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THE APPLICATION OF ESCA TO THE STUDY OF BONDING IN NITROSYLS

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Summary

A study of a series of nitrosyl complexes by ESCA has provided a complementary method to infrared spectroscopy for distinguishing bent and linear nitrosyls. The relative shifts of the binding energies of O 1*s* and N 1*s* electrons tend to be found in the range of 132 ± 1 eV for linear nitrosyls and 128 ± 2 eV for bent nitrosyls. This approach leads to reversal of previous assignments of N 1*s* binding energies observed in certain complexes. Evaluation of N 1*s* binding energy shifts illustrates that the "NO^-" in a bent nitrosyl may actually have less electron density associated with the nitrogen atom than a "NO^+" in a linear nitrosyl.

Introduction

The binding modes of nitric oxide in transition metal nitrosyls have generally been categorized in terms of a formalism which ascribes a positive charge to a linear $M—N\stackrel{...}{—}O$ arrangement and a negative charge to a bent one. The linear structure formally arises from the transfer of the unpaired π^* electron of nitric oxide to the metal and subsequent sigma bond formation by interaction with the lone pair on nitrogen, as found in the isoelectronic carbonyls. Acceptance of an electron from the metal would produce NO^-, which has two potential lone pairs on nitrogen. Sigma bond formation with the metal leaves an unshared pair of electrons on nitrogen and provides a rationale for the bent structure. Although some structures are considered to contain NO radicals and a limited number of compounds contain bridging nitrosyls, most tend to be categorized as NO^+ if they are linear and NO^- if they are bent [1].

Infrared spectroscopy provides the most convenient method of characterization of nitrosyls. The NO stretching frequency in a linear M—N—O structure generally appears at higher values than that of a bent structure. Snyder and Weaver [2] have suggested, for example, that a range of 1750—2000 cm^{-1} is characteristic of linear nitrosyls; whereas 1500—1750 cm^{-1} is appropriate for the majority of complexes. The recent observations of numerous linear nitrosyls with NO frequencies between 1600 and 1750 cm^{-1} suggest that the border line is not well defined. Previous caveats concerning the correlation of NO stretching frequencies with NO bond angles were published by Eisenberg et al. [3] and Mingos and Ibers [4]. Although other factors contribute, the NO frequency is especially sensitive to the degree of $d\pi - p\pi^*$ back bonding. Thus, for cations in particular, the delocalization of negative charge into the π^* orbital of a linear nitrosyl may lower ν(NO) below 1750 cm^{-1}.

Because of the inadequacy of infrared methods to reliably establish NO binding modes, we have investigated the use of ESCA as a complementary technique for elucidation of structure. The possibility of establishing the charge on the nitrosyl from the binding energies suggested the potential of providing some detailed information on the bonding as well.

Results and discussion

The ESCA data, NO stretching frequencies, M—N—O bond lengths and angles of some nitrosyl complexes are summarized in Table 1. It is clear that there is no simple relationship between bond angle and NO stretching frequency, nor between the bond angle and the N 1*s* or O 1*s* binding energies alone. Binding energies for nitrogen 1*s* electrons are in the region of 398—404 eV, which is in good agreement with the data reported by other groups [5-8]. Little information regarding molecular structure can be derived by direct comparison of binding energy of N 1*s* or O 1*s*. However, differences in these values for each compound (O 1*s* — N 1*s*), gave two distinct sets of values for bent and linear nitrosyls, i.e., ~128 and ~132 eV, respectively (Fig. 1). Because of the limited availability of X-ray crystallographic data on bond angles and the experimental error in the (O 1*s* — N 1*s*) values, an extensive rationalization and correlation within the entire range of bond angles was not attempted.

The lack of direct correlation of structure with binding energy was anticipated on the basis of our previous studies on metal sulfoxides [9]. Within a series of neutral complexes, for example, variations in oxidation state of the metals will tend to modify the charge distribution on the nitrosyl. Insofar as previous work indicates a linear correlation of binding energy with "charge" [10], a variation in oxidation state of metal ions should produce variation in binding energies of electrons on the atoms in ligands. The situation is further exacerbated in ionic complexes, where the potential experienced by the photoelectron leaving an atom arises from not only the charge on the atom, but the Madelung potential of the other ions in the sample as well. Further, the inability to adequately compensate for the shift in the observed binding energy due to charging of the sample* virtually assures a large scatter in the data for complexes containing a specific M—N—O bond angle.

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* Since the sample is an insulator which is in contact with a conducting support, a charge can develop due to the loss of electrons from the sample which may produce an offset in the measured potential. The observed binding energy of each element should be shifted the same amount; hence the relative shifts between two elements in the same molecule should not be significantly affected by the charging phenomenon. The use of an electron "flood gun" to neutralize this charge build up appears to minimize the problem.

