J. Chem. Soc. A*, 2572 (1969); (b) cited in ref 19b.

[21] W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973).

[22] W. R. Scheidt and M. E. Frisse, to be published. We are grateful to J. L. Hoard for bringing this work to our attention.

the nitrosyl group should bend in the plane containing the poorer donors. Consider the effect of L′ being a better donor than L, with the L groups in the xz plane, as in **5**. The metal xz and yz orbitals will no longer be degenerate, and yz will come above xz. Both of these orbitals interact with π^* of the nitrosyl. Accordingly the π^* orbital in the linear geometry will split, with π^*_{yz} pushed above π^*_{xz}. This is shown in **6**. **6** is not a diagram for nitrosyl bending but rather a schematic representation of the level structure of a linear complex, with all ligands equivalent at the left and with two stronger donors in the yz plane at the right, as in **5**. Since the main stabilizing interaction which causes the bending is of z^2 with π^* on NO, that interaction may be maximized by bending in the xz plane, as in **7**.



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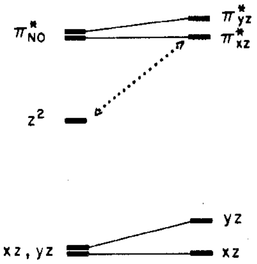

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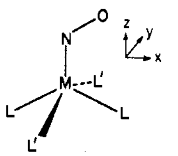

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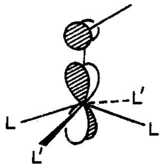
Our argument can be stated in another, simpler way. The better basal donor substituents make the metal a stronger donor in the plane of those donor substituents, here the L′ML′ or yz plane. As the nitrosyl bends, it loses one π interaction and keeps the other one. If it has a choice of which interaction to keep, it will keep the stronger one. This implies bending in the xz plane, the plane of the weaker donors, for in that mode, **8**, the yz-π^*_{yz} interaction is maintained.



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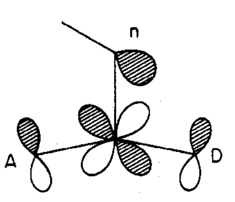
Our argument could alternatively be phrased in terms of the acceptor strength of the basal ligands, in which case we would say that bending will take place in the plane of the most effective acceptors. We should keep in mind, however, that true acceptors as basal substituents will, as noted above, discourage bending.

The electronic factor noted here and checked by some model calculations may explain the puzzling preference of the nitrosyl group to eclipse what appears to be the more sterically crowded Ph_3P-Ir-PPh_3 axes in $IrCl_2(NO)(PPh_3)_2$.[2] The preference for eclipsing certain bonds has already been noted by Mingos and Ibers.[2] In less symmetrical cases the effect is more difficult to analyze. Experimentally in IrI(CH_3)(NO)(PPh_3)$_2$[23,24] the NO eclipses the P-M-P axis, while in $RuCl(NO)_2(PPh_3)_2^+$,[4] $IrCl(NO)(CO)(PPh_3)_2^+$,[25] and IrI(NO)(CO)(PPh_3)$_2^+$ [25,26] that axis appears to be avoided. If the π-acceptor order Me < Cl < I < PR_3 << CO < NO is assumed, then the observed preferences can be rationalized. However, other effects may be operative in setting the sense of bending in these less clear-cut cases.

We include in our survey of structures even those which may be closer to a trigonal bipyramid than to a square pyramid. The tendency to eclipse a certain bond[27] may be due to the establishment of a better donor plane by basal ligand differentiation, or, as will be seen below, it may be due to the electronic effects of the distortion toward the trigonal-bipyramid extreme.

3. In a compound of the type $ML_2DA(NO)$, D = π donor trans to A = π acceptor, if the NO group bends in the DMA plane, then it should bend toward the acceptor. The crucial feature here is that the basal π-acceptor orbital mixes into xz in a bonding way, but the π-donor orbital mixes in an antibonding manner. The result is that there is a secondary node between xz and the basal donor orbital, but no such node on the acceptor side. Given that the NO bends, it will prefer to do so in such a way as to minimize the growing antibonding n-xz interaction, which is best accomplished by having n point toward the node, as in **9**. The same distortion better preserves the fading π^*_{xz}-xz bonding interaction by pointing the π^*_{xz} toward the nodeless side, as in **10**. The predicted bending direction is indeed observed in IrX(CO)(NO)(PPh_3)$_2^+$ (X = Cl, I[25,26]) and in $RuCl(NO)_2(PPh_3)_2^+$.[4] The sense of bending has been attributed to a direct O-NO (basal) interaction.[4]



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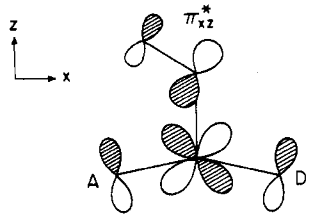

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Before we leave the square-pyramid geometry we must return to one important feature of the basic electronic structure of this geometry. Figures 2 and 3 are based on the assumption that the ML_4 fragment z^2 orbital is below the nitrosyl π^*. Let us trace carefully the consequences of that level ordering on the electron distribution in the molecule as the nitrosyl bends.

