Structure and Reactivities of Six-co-ordinate First-row Transition-metal Nitrosyl Complexes

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A molecular-orbital study of the [ML_5(NO)] complexes [$Fe(CN)_5(NO)]^{2-}$, [$Mn(CN)_5(NO)]^{3-}$, and [$V(CN)_5(NO)]^{3-}$ as well as of the presently non-existent model compound [$FeCl_5(NO)]^{2-}$ has been made using the INDO approximation. It has been shown that the highest occupied molecular orbital (h.o.m.o.) is an orbital of π symmetry localised on the ligands and the lowest unoccupied molecular orbital (l.u.m.o.) is a degenerate π^* (MNO) orbital localised mainly on the nitrogen, but with varying amounts of metal and *cis*, but no *trans*, ligand character. Analysis of the composition of this l.u.m.o. orbital as a function of ligand electronegativity, number of electrons in the complex, and nature of the metal shows that nucleophilic attack or reduction at the nitrogen atom is favoured over the same reactions at the metal site for complexes to the right of the transition-metal series with a high formal charge on the metal. For four to six [metal $d + \pi^*$(NO)] electrons the site of nucleophilic attack or reduction is independent of the number of electrons, and of the nature of the L ligand. As the L ligand becomes less electronegative the contribution of *cis*-ligand orbitals to the l.u.m.o. orbital increases, and it is shown that addition of electrons to the l.u.m.o. results in the expected bending of the MNO group and destabilisation of the *cis* M–L bond in the plane of the MNO bending. Hence, with an electropositive L ligand, loss of a *cis* ligand is favoured by reduction or nucleophilic attack. The energy of the l.u.m.o. decreases with the number of electrons, with increasing electronegativity of the L ligands, and on going from left to right across the transition-metal series, making nucleophilic attack, at any site, more facile in the order given. It is shown that the *trans* influence of the NO ligand in these complexes cannot be measured by bond-distance data because the energy required for M–L bond-distance changes of up to 0.15 Å is extremely small. Overlap criteria cannot be used since they are dependent on the M–L distance assumed. Comparison of the total energy of [ML_5(NO)], *cis*-[ML_4(NO)], and *trans*-[ML_4(NO)] indicates that the *trans* M–L bond is stronger than the *cis* M–L bond in [ML_5(NO)] complexes.

OF the known nitrosyl complexes by far the oldest and most studied are the complexes of formula [$M(CN)_5(NO)]^{n-}$ (M = V, Cr, or Mn for $n = 3$; M = Fe, Ru, or Os for $n = 2$).[1-6] Of particular importance to the present work are two previous molecular-orbital studies of [$M(CN)_5(NO)]^{n-}$ complexes.[7-9] The study by Manoharan and Gray [7,8] focused on the electronic energy levels and spectra of the complexes, and has been used as the basis for the interpretation of the spectra of other six-co-ordinate mononitrosyls; such complexes will be referred to as [ML_5(NO)] complexes in the present work, charges being omitted for clarity. The study by Fenske and DeKock [9] focused on the metal–ligand bonding and has also been the basis of general interpretations of the bonding in [ML_5(NO)] complexes. Both of the cited studies stated that the occupied orbital of highest energy (h.o.m.o.) was the b_2 orbital, largely consisting of metal d_{xy} character, with some *cis* CN π character. However, there is recent evidence that the h.o.m.o. is not located on the metal,[10] but very largely on the CN ligands.[11] These results cast doubt on the previous spectral assignments and necessitate a complete reinvestigation of the energy-level diagrams.

The earlier studies [7-9] used fixed geometries taken from the then available *X*-ray crystal-structure determinations. There have been however a number of more recent structural studies of [ML_5(NO)] complexes, from which a rather varied picture has emerged. For complexes such as [$RuCl_5(NO)]^{2-}$,[12] [$Ru(NH_3)_5(NO)]^{3+}$,[13] or [$IrCl_5(NO)]^{-}$,[14] the *trans* M–L distance is significantly shorter than the *cis* M–L distance. For [$Fe(CN)_5(NO)]^{2-}$ the *trans* and *cis* distances are equal,[15,16] whereas for [$Mn(CN)_5(NO)]^{3-}$,[17] [$Cr(CN)_5(NO)]^{3-}$,[18] and (less certainly because of disorder) [$V(CN)_5(NO)]^{3-}$,[19] the *trans* distance is longer. Explanations for the short M–*trans* L distances in [ML_5(NO)] complexes have concentrated on the poor σ-donor and good π-acceptor characteristics of the linear nitrosyl ligand (formally NO^+) which shares metal orbitals with good σ-donor and poor π-acceptor (or even π-donor) *trans* ligands.[12-14,20,21] There has been no explanation for the long *trans* bond distances observed in [$M(CN)_5(NO)]^{3-}$ (M = V, Cr, or Mn). In order to test the available explanations an investigation of the total energy of [ML_5(NO)] complexes as a function of the various M–L distances is required.

When the previous two molecular-orbital investigations of [$M(CN)_5(NO)]^{n-}$ complexes were made it was known that [$M(CN)_5(NO)]^{2-}$ (M = Fe, Ru, or Os) took part in reactions in which a nucleophile attacked the nitrosyl N atom.[1,22,23] At that time such reactions were confined to those complexes; more recently it has been shown that a variety of other [ML_5(NO)] complexes undergo similar reactions.[6] It has also been found that some [ML_5(NO)] complexes undergo substitution of an L ligand on reaction with a nucleophile, with no apparent change at the NO ligand.[24] Also, on reduction of [ML_5(NO)] complexes by one electron, loss of an L ligand can occur.[3,4,25] An empirical attempt to predict the reactivity of [ML_5(NO)] complexes towards nucleophiles, at least for the type of reaction in which the nucleophile attacks the N atom of the NO ligand, has been made.[26] Although practically useful, it would be more desirable to be able to make predictions based on molecular-orbital energies and their atomic-orbital contributions.