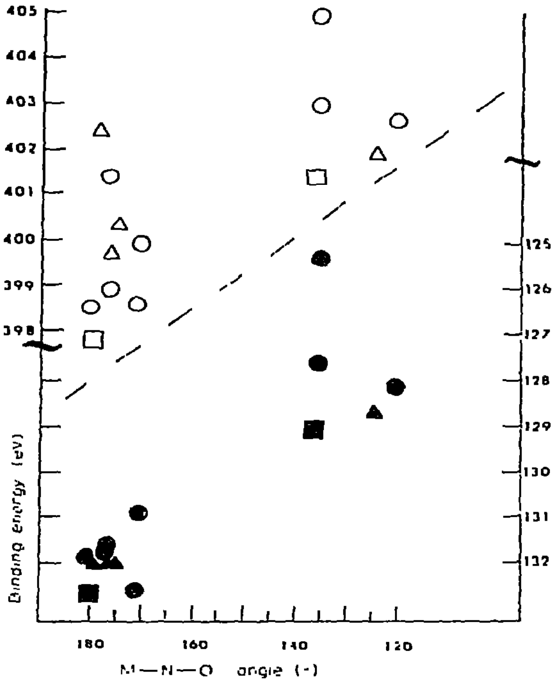

Fig. 1. Binding energies as a function of M—N—O bond angle. The lefthand ordinate and unfilled figures refer to N 1s binding energies. The right-hand ordinate and filled figures refer to the difference between the O 1s and N 1s binding energy. △, ▲, ionic complexes; ○, ●, neutral complexes; □, ■, $Ru(PPh_3)_2(NO)_2Cl^+$ for which the assignments to angles could be reversed. No cobalt compounds are shown.

Examining differences between binding energies of electrons in different atoms in the ligands tends to cancel many of the effects above. Thus, a difference in relative shift, (O 1s — S $2p_{3/2}$), ~365.0 for oxygen-bound sulfoxides and ~365.8 eV for sulfur-bound sulfoxides provides a valuable observable characteristic for use in elucidation of structure [9]. These variations in shift can be rationalized by the greater effect of the metal ion positive charge on the donor atom in the ligand. However, the large difference in relative shift for straight and bent nitrosyls appears to be intrinsic in the electronic structure of NO and requires more detailed consideration.

Although the trends in Table 1 indicate values of ~128 and ~132 eV for bent and linear nitrosyls respectively, the difference of approximately three to four eV is clearly evident in $Ru(PPh_3)_2Cl(NO)_2^+$ which contains both a bent and a linear nitrosyl. In this complex, the O 1s binding energies are similar (~530.5), whereas the N 1s binding energies differ significantly (397.8 and 401.4 eV). If one were to accept the formalized view of the bonding of NO^+ and NO^-, then a lower binding energy would be anticipated for the negative species and the 397.8 eV value assigned to the bent NO [5]. This, however, conflicts with the observation that the (O 1s — N 1s) difference of ~128 eV can usually be associated with a bent nitrosyl. This dilemma can be resolved by reevaluating the relationship of the formalism to the actual charge on the atom.

Within the formalism, both structures contain N—M σ bonds, but differ because a linear structure assumes complete transfer of an electron from N to

(continued on p. 58)