The z^2 orbital starts out in the linear geometry reasonably localized on the metal, but with some nitrosyl n mixed in an antibonding way. As the NO bends, it begins to interact more and more with nitrosyl π^*_{xz}. The following consequences ensue: (a) the NO bond weakens as the π^* orbital is populated; (b) the nitrosyl group as a whole gains electron density from the ML_4 fragment. The xz and yz orbitals show a different trend. They begin in the linear form with strong π bonding with the π^* orbitals of the nitrosyl group. As the nitrosyl group bends, half of that interaction is gradually lost. The expected trends are precisely the reverse of (a) and (b) above. In fact the effect as set by the z^2 orbital dominates. The primary reason for this is that the z^2 orbital is closer in energy to π^* than is the xz.

The conclusion reached above, that as the nitrosyl bends it becomes more negative, is in accord with the accepted picture of the linear ligand as NO^+ and the bent one as NO^-.

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(23) C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).

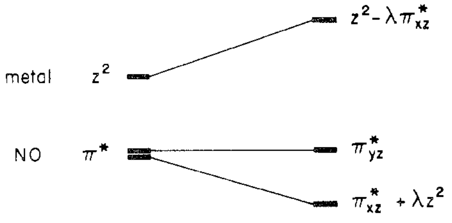
(24) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, 10, 1043 (1971).

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

(26) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 8, 1282 (1969).

(27) Our model calculations on bent $IrCl_4(NO)^{2-}$ and $Mn(CO)_4$-NO, in which the barrier to rotation of a nitrosyl is perfectly fourfold, yield a very small barrier of the order of 0.2 kcal/mol, favoring a staggered conformation. The observed structures, with the exception of nitrosyl-α,β,γ,δ-tetraphenylporphinatocobalt[21] are eclipsed.

It is interesting to note that the charge transfer as a function of bending need not necessarily be in the direction noted. Depending on the metal, its oxidation state, and the ligands, it is conceivable, as noted by Mingos and Ibers,[6] that the metal z^2 orbital enters the interaction picture above the π^* orbitals of the nitrosyl group. Let us trace the consequences of that hypothesis. The strong interaction is still between z^2 and π^*_{xz}. Interaction diagram **11** shows that *bending is still favored.*



11

Some of our general conclusions will change in case z^2 is above π^*, some will not. For instance, better basal donors which, as we argued above, raise the energy of z^2, now would decrease the tendency to bend because a rise in the energy of z^2, when it is above π^*_{NO}, actually diminishes the interaction of those two orbitals. One interesting reversal is in the sense of charge transfer. In the linear geometry we would begin by populating a nitrosyl π^* orbital, with much density on N and O and a weakened NO bond. It need not be that the M-N bond has been weakened, because two electrons have switched from a σ-antibonding MO (z^2-λn) to a π-antibonding one (π^*_{xz}-$\lambda(xz)$). As the nitrosyl bends, π^*_{xz} would begin to mix into itself some z^2 character. The result would be an interesting trend where the NO gets more positive as it bends and the NO bond becomes stronger. We checked some of these qualitative conclusions with detailed calculations on $Ir(NO)Cl_4^{2-}$ with two sets of parameters. The first, described in the Appendix, was the one that led to Figure 3. The second created a situation in which z^2 began above π^* of NO by arbitrarily raising all the metal Coulomb integrals by 1.5 eV. Interaction diagram **11** was checked by the calculation with these modified parameters. Figure 4 presents the charge distribution trends as a function of bending for both cases. We focus on the charges because ESCA studies may provide information on these[28] and thus indirectly on the relative position of z^2 and π^* NO levels.

We turn to an analysis of the nitrosyl group in a trigonal bipyramid. First we will look at this ligand in the equatorial position, since that substitution site is easily connected to the apical site in a square pyramid by a Berry pseudorotation.[15,29]

There is a minor initial problem with geometrical notation which should be clarified. The usual analysis of bonding in the trigonal bipyramid identifies the z axis with the threefold axis,[15] as in **12**. However, the correspondence with the square pyramid is more convenient if the trigonal bipyramid is reoriented with the z axis chosen along one equatorial ligand, as in **13**. In the latter coordinate system the metal d orbitals subduce the following representations in the reduced C_{2v} symmetry appropriate to nitrosyl substitution: z^2 and x^2-y^2, both a_1; xy, a_2; xz, b_1; yz, b_2.

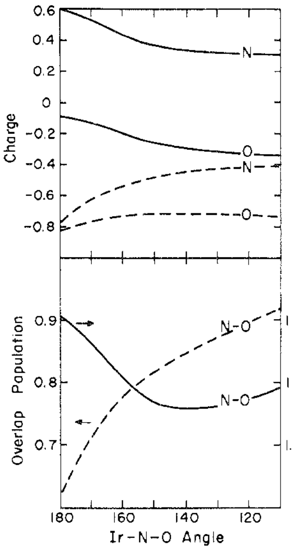


Figure 4. Charges on N and O (top) and NO overlap populations (bottom), as a function of bending. The solid lines refer to the "normal" parameters, which put z^2 below π^*_{NO}. The dashed lines refer to "modified" parameters, described in the text, which reverse the level ordering. Note two different scales for the overlap populations.

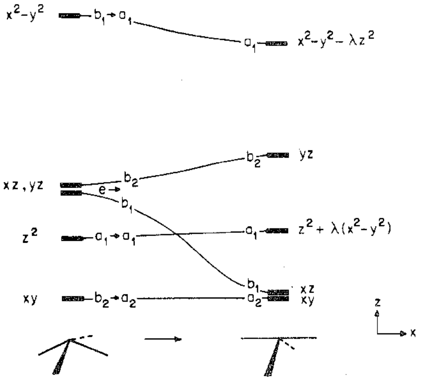
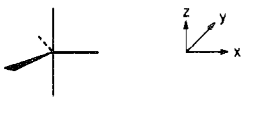


Figure 5. A schematic representation of the energy changes attending Berry pseudorotation in an ML_4 fragment.