In order to investigate all three of the above problems we have performed the necessary molecular-orbital calculations on $[V(CN)_5(NO)]^{3-}$, $[Mn(CN)_5(NO)]^{3-}$, and $[Fe(CN)_5(NO)]^{2-}$, as well as on a variety of presently non-existent models: $[FeCl_5(NO)]^{2-}$ (in most detail), $[FeX_5(NO)]^{2-}$ (X = H or F), $[Fe(CN)_5(NO)]$, and $[FeL_4(NO)]$ complexes.

METHODS

Calculations were performed by the INDO method, using $3d$, $4s$, and $4p$ orbitals for the transition elements and $2s$ and $2p$ orbitals for all other atoms except hydrogen, for which $1s$ was used. The program used, which was written by M. C. Zerner, J. E. Ridley, and A. D. Bacon, is a modified version of that given in ref. 27.

For $[Fe(CN)_5(NO)]^{2-}$, beginning with the published distances,[15] a series of calculations were performed in which each of the Fe–*trans* CN, Fe–*cis* CN, Fe–NO, C–N, and N–O distances were varied one at a time (C_{4v} symmetry being maintained, *i.e.* all *cis* distances were altered simultaneously), the other distances being held constant. The distance having the minimum total energy in each case was used for the next series of calculations. Successive iteration yielded the final minimum energy. For $[Mn(CN)_5(NO)]^{3-}$ and $[V(CN)_5(NO)]^{3-}$ the procedure was similar except that the C–N and N–O distances obtained from $[Fe(CN)_5(NO)]^{2-}$ were used as fixed quantities in the calculation. For $[FeCl_5(NO)]^{2-}$ the Fe–NO, Fe–*trans* Cl, Fe–*cis* Cl, and N–O distances were varied, starting with the distances from the structure of $[FeCl(PPh_3)(NO)_2]$.[28] The distances at which the total energy was a minimum are listed in Table 1 and compared to the values determined by *X*-ray diffraction. The agreement is as good as is generally observed using INDO or similar approximations.[29] In the calculations all angles were constrained to 180 or 90° as appropriate. In the known structures of $[ML_5(NO)]$ complexes the most striking deviation from the idealised symmetry adopted here is that the *cis* L ligands are always bent (as much as 10°) away from the NO ligand. A set of calculations for the $[M(CN)_5(NO)]^{n-}$ complexes using the exact distances and angles found in the *X*-ray structures showed that the assumption of idealised symmetry did not affect the conclusions.

TABLE 1

Calculated and observed distances (Å) for $[ML_5(NO)]$ complexes

	$[Fe(CN)_5(NO)]^{2-}$		$[Mn(CN)_5(NO)]^{3-}$		$[V(CN)_5(NO)]^{3-}$		$[FeCl_5(NO)]^{2-}$	
	m.o.	*X*-Ray [a]	m.o.	*X*-Ray [b]	m.o.	*X*-Ray [c]	m.o.	*X*-Ray [d]
M–N	1.52	1.653(5)	1.81	1.66(1)	1.62	1.66(4)	1.85	1.68
N–O	1.20	1.124(7)	[1.20] [e]	1.21(2)	[1.20] [e]	1.29(5)	1.17	1.14
M–*trans* C	1.81	1.918(6)	2.26	2.01(1)	2.18	2.19(1)	2.33 [f]	2.21
M–*cis* C [h]	1.73	1.932(3)	2.23	1.98(1)	2.14	2.14(1)	2.26 [g]	2.21
cis C–N [h]	1.24	1.15(1)	[1.24] [e]	1.16(2)	[1.24] [e]	1.13(2)		
trans C–N	1.24	1.15(1)	[1.24] [e]	1.16(2)	[1.24] [e]	1.15(1)		

[a] See ref. 16. [b] See ref. 17. [c] See ref. 19. The structure of this complex is disordered. [d] $[FeCl_5(NO)]^{2-}$ is not a presently known complex; the distances given are taken from the structure of $[FeCl(PPh_3)(NO)_2]$. See ref. 28. [e] Fixed distances, see text. [f] Fe–*trans* Cl. [g] Fe–*cis* Cl. [h] Average distances.

The force constants for the $[ML_5(NO)]$ complexes were obtained from the calculated energy against M–L distance curves, assuming a cubic form for the equation of the curve.

RESULTS AND DISCUSSION

The trans-*Influence of the Nitrosyl Ligand.*—Previous discussions of the *trans* influence of the nitrosyl ligand in $[ML_5(NO)]$ complexes have concentrated on the analysis of relative σ and π overlap in the M–*trans* L, M–*cis* L, and M–NO groups.[12-14,30] It was found that NO was a poor σ-bonding ligand. This allowed good σ bonding to the metal by the L ligand *trans* to NO (which shares orbitals with NO) as compared to the same L in the *cis* position. Because NO was also a good π-acceptor ligand, a *trans* L ligand such as Cl was also able to act as a better π donor than the corresponding *cis* L. Evidence for these effects was the short M–*trans* L distances, compared to the M–*cis* L, in complexes such as $[RuCl_5(NO)]^{2-}$,[12] $[Ru(NH_3)_5(NO)]^{3+}$,[13] and $[IrCl_5(NO)]^{-}$.[14] In order to test the usefulness of this evidence we have varied the M–L distances in the $[ML_5(NO)]$ complexes studied here by up to 0.20 Å on either side of the position at which the total energy was a minimum. The results are shown in the form of distance against energy curves in Figure 1. It is seen by comparing (*a*) with (*b*) and (*d*) with (*e*) that the shape of the curves is not greatly affected by the fixed M–L or M–NO distances adopted for the calculations.

The most obvious fact which emerges from the curves in Figure 1 is that a change of 0.1 Å in the M–*cis* L or M–*trans* L distance requires less than 10 kJ mol^{-1}. Hence, the *cis* to *trans* M–L bond distance ratio is of no use in assessing the relative bond strengths. This result is actually in agreement with the wide variation in *cis* and *trans* M–L distances in $[ML_5(NO)]$ complexes: from $[IrBr_5(NO)]^-$ in which the *trans* Ir–Br distance is 0.06 Å shorter than the *cis* distances,[14] to $[M(CN)_5(NO)]^{3-}$ (M = Mn[17] or Cr[18]) where the *trans* M–CN is 0.04 Å longer than the *cis*. The ratio of the observed *cis* to *trans* distances must be dependent on external packing forces to a greater extent than any differences which are due to inherent bond strengths.