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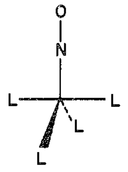

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Figure 5 shows schematically what happens to the molecular orbitals of a square-pyramidal ML_4 fragment in the course of a C_{2v} distortion to the ML_4 part of a trigonal bipyramid (**14** → **15**). The slopes of the various levels are easily understood. The z^2 orbital of **14** changes little in energy along the pseudorotation itinerary. The square-pyramid e orbital splits into a b_1 and b_2 pair. The xz orbital, b_1, moves to lower energy since it loses metal-ligand antibonding character, as shown in **16**. In fact, if the ligands were to carry no π orbitals, xz would be a pure metal orbital in the idealized

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15

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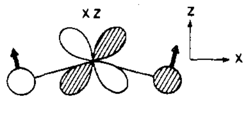
[28] C.-C. Su and J. W. Faller, *J. Organometal. Chem.*, in press.

[29] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); *Rev. Mod. Phys.*, **32**, 447 (1960). See also E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, **96**, 1748 (1974); E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

trigonal-bipyramid fragment geometry. On the other hand yz rises in energy as its antibonding interaction with the "equatorial" ligands increases; this is shown in **17**. We are now ready to bring in a linear or a bent nitrosyl group. The interactions are much the same as in the square pyramid geometry. The nitrosyl n orbital interacts in an antibonding way with z^2 while the nitrosyl π^* orbitals mix with xz and yz. The level scheme is much like that of Figure 2, except that the xz and yz levels are split, as detailed above. And it should be no surprise that the level interaction diagram is similar to the square-pyramid case, given the small atomic motions that the Berry pseudorotation entails.



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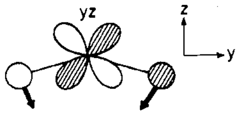
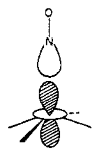


17

There is, however, one crucial difference between the linear NO geometries of the square pyramid and the trigonal bipyramid. The antibonding $z^2-\lambda n$ combination in the square pyramid, which it will be recalled was the controlling orbital for nitrosyl bending, is significantly higher in energy than in the trigonal-bipyramid geometry. The reason for this can be traced to the reduced symmetry of the trigonal-bipyramid fragment. In the square pyramid the z^2 orbital is the only metal orbital of a_1 symmetry. In the trigonal bipyramid fragment both z^2 and x^2-y^2 are of a_1 symmetry. They mix slightly in the fragment, but much more so when the nitrosyl comes in. The primary interaction in both the square pyramid and the trigonal bipyramid is between n and z^2, and it is antibonding. In the square pyramid, **18**, that antibonding cannot be avoided.[30] But in the trigonal bipyramid x^2-y^2 can also be utilized. The linear combination "z^2" + $(x^2-y^2) \sim 3z^2-r^2+x^2-y^2 \sim z^2-y^2$, shown in **19**, takes some electron density from the nitrosyl axis and puts it into the relatively harmless region along the y axis.[31]



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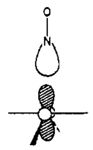
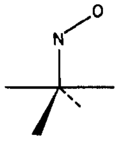


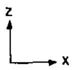
19

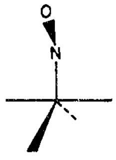
We proceed to draw the consequences of this level scheme for the trigonal bipyramid, equatorially substituted by a nitrosyl.

4. The nitrosyl is less likely to bend in the equatorial position of a trigonal bipyramid than in the apical site of a square pyramid. This follows from the lower energy of the z^2 orbital, analyzed above. Just as in the square pyramid it is the balance of the z^2 trend, favoring bending, and the movement of the xz and yz levels, favoring linearity, which must be superimposed. The balance is much closer in the trigonal bipyramid. Depending on the parameters we use for the metal orbitals, our calculations yield either a linear or a bent nitrosyl group in the model $\mathrm{IrCl_4(NO)^{2-}}$, but only a linear geometry in $\mathrm{Mn(CO)_4NO}$. The available crystal structures all show a linear or nearly linear nitrosyl group in $\mathrm{Mn(NO)(CO)_{4-x}(PPh_3)_x}$ (x = 0, 1, 2[3,32,33]), $\mathrm{Ru(NO)(Ph_2PCH_2CH_2PPh_2)_2^+}$,[34,35] $\mathrm{Co(NO)Cl_2(PCH_3Ph_2)_2}$,[36] $\mathrm{CoNO(C_6H_4[As(CH_3)_2]_2)_2^{2+}}$,[37] and $\mathrm{Os(NO)(CO)_2(PPh_3)_2^+}$.[38]

*5. If a nitrosyl in the equatorial position of a trigonal bipyramid bends, then it would prefer to do so in the axial plane, **20**, rather than the equatorial one, **21**.* This follows from the clear ordering yz above xz in Figure 5. The metal yz orbital is not only at higher energy, better able to interact with the π^*_{yz} of NO, but as a result of its σ-antibonding character it is hybridized toward the nitrosyl.[15,16] To put it another way, the distortion from a square pyramid to a trigonal bipyramid by itself, without differential ligand substitution, produces a characteristic difference between the xz and yz direction. The yz plane becomes the better donor plane. Thus as the nitrosyl bends, it should do so preserving the yz-π^*_{yz} interaction, which implies bending in the xz plane. This result, checked by model calculations, is also consistent with our general theory of substituent orientational preferences in pentacoordinate molecules.[15]







20 **21**

Among the bent nitrosyl structures there appear to be no perfect trigonal bipyramids. Yet, as mentioned above, many of the structures identified as square pyramids are in fact intermediate in geometry between the two extremes. In $\mathrm{IrCl_2(NO)(PPh_3)_2}$ the PIrP angle is 170°, while ClIrCl is 157°.[2] The bent nitrosyl eclipses the PIrP axis, which better approximates the axial locus of the trigonal bipyramid. A similar situation occurs in $\mathrm{IrI(CH_3)(NO)(PPh_3)_2}$[24] but not in $\mathrm{IrX(CO)(NO)(PPh_3)_2^+}$ (X = I, Cl[25,26]). $\mathrm{Co(NO)Cl_2(PCH_3Ph_2)_2}$ has a Co-N-O angle of 164° in the solid state. As slightly bent as it is, the direction of the bending is counter to the theoretical conclusion of this section as well as conclusion 2.

To complete our analysis of various substitution patterns we will look at an axial NO in a trigonal bipyramid and a basal NO in a square pyramid. These are again related by a Berry pseudorotation. The basal substitution and associated bending modes are of low symmetry—it is convenient to treat the more symmetrical trigonal bipyramid and then view the square pyramid as a perturbation thereof.

The natural coordinate system for a trigonal bipyramid is with the z axis along the threefold rotation axis, as in **22**. Note that this differs from our convention for equatorial substitution. The well-known energy levels of a trigonal-

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[30] Except by mixing in a little metal 4p character, which indeed happens.

[31] With our parameters the 3d contributions to this orbital in $\mathrm{IrCl_4(NO)^{2-}}$ partition approximately 65% z^2 and 35% x^2-y^2. Mingos[7] identified the corresponding a_1 orbital (his Figure 2c) as x^2-y^2.

[32] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967); W. Hieber and H. Tengler, *Z. Anorg. Allg. Chem.*, **318**, 136 (1962).

[33] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2339 (1968); R. F. Lambert and J. D. Johnston, *Chem. Ind. (London)*, 1267 (1960).

[34] R. E. Townsend, K. J. Coskran, and M. H. B. Stiddard, in footnote 4 of ref 35.

[35] C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3050 (1971); C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1094 (1972). See also ref 8b.

[36] 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).

[37] J. H. Enemark and R. D. Feltham, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3534 (1972).

[38] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Water, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 119 (1972).

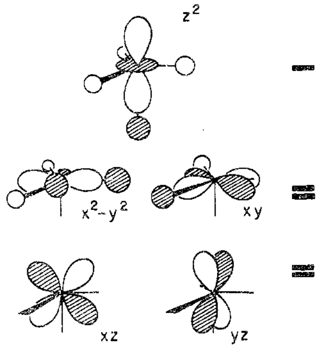
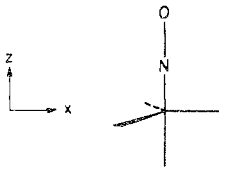


Figure 6. Schematic representations of the energy levels of a C_{3v} ML_4 fragment.

pyramidal fragment, 22, are shown in Figure 6. There is a low-lying degenerate *xz, yz* set, pure d in the absence of π interactions, followed by the x^2-y^2, *xy* orbitals, slightly metal-ligand σ antibonding, and finally the more strongly antibonding metal z^2 orbital.

22

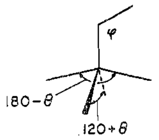


23

As the nitrosyl approaches linearly along the *z* axis, it will π bond strongly to the *xz, yz* set. Even though the C_{3v} symmetry allows an interaction with x^2-y^2 and *xy*, the linear pseudosymmetry of the interaction makes that mixing minimal. For five-coordinate $\{MNO\}^8$ systems the fragment z^2 orbital is unfilled. This is a very different situation from the apical square pyramid and the equatorial trigonal bipyramid. We have no analog in 23 of a z^2 orbital favoring bending. Instead the z^2 orbital actually helps to make the nitrosyl linear by virtue of its strong mixing with the NO n orbital. Moreover, as one bends, back-bonding between NO π^* and *xz* and *yz* is lost. There is a strong preference for a linear geometry. The basal site of a square pyramid is essentially a perturbation on the above scheme and also prefers a linear MNO bond. Thus: *6. Nitrosyl groups in axial positions in a trigonal bipyramid and basal sites in a square pyramid prefer to be linearly coordinated.*

The available structures are in accord with this conclusion. In $IrH(NO)(PPh_3)_3^+$ [6,23] and $RuH(NO)(PPh_3)_3$[35,39] the hydride was not specifically located but was inferred to lie trans to a linear NO along the axis of a distorted trigonal bipyramid. The two structures we know with nonequivalent nitrosyls, namely, $RuCl(NO)_2(PPh_3)_2^+$ [4] and $Os(OH)(NO)_2(PPh_3)_2^+$,[40,41] both possess a linear NO group in the base of a square pyramid.