That the distance–energy curves in Figure 1 are reasonable approximations to reality is shown when they are treated as potential-energy curves from which force constants may be calculated. Using the calculated distances for the $[M(CN)_5(NO)]^{n-}$ and $[FeCl_5(NO)]^{2-}$ complexes listed in Table 1, the curves yield the M–L stretching force constants listed in Table 2. To date no reliable force-constant values for $[M(CN)_5(NO)]^{n-}$ complexes are available. Therefore, the ν(M–CN) frequencies have been calculated assuming no coupling between a single M–CN stretching vibration and other vibrations.

These are compared with the observed frequency, where available, in Table 2. The agreement is satisfactory except for $[Fe(CN)_5(NO)]^{2-}$ where all calculated M–CN force constants are much greater than the true values.

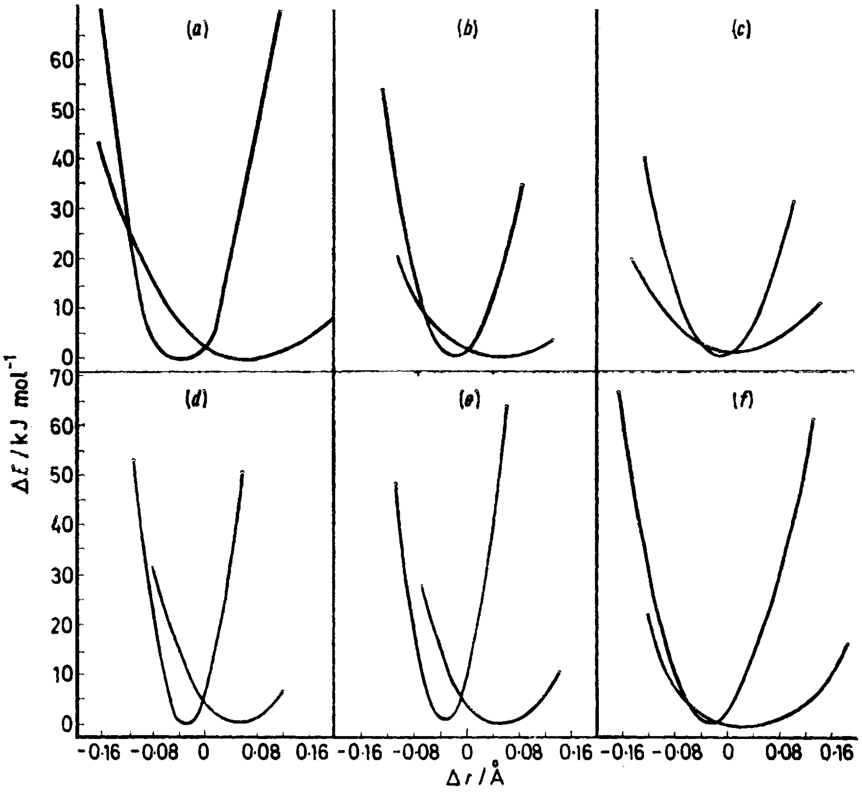

FIGURE 1 Calculated total energy plotted against *cis* or *trans* M–L distance for $[ML_5(NO)]$ complexes. In each diagram the curve of greatest slope is for the movement of four *cis* ligands, the shallow slope curve for the single *trans* ligand. During the movement of one *cis* or *trans* distance the other distances are fixed at the values given below (in Å). Curve (*a*): $[FeCl_5(NO)]^{2-}$, Fe–N = 1.75, N–O = 1.22, Fe–*trans* Cl = 2.34, Fe–*cis* Cl = 2.21; ΔE_0 = 154.892 31 a.u. (≡ 406.7996 MJ mol⁻¹), Δr_0 = 2.28. Curve (*b*): $[FeCl_5(NO)]^{2-}$, Fe–N = 1.85, N–O = 1.17, Fe–*trans* Cl = 2.33, Fe–*cis* Cl = 2.26; ΔE_0 = 154.892 31 a.u. (≡ 406.7996 MJ mol⁻¹), Δr_0 = 2.28. Curve (*c*): $[Mn(CN)_5(NO)]^{3-}$, Mn–N = 1.81, N–O = 1.20, Mn–*trans* C = 2.26, Mn–*cis* C = 2.22, C–N = 1.24; ΔE_0 = 156.863 19 a.u. (≡ 411.9758 MJ mol⁻¹), Δr_0 = 2.25. Curve (*d*): $[Fe(CN)_5(NO)]^{2-}$, Fe–N = 1.62, N–O = 1.22, Fe–*trans* C = 1.81, Fe–*cis* C = 1.73, C–N = 1.24; ΔE_0 = 167.277 08 a.u. (≡ 439.3263 MJ mol⁻¹), Δr_0 = 1.77. Curve (*e*): $[Fe(CN)_5(NO)]^{2-}$, Fe–N = 1.52, N–O = 1.22, Fe–*trans* C = 1.81, Fe–*cis* C = 1.73, C–N = 1.24; ΔE_0 = 167.289 61 a.u. (≡ 439.3592 MJ mol⁻¹), Δr_0 = 1.76. Curve (*f*): $[V(CN)_5(NO)]^{3-}$, V–N = 1.62, N–O = 1.20, V–*trans* C = 2.18, V–*cis* C = 2.14, C–N = 1.24; ΔE_0 = 146.94280 a.u. (≡ 385.9216 MJ mol⁻¹), Δr_0 = 2.17

It is clear that the potential-energy curves in Figure 1 are in the correct energy range.