We have treated the square pyramid and trigonal bipyramid separately, and now we must consider the surface connecting these extremes. It is not a simple surface, but let us reduce it to the two essential degrees of freedom—M-N-O bending and an idealized Berry pseudorotation. We constrain our system to C_s symmetry and define the two angular degrees of freedom as in 24: (1) a pseudorotation angle θ, such that



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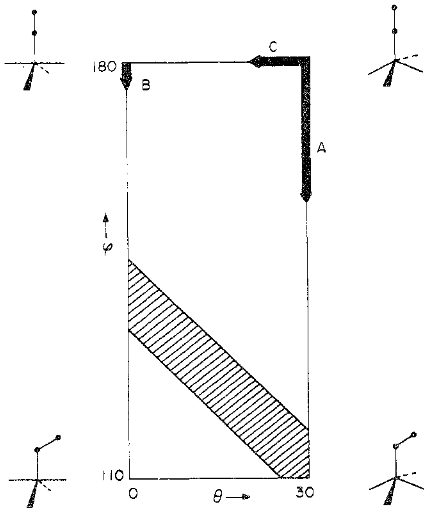
L_{ax}-M-L_{ax} is 180° $-\ \theta$ and at the same time L_{eq}-M-L_{eq} 120° + θ, and (2) a bending angle φ, the bending taking place in the axial plane. $\theta = 0°$ defines a trigonal bipyramid with an equatorial nitrosyl; $\theta = 30°$, a square pyramid with L-M-L = 150°.

What can we predict qualitatively about the shape of this surface and the effect of donors and acceptors thereon? It is easiest to begin with the case of strong donor substitution. We have already noted that the energy of the crucial z^2 orbital is lower in the trigonal bipyramid than in the square pyramid. This led to the conclusion that with strong donor substitution the nitrosyl would bend, but more so in the square pyramid than in the trigonal bipyramid. We can summarize this trend by arrows A and B in the schematic two-dimensional surface 25. We can also deduce that independent of donor or acceptor substitution the linear square pyramid will distort toward the linear trigonal bipyramid. The argument is as follows. From Figure 5 we see that the π-bonding ML_4 orbitals, *xz* and *yz*, split in the trigonal bipyramid, one moving up and one moving down. In their interaction with π^*_{NO} the net differential on distortion is small—what one interaction gains the other loses. The determining factor is once again the z^2 orbital. As explained above, even though it is at the same energy in the square-pyramid and trigonal-bipyramid fragments, it has a different composition, being less localized along the *z* direction in the trigonal bipyramid. Its antibonding interaction with nitrosyl n is then less in the trigonal bipyramid than in the square pyramid. Thus pseudorotation away from the square pyramid is favored for a linear nitrosyl. This is indicated by arrow C in 25.



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We can thus predict qualitatively the nature of this two-dimensional surface. The trends represented by A, B, and C in 25 translate into a set of contours that will produce a lowest energy in the region indicated by shading in 25. Where in that region the absolute minimum will lie we dare not predict. There should be a range of structures of similar energy combining the pseudorotation coordinate θ with the bending φ in the way indicated. If the region of

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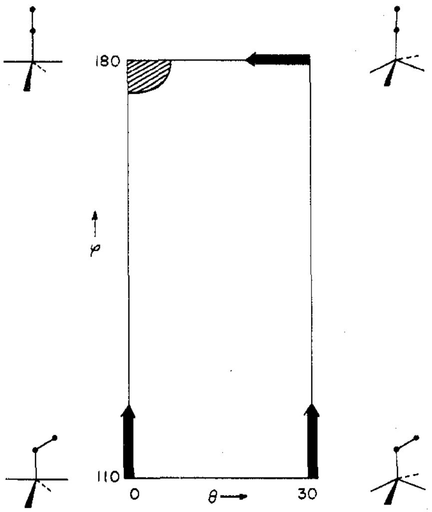
(39) S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3068 (1971).

(40) J. M. Waters and K. R. Whittle, *Chem. Commun.*, 518 (1971).

(41) K. R. Grundy, K. R. Laing, and W. R. Roper, *Chem. Commun.*, 1500 (1970).

similar energy is sufficiently great, then the solid-state structures may not even be good guides to the geometry of the isolated molecule.[29]

We turn to the other extreme—substitution by excellent π acceptors. As we noted previously, the tendency to bend will then be greatly diminished. Indeed the tendencies represented by arrows A and B may entirely disappear. In the limiting case the square pyramid and trigonal bipyramid will both prefer to remain linear. But the preference for the trigonal bipyramid represented by C will remain. The resulting surface, **26**, will contain a single minimum for the linear trigonal bipyramid. We summarize our conclusion:



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7. In ML_4NO species, if L are strong π-acceptor substituents, a trigonal bipyramid with an equatorial nitrosyl will be preferred. If the ligands L are strong π donors, a range of geometries is possible, from a strongly bent square pyramid to a less bent trigonal bipyramid.

Two model surfaces were calculated, one for $IrCl_4NO^{2-}$ and the other for $Mn(CO)_4NO$. The results are shown in Figure 7. The results generally confirm the qualitative analysis of **25** and **26**. The details cannot be considered in any way reliable, since these surfaces are unfortunately extremely sensitive to the parameters of the calculation, even to relatively small shifts in the energy of the metal 4p orbitals.

It is interesting that the calculated $IrCl_4(NO)^{2-}$ surface has its minimum energy at an intermediate point on the pseudorotation itinerary. This is probably partially due to the fact that we forced an "ideal" pseudorotation, making the increment in the L_{ax}-M-L_{ax} angle equal to that in the L_{eq}-M-L_{eq} angle. That constraint forced us into a C_{4v} structure with an apex-base angle of 105°, which is not necessarily optimum. Indeed our energy minimum in the $IrCl_4(NO)^{2-}$ model is for a smaller angle of 101° when the nitrosyl is linear. However, conclusion 5 also implies that if the basal ligands are free to distort, they will tend to move toward a trigonal bipyramid with the bent NO eclipsing the axial plane.

We also must mention the interesting consequences of a possibility alluded to earlier, namely, a reversal in the ordering of z^2 and π^*_{NO} in the square-pyramidal geometry. Such a reversal could occur upon strong donor substitution. Given that z^2 falls in energy on moving from the square pyramid to the trigonal bipyramid, we think that even if the conditions were created for z^2 above π^*_{NO} in the square pyramid, it is extremely unlikely that such an ordering would persist in the trigonal bipyramid. The result would be an effective level crossing along the pseudorotation coordinate, a large barrier for that simple process, and a very different charge distribution on either side of that barrier. A reversal of the ordering of z^2 and π^*_{NO} is a central theme in the important analysis of Enemark and Feltham.[11-13]

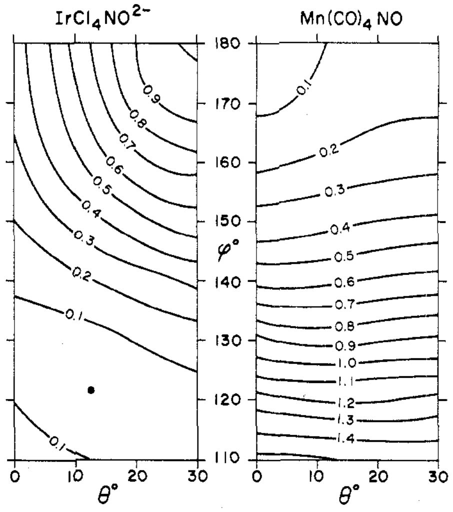
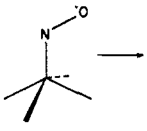


Figure 7. Calculated potential energy surfaces for Berry pseudorotation and bending in $IrCl_4NO^{2-}$ and $Mn(CO)_4NO$. The angles θ and φ are described in the text and structure **24**. The energy contours are in electron volts relative to the minimum energy points of the graph: $\varphi = 180°$, $\theta = 0°$ for $Mn(CO)_4NO$, the dark dot for $IrCl_4NO^{2-}$.

We next discuss a degree of freedom which has not entered our study before, namely, motion of a bent nitrosyl sideways, so that the M-N bond is no longer along the (approximate) fourfold axis of the ML_4 fragment. This is shown in **27** and **28**. This degree of freedom establishes a connection between the present discussion of the nitrosyls and the more general treatment of a diatomic ligand complexed to an ML_4 fragment. In a general discussion of the diatomic coordination problem, including O_2 and N_2 ligands, as well as CO and NO, the extreme of π coordination, **29**, must be considered.



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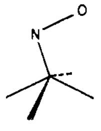

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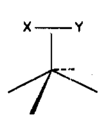

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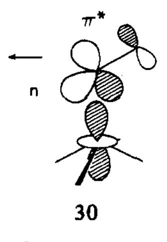
8. A bent nitrosyl will move its nitrogen off the coordination axis in the direction of π coordination, as indicated in **28**. The demonstration of this effect follows from the dominant role of the z^2 orbital. Its significant interactions are repeated in **30**. The destabilizing mixing with n, stabilizing interaction with π^* of NO, should be familiar by now. It is clear that a motion of the NO group as a whole to the left would lower the n-z^2 overlap and increase that of z^2 with π^*.



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The effect we seek is just perceptible in some of the crystal structures. In $IrCl_2(NO)(PPh_3)_2$ one N-Ir-P angle is 100.5°;

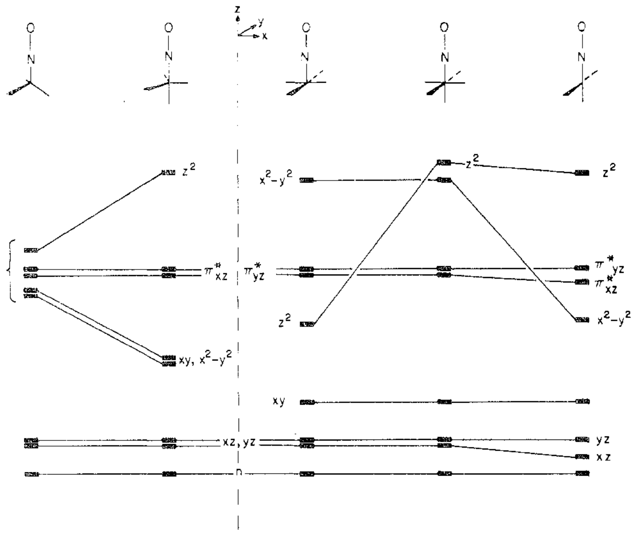

Figure 8. Level-ordering schemes. To the right of the dashed line are the orbitals of a flat square pyramid ML_4NO, with MNO linear and L bearing only σ-bonding orbitals. Next on the right there is shown a schematic representation of the effect of adding another ligand trans to the NO. At the extreme right two ligands along the *x* axis are removed to make a square-planar ML_3NO. To the left of the dashed line are the orbitals of a trigonal bipyramid ML_4NO, with NO axial. At the extreme left the orbitals of a tetrahedrally coordinated ML_3NO are constructed. The brace implies that the precise level ordering is uncertain. In all the level schemes we have focused on the crucial levels, leaving n, *xz, yz,* and *xy* at one level, even though these orbitals will in fact differ somewhat in energy in each coordination geometry.

the other is 89.3°.[2] In $IrI(CH_3)NO(PPh_3)_2$,[24] the similar N-Ir-P angles are 103 and 88°. A similar distortion has been noted for a nitrosylcobalt porphyrin derivative,[21] though in this situation a convincing case for the steric origin of the distortion was presented. Other bent nitrosyl structures do not seem to show this distortion.