The INDO approximation is not ideal for discussing overlap approaches to bonding since an artificial introduction of an overlap matrix is necessary. For comparison with earlier work an overlap population analysis was performed. It showed that overlap to both *cis* and *trans* L ligands was similar, and that the magnitudes of the *cis* and *trans* M–L bonds as measured by overlap criteria were dependent on the M–L distances. In general, overlap decreased as distance increased, though the cross-over point (*cis* to *trans* overlap ratio = 1.0 : 1.0) was not necessarily at equal *cis* and *trans* M–L distances. Since, as discussed above, the M–L distances can be varied independently at the expense of a few kJ mol⁻¹, it is clear that overlap arguments for either a strong *cis* or a strong *trans* M–L bond cannot be used. Nikol'skii and co-workers [21,30] used INDO calculations in coming to

TABLE 2

Force constants (Nm⁻¹) and frequencies (cm⁻¹) for $[ML_5(NO)]$ complexes

	Calculated				Observed [a]
Complex	$k_{M\text{-}trans\ L}$	$k_{M\text{-}cis\ L}$	$\nu_{M\text{-}trans\ L}$	$\nu_{M\text{-}cis\ L}$	$\nu_{(ML)}$
$[Fe(CN)_5(NO)]^{2-}$	497	646	740	640	469, 416
$[Mn(CN)_5(NO)]^{3-}$	242	228	482	386	453, 405
$[V(CN)_5(NO)]^{3-}$	181	228	422	386	*b*
$[FeCl_5(NO)]^{2-}$	189	315	385	454	422 [c]

[a] The M–L stretching frequencies are made up of $2A_1 + B_1 + E$ in C_{4v} symmetry; the frequencies given are for the A_1 vibrations; see M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372 for assignments. [b] Not known. [c] Calculated from the reported spectrum of $FeCl_4^-$, see L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 1960, 4473.

their conclusion that the *trans* Ru–Cl bond in $[\mathrm{RuCl_5(NO)}]^{2-}$ is stronger than the *cis*, but since they used an Ru-*trans* Cl distance which was shorter than the Ru-*cis* Cl, their argument may well be circular. Whether the approximation used by Fenske and DeKock (a modified CNDO procedure in which M–L overlap is implicitly included) suffers similarly is unknown. Their calculations used only one fixed set of distances.

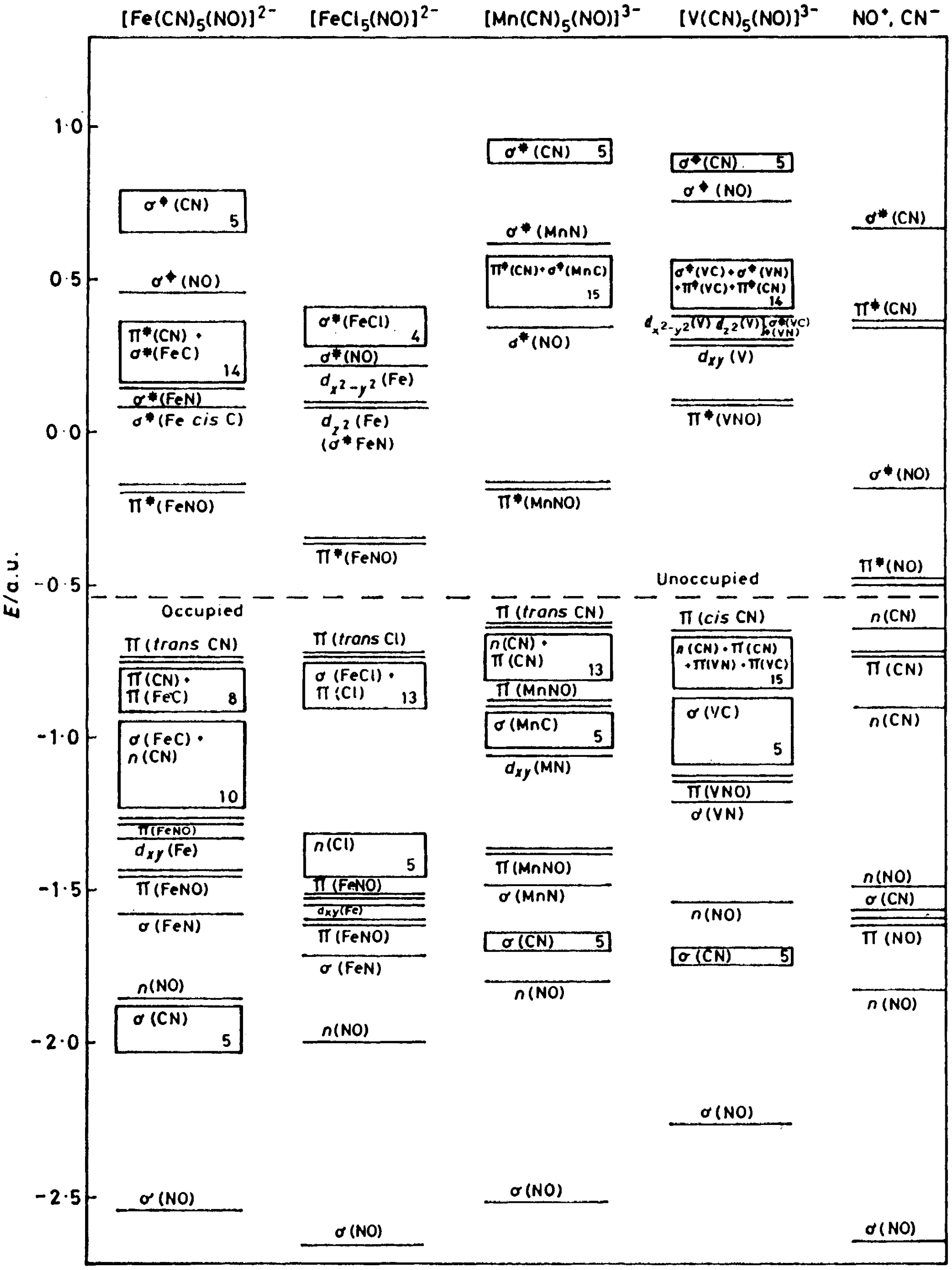

FIGURE 2 Energy levels in $[\mathrm{ML_5(NO)}]$ complexes

Some overlap results were independent of M–L distance and are therefore useful. The M–L π overlap was never more than 14% of the M–L σ value, in contrast to the M–NO π overlap which varied between 25% {for $[\mathrm{FeCl_5(NO)}]^{2-}$} and 75% {for $[\mathrm{V(CN)_5(NO)}]^{3-}$} of the σ value. Hence, though the CN ligand is potentially capable of competing with NO as a π-acceptor ligand, it in fact acts as an essentially pure σ donor in these complexes. This is because the π^* (CN) acceptor orbital is much higher in energy than π^* (NO) (see Figure 2). Also, although the M–NO σ overlap was always less than the M–L σ overlap, it was never less than 70% of the σ

M–L value. We believe this apparently high σ-donor capability of NO is simply due to the extremely short M–NO bond, which produces a high M–NO σ overlap independent of the inherent electropositivity of NO.

A further method for the determination of the relative strengths of the *cis* and *trans* M–L bonds is to compare the energy of *cis*- and *trans*-$[ML_4(NO)]$ complexes with $[ML_5(NO)]$. Such an approach also appears to have been adopted in the ' diatomic component of the total energy ' referred to by Nikol'skii *et al.*[21] In the present case the results show that it always required more energy to remove *trans* L than a *cis* L from $[ML_5(NO)]$, and this result is independent of the *cis* or *trans* M–L bond distances within the range investigated. This result therefore supports the idea that NO produces a strong *trans* M–L bond in $[ML_5(NO)]$ complexes.

The Energy Levels in the Complexes.—The energy levels in the $[ML_5(NO)]$ complexes are presented schematically in Figure 2. We note that in all cases the h.o.m.o. is an orbital of π symmetry localised almost completely on the L ligands. For $[V(CN)_5(NO)]^{3-}$ this orbital is localised on a *cis* ligand, for the other complexes {including $[FeCl_5(NO)]^{2-}$} on a *trans*. However, the small energy differences between the orbitals of π symmetry on the *cis* or *trans* ligands make it unwise to differentiate between them. This conclusion is independent of the M–L distances used, and is in agreement with theoretical and experimental studies by Nikol'skii *et al.* on $[RuCl_5(NO)]^{2-}$.[11,31] It is however in disagreement with previous calculations and interpretations of the spectra of $[ML_5(NO)]$ complexes in which an orbital mainly localised on the metal [d_{xy}, with some π (L) contribution] has been calculated or assumed as the h.o.m.o.[7,8,32–34] Since, as discussed more fully below, the unoccupied orbital of lowest energy (l.u.m.o.) can be well described as π^* (MNO), the lowest energy transition is best described as π(L)—π^* (MNO), *i.e.* mainly ligand-to-ligand charge transfer rather than *d-d*. Because of the approximate nature of INDO calculations we do not feel that a more detailed analysis is warranted.

One interesting test should be possible if our contention that the h.o.m.o. is a π orbital on an L ligand is correct. Oxidation of $[ML_5(NO)]$ complexes by one electron should not result in rapid decomposition of the complex since the oxidation involves a ligand not the metal centre. While reduction has been well studied, we have found only one report of the oxidation of a $[ML_5(NO)]$ complex, $[ReCl_2(NO)(PMePh_2)_3]$.[35] This gave a well behaved reversible oxidation wave followed by decomposition of the oxidised species with a half-life of 17 s. The product of decomposition was not established.

Reactions of $[ML_5(NO)]$ *Complexes.*—In general the chemistry of $[ML_5(NO)]$ complexes is dominated by reactions in which the complex behaves as an electrophile. Reactions with nucleophiles lead either to changes at the NO ligand, with retention of the M–N bond, or to replacement of an L ligand by the nucleophile. Examples are (1) and (2). Stepwise reduction of $[ML_5(NO)]$ complexes results in initial formation of a one-electron reduced species which loses a ligand at a rate which depends on the complex. Examples are (3)—(6). The rate constant for reaction (4) is 2.6×10^2 s^{-1},[4] and for reaction (6) 1.8×10^{-2} s^{-1}.[38] The structure of $[Fe(CN)_4(NO)]^{2-}$ has been determined; it is a square pyramid with a linear apical FeNO unit.[39] The product $[Ru(NH_3)_4(OH_2)(NO)]^{2+}$ is believed to be *trans*.[38] We will discuss these results later.

$$[Fe(CN)_5(NO)]^{2-} + 2OH^- \rightleftharpoons [Fe(CN)_5(NO_2)]^{4-} + H_2O \quad (1)\ (\text{ref. }1)$$

$$[RuCl(NH_3)_4(NO)]^{2+} + OH^- \longrightarrow [RuOH(NH_3)_4(NO)]^{2+} + Cl^- \quad (2)\ (\text{ref. }36)$$

The primary electrophilic reactions (1), (3), and (5) are clearly bimolecular. Ligand substitution reactions in six-co-ordinate complexes, of which reaction (2) is an example, generally tend towards a unimolecular mechanism.[40] However, the presence of a low-energy π^* (MNO) orbital in $[ML_5(NO)]$ complexes, which is not found in the usual complexes for which the mechanism of ligand substitution has been studied, make it not surprising that different reactions and mechanisms may occur. As will become apparent, a great deal of chemistry may be rationalised if it is assumed that the initial step in reaction (2) is bimolecular attack of a nucleophile; the actual mechanism is unknown.

$$[Fe(CN)_5(NO)]^{2-} + e^- \longrightarrow [Fe(CN)_5(NO)]^{3-} \quad (3)\ (\text{refs. }3\text{ and }4)$$

$$[Fe(CN)_5(NO)]^{3-} \longrightarrow [Fe(CN)_4(NO)]^{2-} + CN^- \quad (4)\ (\text{refs. }3\text{ and }4)$$

$$[Ru(NH_3)_5(NO)]^{3+} + e^- \longrightarrow [Ru(NH_3)_5(NO)]^{2+} \quad (5)\ (\text{refs. }37\text{ and }38)$$

$$[Ru(NH_3)_5(NO)]^{2+} + H_2O \longrightarrow [Ru(NH_3)_4(OH_2)(NO)]^{2+} + NH_3 \quad (6)\ (\text{refs. }37\text{ and }38)$$

All calculations, both here and previously,[7–9] clearly indicate that the l.u.m.o. is the doubly degenerate 9*e* orbital for the $[M(CN)_5(NO)]^{n-}$ complexes and 8*e* for $[FeL_5(NO)]^{2-}$ (L = Cl or F) complexes. This orbital is overwhelmingly π^* (MNO) in character. Hence, when $[ML_5(NO)]$ complexes behave as electrophiles, electrons are initially accepted into this orbital, and there are several consequences of this. The most obvious results from the degeneracy of the 9*e* (8*e*) orbitals. Acceptance of a single electron must, by the Jahn–Teller theorem, result in bending of the MNO group, or in some change in the geometry of the *cis* L ligands which removes the degeneracy. The product complex of a nucleophilic attack of the type represented by reaction (1) will of necessity be of lower symmetry, where the 9*e* (8*e*) orbitals are no longer degenerate.