Four- and Six-Coordinate Nitrosyls

Our discussion to this point has been confined to the pentacoordinate nitrosyls. The tetra- and hexacoordinate compounds have been discussed elsewhere,[6-8,11-13] and we may return to them on another occasion. However, it would be a pity to forego the opportunity that a detailed understanding of the electronic structure of the pentacoordinate species offers for a qualitative analysis of the bending tendencies of the species with one less or one more ligand.

Figure 8 carries the requisite information. At center of the figure is the level ordering of a square-pyramidal ML_4-NO, L being model ligands with σ-bonding capability alone, and a linear MNO grouping. For convenience, in the transition to an octahedron we take the square pyramid as flat. The level ordering is essentially that of Figure 2.

Consider the addition of another σ-bonding ligand to complete the octahedron. To a first approximation that ligand will perturb only the z^2 (really z^2-λn) combination, pushing it to higher energy. The level ordering z^2 above π^*_{NO} is likely,[6-8,11-13] and there would be expected a greater tendency for $\{MNO\}^8$ systems to bend. In our analysis it is the raised energy of the z^2 orbital which is responsible for the conversion of a linear nitrosyl in the five-coordinate $Co(NO)(das)_2^{2+}$ to a bent one in the six-coordinate NCS adduct $Co(NO)(das)_2NCS^+$.[37]

The octahedral level ordering in Figure 8 is a convenient starting point for the analysis of one limiting four-coordinate geometry, the square planar one. This is accomplished by removing two trans ligands, for instance those along the *x* axis. The primary consequence is a great depression of $x^2 - y^2$. Complexes satisfying the 18-electron rule, $\{MNO\}^{10}$, would have 12 electrons in the level scheme at the extreme right of Figure 8. Such molecules should be bent, a conclusion also reached by Enemark and Feltham.[11-13] However, all the available crystal structures of $Co(NO)(CO)_2(PPh_3)$,[42] $Co(NO)(CO)(PPh_3)_2$,[42] $Ir(NO)(PPh_3)_3$,[43] $Ir(NO)(CO)(PPh_3)_2$,[44] and $Ni(NO)(N_3)(PPh_3)_2$[45] show a quasi-tetrahedral coordination, albeit sometimes distorted toward square-planar coordination. We must then examine the level scheme of the tetrahedral four-coordinate system.

The tetrahedral level scheme is best derived from that of a trigonal bipyramid with an axial nitrosyl, by removing the other axial ligand (left side of Figure 8). This obviously stabilizes the z^2 orbital. The destabilization of the e set, $x^2 - y^2$ and xy, is not related to the removal of the axial ligand trans to the nitrosyl but rather is a consequence of the adjustment of a "flat" trigonal pyramid (N-M-L_{eq} angle 90°) to a tetrahedron (N-M-L_{eq} angle ~109.5°). The net result of these trends is that the tetrahedral geometry has z^2, xy, and $x^2 - y^2$ and the nitrosyl π* levels close to each other in energy. A number of level-ordering schemes are possible, and whether the $\{MNO\}^{10}$ complex bends or not should depend on which levels are occupied. The experimental structures cited above are all linear or nearly linear, with the exception of $Ni(NO)(N_3)(PPh_3)_2$, which has an intermediate MNO angle of 153°.[45]

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Appendix

The following geometries were used in our calculations. $IrCl_4NO^{2-}$ (square pyramid, NO apical): Ir-Cl = 2.348 Å, Ir-N = 1.94 Å, N-O = 1.03 Å, Cl-Ir-Cl = 157.6°, Ir-N-O = 120.0°. $IrCl_2(PH_3)_2NO$ (distorted square pyramid, NO apical): The geometrical parameters were those given for $IrCl_4NO^{2-}$, along with Ir-P = 2.367 Å, P-H = 1.42 Å, P-Ir-P = 170.2°, Ir-P-H = 109.47°. $Mn(CO)_4NO$ (trigonal bipyramid, NO equatorial): Mn-C = 1.80 Å, Mn-N = 1.80 Å, C-O = 1.13 Å, N-O = 1.03 Å.

The parameters for the extended Huckel calculations are summarized in Table I.

The metal d functions were taken as double-ζ functions:

Table I

Orbital	Slater exponent	H_{ii}, eV	Orbital	Slater exponent	H_{ii}, eV
H 1s	1.30	−13.60	Cl 3p	2.033	−15.00
C 2s	1.625	−21.40	P 3s	1.60	−18.60
C 2p	1.625	−11.40	P 3p	1.60	−14.00
N 2s	1.950	−26.00	Ir 6s	2.50	−11.36
N 2p	1.950	−13.40	Ir 6p	2.20	−4.50
O 2s	2.275	−32.30	Mn 4s	0.97	−9.75
O 2p	2.275	−14.80	Mn 4p	0.97	−5.89
Cl 3s	2.033	−30.00			

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for Ir 5d, $\zeta_1 = 5.796, c_1 = 0.6698, \zeta_2 = 2.557, c_2 = 0.5860$;[46] for Mn 3d, $\zeta_1 = 5.15, c_1 = 0.51392, \zeta_2 = 1.70, c_2 = 0.6929$.[47] The d orbital H_{ii}'s were Mn −11.67 eV, Ir −12.17 eV.

In the model studies of comparative donor properties we used a pseudochlorine atom with its 3p H_{ii} shifted up or down by 2 eV to simulate a better or poorer donor.

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Contribution from the Department of Synthetic Chemistry,
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

Novel Rhodium and Palladium Complexes from Benzoyl and Thiobenzoyl Isocyanates

SEIJI HASEGAWA, KENJI ITOH, and YOSHIO ISHII*

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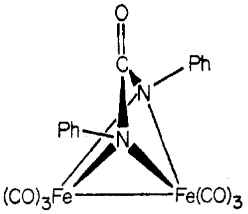
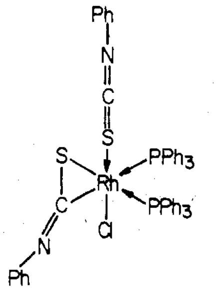
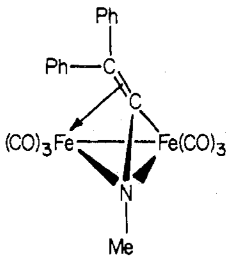
The reaction between benzoyl isocyanate and $RhCl(Ph_3P)_3$ afforded a complex $[RhCl(Ph_3P)_2(PhCONCO)]_2$ (**1**), which was converted to $[(bipy)Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (**2a**) by bipyridine and $NaBPh_4$. The latter complex was also obtained by the reaction of $[(bipy)Rh(cyclooctadiene)]^+BPh_4^-$, triphenylphosphine, and benzoyl isocyanate. An analogous palladium complex (bipy)Pd(PhCONCO) (**3**) was prepared in the reaction of Pd_2(dibenzylideneacetone)$_3$ with bipyridine and benzoyl isocyanate. 2-Phenylthiazoline-4,5-dione (**4**), a precursor of thiobenzoyl isocyanate, gave $RhCl(CO)(Ph_3P)_2(PhCSNCO)$ (**5**) in the reaction with either $RhCl(Ph_3P)_3$ or $RhCl(CO)(Ph_3P)_2$. A cationic complex $[(bipy)Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (**6a**) was also prepared from **4**. The similar reactions of Pd_2(dibenzylideneacetone)$_3$ with **4** and bipyridine or *o*-phenanthroline afforded $(\overset{\frown}{N\;N})$Pd(PhCSNCO) (**7**). Most of these novel complexes have a metallocyclic structure composed of M–O–C–N–C or M–S–C–N–C skeltons.

Introduction

No systematic investigations of the coordinating properties of benzoyl and thiobenzoyl isocyanates with low-valent transition metals have been reported, although some transition metal complexes of simple heterocumulene compounds were known.[1-5] Manuel originally reported $[(CO)_3Fe(PhNCO)]_2$ in the reaction of phenyl isocyanate with $Fe_3(CO)_{12}$;[1a] however, later structural investigations[1b-1d] concluded that the original complex was a diphenylurea complex of diiron hexacarbonyl. Similar types of urea complexes were isolated recently in the case of arylsulfonyl isocyanates.[1e] Baird and Wilkinson[2] prepared π- and S-bonded phenyl isothiocyanate complexes of nickel, palladium, platinum, rhodium, and iridium. The preparation and X-ray study of ketenimine complexes of iron were achieved by Otsuka.[3,4] Bycroft and Cotton[5] obtained carbodiimide-palladium(II) complexes with the formula $(RN{=}C{=}NR')_2PdX_2$. The representative structures of some transition metal complexes induced from simple heterocumulene compounds are shown below.

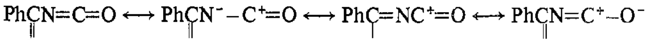






On the other hand, the five-membered metallocyclic complexes containing heteroatoms as the ring member have attracted much attention in recent years.[6-9] In particular, *N*-acylhydrazine or diazenes were found to be an excellent precursor to generate various five-membered metallocyclic systems (M-O-C-N-N), for instance, $[(PhCON{=}N)_2Cu]^+$,[6] $MoCl_2(NAr)(ArCON{=}NAr)(PhMe_2P)$,[7] $[(diphos)_2WCl(N{=}NCOR)]$,[8] and $Pt(Ph_3P)_2(PhCON{=}NCOPh)$.[9] The five-membered structure was definitely concluded by Ittel and Ibers[9] for the final complex by means of X-ray structural determination.

The following canonical structures (X = O or S) can be represented for (thio)benzoyl isocyanate and are corresponding to three possible modes of coordination.



$$\underset{\substack{\|\\ X}}{PhC}N{=}C{=}O \longleftrightarrow \underset{\substack{\|\\ X}}{PhC}N^-{-}C^+{=}O \longleftrightarrow \underset{\substack{|\\ X^-}}{PhC}{=}NC^+{=}O \longleftrightarrow \underset{\substack{\|\\ X}}{PhC}N{=}C^+{-}O^-$$

a b c

Our studies on the addition-elimination reactions of benzoyl and thiobenzoyl isocyanates with group IVb organometallic compounds disclosed a lot of interesting results indicative of the occurrence of the 1,4 addition of these hetero-

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