The product obtained as a result of attack by a nucleophile or on reduction of the complex will depend on the orbital contributions to the 9*e* (8*e*) molecular orbital. Although in our calculations atomic orbitals were used for all ligands, the analysis is simplified if the contributions are referred to a formal MNO group made up of

M atomic orbitals and NO^+ molecular orbitals. Similarly, where L = CN, the molecular orbitals of CN^- provide the basis for discussing the ligand contributions. As has been discussed by Hoffmann and co-workers,[41,42] the interaction of the π orbitals on the metal with both the occupied π and unoccupied π^* orbitals on the NO^+ ligand must be considered. This interaction results in three doubly degenerate MNO fragment molecular orbitals. Two are occupied, of which one is located mainly on the metal and the other mainly on the oxygen atom, and one is unoccupied, it being located mainly on the nitrogen atom.† This latter is the $9e$ ($8e$) orbital referred to above, and the approximate metal, nitrogen, oxygen, and L ligand contributions to this $9e$ ($8e$) orbital are listed in Table 3 for the $[ML_5(NO)]$ complexes investigated here. The charge separation induced in the MNO fragment by interaction between the metal π orbitals and the π and π^* orbitals on NO^+ is enhanced by the σ donation of electrons from NO^+ to M, and further modified by the L ligand electrons. The results are the total formal charges on the individual atoms of the $[ML_5(NO)]$ complexes which are listed in Table 4. These charges should be considered as of relative rather than of absolute magnitude. From these Tables it is seen that the metal contribution to the $9e$ ($8e$) orbital is very low except in the cases of $[Mn(CN)_5(NO)]^{3-}$ and $[V(CN)_5(NO)]^{3-}$, and that for $[Fe(CN)_5(NO)]^{2-}$ and $[FeCl_5(NO)]^{2-}$ the MNO nitrogen atom carries the highest formal positive charge in the complex. We would therefore expect that nucleophilic attack or reduction would take place at the nitrogen atom in all cases except the manganese and vanadium complexes. For $[Fe(CN)_5(NO)]^{2-}$ (the only one of the iron complexes in Table 4 which has actually been prepared) a variety of electrophilic reactions in which a nucleophile attacks the nitrogen atom are known, of which reaction (1) is an example.[1] In the reduction product $[Fe(CN)_5(NO)]^{3-}$ the odd electron appears to reside mainly on the NO ligand;[1] we would expect this complex to have a bent FeNO group (its structure is unknown). For $[V(CN)_5(NO)]^{3-}$ the $9e$ orbital contains 41% V character and the V atom carries by far the largest positive charge in the complex. In this case nucleophilic attack or reduction will therefore occur at the metal. Nucleophilic attack at the metal could be accommodated in the case of $[V(CN)_5(NO)]^{3-}$ (though the high energy of the $9e$ orbital does not favour the reaction) since the metal formally has only 16 electrons (d_{xy} is empty). The direct reaction of CN^- with $[V(CN)_5(NO)]^{3-}$ has not been reported but the product which would be expected, $[V(CN)_6(NO)]^{4-}$, with a linear VNO group and a pentagonal-bipyramidal structure, is a known stable complex.[43] Reduction of $[V(CN)_5(NO)]^{3-}$ has not been reported, and in view of the high energy of the $9e$ orbital is unlikely to be easy.

TABLE 3

Contributions (%) to the l.u.m.o. orbitals of $[ML_5(NO)]$ complexes

Complex	M	N	O	*trans* C	*trans* N	*cis* C	*cis* N	Energy (a.u.)[a]
$[Fe(CN)_5(NO)]^{2-}$	7.5	66.9	5.4	0.0	0.0	13.2	6.6	−0.1914
$[Fe(CN)_5(NO)]^0$	5.5	59.6	5.8	0.2	1.5	18.5	8.2	−0.5258
$[FeCl_5(NO)]^{2-}$	0.5	76.0	13.0	0.0 [b]		10.4 [b]		−0.3541
$[Mn(CN)_5(NO)]^{3-}$	17.8	70.5	7.9	0.0	0.0	3.1	0.5	−0.1634
$[V(CN)_5(NO)]^{3-}$	41.0	51.8	3.3	0.3	0.7	2.2	0.6	0.0983
$[FeH_5(NO)]^{2-}$	0.3	60.0	10.2	0.0 [b]		29.5 [b]		−0.2442($4e$)
$[FeF_5(NO)]^{2-}$	3.2	82.4	13.3	0.0 [b]		0.9 [b]		−0.4289
NO^+		65.4	34.5	0.0		0.9		

[a] 1 a.u. ≡ 2.6263 MJ mol^{-1}. [b] *trans* or *cis* Cl, F, or H

TABLE 4

Total formal charges

Complex	M	N	O	*trans* C	*trans* N	*cis* C	*cis* N
$[Fe(CN)_5(NO)]^{2-}$	−0.619	0.787	−0.590	0.257	−0.787	0.470	−0.732
$[Fe(CN)_5(NO)]^0$	−0.346	0.661	−0.521	0.485	−0.498	0.398	0.343
$[FeCl_5(NO)]^{2-}$	0.941	1.039	−0.365	−0.792 *		−0.706 *	
$[Mn(CN)_5(NO)]^{3-}$	0.599	0.785	−0.527	0.067	−0.851	0.046	−0.814
$[V(CN)_5(NO)]^{3-}$	1.103	0.183	−0.713	0.045	−0.790	0.040	−0.747
$[FeH_5(NO)]^{2-}$	1.162	0.494	−0.507	−0.876 *		−0.578 *	
$[FeF_5(NO)]^{2-}$	1.589	1.209	−0.295	−0.923 *		−0.895 *	
NO^+		0.761	0.239				

* *trans* or *cis* Cl, F, or H.

For a $[ML_5(NO)]$ complex having formally 18 electrons around the metal and a high metal contribution to the $9e$ ($8e$) orbital, electrophilic behaviour would not be expected to lead to a stable species (see the correlation diagram in refs. 24 and 41) since the metal electron count would now be greater than 18. This situation can be relieved by loss of a ligand other than NO, the net result of the reaction being ligand replacement. We discuss below the factors which determine which ligand may be lost. For $[Mn(CN)_5(NO)]^{3-}$ the $9e$ orbital has 17% Mn character and the Mn and N charges are both positive and similar in magnitude. Hence, the site and products of electrophilic behaviour are difficult to predict. The

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† For $[V(CN)_5(NO)]^{3-}$ the two occupied orbitals have considerable CN character and the simple charge distribution description is not valid.

complex $[Mn(CN)_5(NO)]^{3-}$ is not apparently susceptible to nucleophilic attack at the nitrogen and its reduction occurs only at such negative potentials that complete complex decomposition occurs.[2] Another complex which behaves in a manner similar to that discussed here is $[RuCl(bipy)_2(NO)]^{2+}$ (bipy = 2,2'-bipyridyl) which can be attacked at the nitrogen atom by a variety of nucleophiles and reduced to $[RuCl(bipy)_2(NO)]^{+}$ in which the odd electron lies on the nitrogen atom.[6,44-46] Again, we predict a bent RuNO group in the reduced complex. The complex $[Ru(NH_3)_5(NO)]^{3+}$ undergoes a variety of reactions in which the nitrogen atom is attacked by a nucleophile; reduction to $[Ru(NH_3)_5(NO)]^{2+}$ is followed by rapid loss of a ligand.[6,38]

Since the products of the electrophilic behaviour of $[ML_5(NO)]$ complexes depend on the atomic-orbital contributions to the $9e$ ($8e$) orbital, it is necessary to investigate the factors which produce a high M or N component in this orbital. Fenske and DeKock[9] have pointed out that particular electron densities and orbital energies are a function of all constituents of the molecule. However, the unoccupied $9e$ ($8e$) orbital of interest to us is never less than 70% a π^* (MNO) orbital (see Table 3), and for the complexes which are actually known to exist it is over 80%. Any changes in this orbital will therefore in the first instance be the result of changes in the metal and the number of electrons associated with it. As one moves from left to right across the transition-metal series, or increases the nuclear charge, the metal *d*-orbital energies decrease, becoming closer in energy to the occupied π orbitals of the isolated NO^+ ligand, and further from the unoccupied π^*. Hence, overlap of the metal d_π orbitals with π^* (NO^+) will decrease and the contribution of metal d_π orbitals to the $9e$ ($8e$) orbital in the complex will also decrease. Nucleophilic attack or reduction at the nitrogen atom of the NO^+ ligand will therefore be preferred over attack at the metal in complexes of metals at the right-hand side of the transition metals, with a high formal positive charge on the metal. Similarly, since the *d*-orbital energies lie in the order 1st row < 2nd row ≈ 3rd row, nucleophilic attack or reduction at the nitrogen atom will be favoured with respect to attack or reduction at the metal in complexes of the first-row metals, when analogous complexes of all three rows can be compared. To date all known cases in which nucleophilic attack at the nitrogen atom of an $[ML_5(NO)]$ complex occurs are for Group 8 metals (in fact all postulated cases of such reactions of whatever geometry occur for Group 8 metals) with formal metal charges of +2 or +3. Similarly, the only known stable reduced species are for Group 8 metal complexes. Only one relevant and complete series of analogous complexes, $[M(CN)_5(NO)]^{2-}$ (M = Fe, Ru, or Os) is known; nucleophilic attack, at least by OH^-, apparently takes place in all three cases at the nitrogen atom of the NO ligand; however, the extreme insolubility of $[M(CN)_5(NO)]^{2-}$ (M = Ru or Os) has meant that their chemistry has been very little investigated.[6,22,23]

The number of electrons associated with the complex is best described by the $(MNO)^n$ (n = number of metal *d* electrons when the nitrosyl ligand is considered to be NO^+) notation of Enemark and Feltham[47] (but see below for an exception). Complexes of the type $[ML_5(NO)]$ are known for n = 4—8; those with n = 7 or 8 are obtained by reduction of the n = 6 complexes, and are therefore the products of the electrophilic reactions of $[ML_5(NO)]$ complexes referred to above. The requirements of the NO^+ ligand for back donation from the metal, combined with the fact that for n = 1 or 3 a Jahn–Teller distortion giving a non-linear MNO group is expected, means that complexes with $n < 4$ are either unlikely to be stable or do not conform to the limits of our investigation (a linear MNO group). Hence, we restrict ourselves to n = 4 or 6. From Tables 3 and 4 we see that rather minor changes in the contributions to the $9e$ orbital, and in the formal charges of the MNO group atoms, occur when $[Fe(CN)_4(NO)]^{2-}$ and $[Fe(CN)_5(NO)]^0$ are compared. This is to be expected, since formally the two extra electrons are being placed in the d_{xy} orbital, which is not involved in MNO bonding. We can therefore say that for n = 4—6 the site of reaction in an $[ML_5(NO)]$ complex is independent of the number of electrons. The difference in the chemistry of $[V(CN)_5(NO)]^{3-}$ (which does not undergo nucleophilic attack at nitrogen, or reduction) $[(MNO)^4]$ and $[Fe(CN)_5(NO)]^{2-}$ $[(MNO)^6]$ is a function of the different metal *d*-orbital energies, not of the different number of electrons.

Although the constitution of the $9e$ ($8e$) orbital depends in the first instance on the metal *d*-orbital energies, the other ligands do have an effect. Analysis of the 4—20% of the $9e$ ($8e$) orbital which is not from MNO shows that the secondary contribution is essentially completely from the *cis* L ligands and is antibonding with respect to them. In order to investigate the role of the ligands further, model calculations on $[FeH_5(NO)]^{2-}$ and $[FeF_5(NO)]^{2-}$ were performed; the results are included in Tables 1 and 2. When $[FeL_5(NO)]^{2-}$ (L = H, F, Cl, or CN) are compared it is seen that the contribution of L to $9e$ {$8e$, or $4e$ in the case of $[FeH_5(NO)]^{2-}$} increases markedly at the expense of the N contribution as the electronegativity of L decreases. In other words, the contribution of L to the l.u.m.o. increases as the Lewis basicity of L increases. The contribution of N still remains the largest single contribution, and that of iron remains small. Hence, electrophilic behaviour will still be at the MNO nitrogen atom, rather than at the metal; however, with electropositive ligands in the *cis* position, the incoming electrons enter an orbital which is destabilising with respect to the *cis* ligands. We therefore expect that in such cases loss of a *cis* ligand may be possible. This conclusion is reinforced by calculations on the hypothetical complexes $[V(CN)_5(NO)]^{5-}$, $[Mn(CN)_5(NO)]^{5-}$, $[Fe(CN)_5(NO)]^{4-}$, and $[FeCl_5(NO)]^{4-}$ having an MNO angle of 120° [*i.e.* an approximation to the situation which would occur on addition of electrons to the $9e$ ($8e$) orbital]. The h.o.m.o. has now *ca.* 50% *cis* ligand character, antibonding with respect to the metal *cis* ligands, and *ca.* 15% *trans* ligand character, also antibonding. Note that the essentially (75%) empty d_{z^2} orbital in $[Fe(CN)_5(NO)]^{2-}$ remains empty (75%) in $[Fe(CN)_5(NO)]^{4-}$; in both cases its occupied component is bonding with respect to the *trans* CN. On the other hand $d_{x^2-y^2}$, which is largely (60%) occupied in $[Fe(CN)_5(NO)]^{2-}$ becomes unoccupied (60%) in $[Fe(CN)_5(NO)]^{4-}$ and its occupied component changes from bonding to antibonding with respect to the *cis* ligands. Calculations on *cis* and *trans* $[V(CN)_4(NO)]^{4-}$, $[Mn(CN)_4(NO)]^{4-}$, $[Fe(CN)_4(NO)]^{3-}$, and $[FeCl_4(NO)]^{3-}$ with MNO = 120° show in all cases except $[FeCl_4(NO)]^{3-}$ that it requires less energy to remove a *cis* than a *trans* ligand. For $[FeCl_4(NO)]^{3-}$ the *cis* and *trans* complexes have the same energy within experimental error.

These results are significant for the loss of the ligand by the reduced species $[Fe(CN)_5(NO)]^{3-}$ and $[Ru(NH_3)_5(NO)]^{2+}$ [reactions (4) and (6) respectively]. The complex $[Fe(CN)_4(NO)]^{2-}$ has a square-pyramidal structure with a linear FeNO group,[39] despite the formal $(FeNO)^7$ electron count. This structure is predicted by our results, because the odd electron does not reside in the FeNO π system, but largely on the CN^- ligands. It has been previously assumed that a *trans* CN^- has been lost from $[Fe(CN)_5(NO)]^{3-}$,[4] but neither the structure nor the mechanistic evidence proves this. Similarly, it is presumed that a *trans* NH_3 is lost from $[Ru(NH_3)_5(NO)]^{2+}$,[38] though this is not proved by the evidence. We propose that it is in fact a *cis* ligand which is lost. It has been stated that *cis*- and *trans*- $[RuCl(NH_3)_4(NO)]^{2+}$ undergo aquation on reduction, though the products were not given;[48] our results indicate that *trans*-$[RuCl(NH_3)_4(NO)]^{2+}$ will give *mer*-$[RuCl(OH)(NH_3)_3(NO)]^+$ {or possibly *mer*-$[Ru(OH)_2(NH_3)_3(NO)]^+$} and *cis*-$[RuCl(NH_3)_4(NO)]^{2+}$ will give a mixture of *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ and *mer*-$[RuCl(OH)(NH_3)_3(NO)]^+$ {or *mer*-$[Ru(OH)_2(NH_3)_3(NO)]^+$}. Finally, the proposed *cis*-ligand replacement would explain the remarkably rapid base hydrolysis of *cis*-$[RuCl(NH_3)_4(NO)]^{2+}$,[49] though here an S_N1CB mechanism [40] may be possible.

The energy of the 9*e* (8*e*) orbital is obviously important in determining the ease with which nucleophilic attack or reduction will take place, and hence also in determining the products of the reactions. The calculated energies are given in Table 3. As discussed above, since the energy of the metal *d* orbitals decreases on going from left to right across the transition-metal series, the energy of the 9*e* orbital also decreases in the order $[V(CN)_5(NO)]^{3-} > [Mn(CN)_5(NO)]^{3-} > [Fe(CN)_5(NO)]^{2-}$. Note that of all the complexes studied only for $[V(CN)_5(NO)]^{3-}$ is the 9*e*-orbital energy positive; in this case a significant barrier to electrophilic behaviour is present.

The energy of the 9*e* (8*e*) orbital decreases as the number of electrons [n in $(MNO)^n$] decreases, and also decreases as the electronegativity (Lewis acidity) of the L ligands increases. This is a reflection of the increase in the charge at the metal which increases the *d*-orbital energies, leading to an increase in the 9*e* (8*e*)-orbital energy as discussed above. We may therefore expect electrophilic behaviour of the $[ML_5(NO)]$ complex (reduction or nucleophilic attack, at the metal or at the nitrogen) will be favoured for $[ML_5(NO)]$ complexes on the right-hand side of the transition-metal series, with high formal oxidation states and weak Lewis bases as co-ligands (subject to the requirement that M–NO bonding requires a strong M–NO π overlap *via* the 2*e* orbital). Note that as the energy of the 9*e* (8*e*) orbital increases the activation energy for electrophilic behaviour increases and the possibility of other reactions, such as ligand dissociation, increases. Hence, the net effect of an increase in the 9*e* (8*e*)-orbital energy will be to favour ligand replacement over nucleophilic attack at the nitrogen atom of the MNO group.

We thank Drs. W. V. F. Brooks and N. A. Lewis for very helpful discussions and the National Science and Engineering Research Council of Canada for support of this work. We are grateful to Dr. M. C. Zerner for providing us with a copy of his computer program.

[9/1413 *Received, 5th September,* 1979]

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