TABLE 1

ESCA DATA, NO STRETCHING FREQUENCIES, M—N—O BOND LENGTHS AND ANGLES OF SOME NITROSYL COMPLEXES

Compound[a]	O 1s (eV)	N 1s (eV)	(O 1s — N 1s)	M	Ref. Peak[b]	(M—N; N—O(Å); ∠MNO(°))	NO (cm^{-1})
$K_3[Cr(CN)_5(NO)]$	531.7	399.7	132.0	Cr $2p_{3/2}$ 575.9	A	(1.71; 1.21; 175.6)[h] [18]	1645 [23]
$K_3[Mn(CN)_5(NO)] \cdot xH_2O$	532.3	400.3	132.0	Mn $2p_{3/2}$ 640.2	A	(1.66; 1.21; 174.3) [17]	(1693, 1713) [15] 1730 [24]
$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$	534.4	402.4 403.3 [5]	132.0	Fe $2p_{3/2}$ 710.2	A	(1.63; 1.13; 178.3) [11b]	1944 [15]
$Fe(dmtc)_2(NO)$	531.2	(398.6)[c]	(132.6)[d]	Fe $2p_{3/2}$ 707.0	A	(1.72; 1.10; 170.4) [19]	1960 [25]
$Ru(dmtc)_3(NO)$	530.8	(399.9)[c]	(130.9)[d]	Ru $3d_{5/2}$ 280.8	A	(1.72; 1.17; 170) [20]	1830 [20]; 1845 [24]
$Ru(PPh_3)_3H(NO)$	530.5	398.9	131.6	Ru $3d_{5/2}$ 278.9	B	(1.795; 1.160; 176) [3]	1640 [26]
$Ru(PPh_3)_2Cl_3(NO)$	533.3	401.4	131.9	Ru $3d_{5/2}$ (281.3)[c]	B	(1.744; 1.132; 176.4) [27]	1877 [28]
$Ir(PPh_3)_3(NO)$	530.4	398.5 400.3 [5] 400.2 [8]	131.9	Ir $4f_{7/2}$ 60.3 61.6 [8]	B	(1.67; 1.24; 180) [29]	1615 [30]; 1600 [31, 32]
$Rh(PPh_3)_2Cl_2(NO)$	(529.9)[f]	401.9 401.5 [5]	128.0	Rh $3d_{5/2}$ 305.9	B		(1632, 1683) [33]; 1630 [34]

Ir(PPh$_3$)$_2$(CH$_3$)I(NO)	530.7	402.6	128.1	Ir 4$f_{7/2}$ 60.2	B	(1.91; 1.23; 120) [35]	1525 [31]
[Ir(PPh$_3$)$_2$Cl(CO)(NO)](BF$_4$)	530.5 533.2	401.9	128.6	Ir 4$f_{7/2}$ 61.4	B	(1.97; 1.16; 124.1) [36, 37]	1680 [36]
[Ru(PPh$_3$)$_2$Cl(NO)$_2$](BF$_4$)	530.5	397.8	132.7	Ru 3$d_{5/2}$	B	(1.738; 1.162; 179.5) [21]	
		401.4 400.2 [5] 402.6 [5]	129.1	(181.3)^c		(1.859; 1.170; 136.0) [21]	(1687, 1845) [21]
CoCl$_2$(diphos)(NO)	531.5	399.4	132.1	Co 2$p_{3/2}$ 779.1	B		1676 [38]
[Co(NCS)(dias)$_2$(NO)](NCS)	530.3	404.9	125.4	Co 2$p_{3/2}$ 780.7	A	(1.85; 1.01; 135) [39]	(1587, 1561) [39]
Co(ttp)NO	(530.5)^g	(403.0)^g	127.5	Co 2$p_{3/2}$ (778.4)	A	(1.833; 1.01; 135.2) [22]	1689 [22]
Co(PPh$_2$Me)$_2$Cl$_2$(NO)	(531.6)^g (530.4)^g	(399.5)^g (401.0)^g 400.5 [7] 402.2 [7] 399.6 [25] 401.7 [25]	132.1 129.4	Co 2$p_{3/2}$ 779.8	B	(1.705; 1.076; 164.5) [7]	(1735, 1640) [7]

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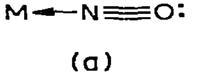
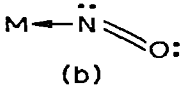
[a] dmtc = dimethyldithiocarbamate; diphos = Ph$_2$PCH$_2$CH$_2$PPh$_2$; dias = *o*-phenylenebis(dimethylarsine); ttp = tetraphenylphorphinato. [b] A, Au 4$f_{7/2}$ = 83.0 eV., B, internal reference, C, 1*s* (phosphine) = 283.0 eV. [c] N 1*s* of NO was obscured by N 1*s* of dmtc. [d] Less accurate. [c] Interference from C 1*s* at 283.0 eV. [f] Less accurate due to gradual decomposition of the sample. [g] Low temperature spectra; peaks observed only during early stages of data collection. (For Co(tpp)(NO) peaks appear at 531.2 and 399.5 eV on prolonged X-ray exposure). [h] Refers to [Co(en)$_3$] [Cr(CN)$_5$NO] · 2H$_2$O.

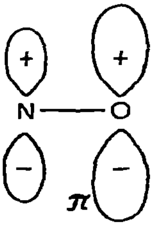
M (a); whereas a bent structure assumes complete transfer from M to N (b). These valence bond descriptions would suggest shifts, on bending,

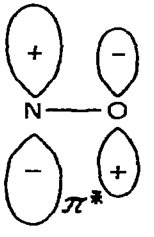

(a)


(b)

of both oxygen and nitrogen binding energies to lower values due to a decrease in formal charge; however, π-bonding between the ligand and the metal is neglected. Since the $\pi^{\star}$ orbital of NO lies very close in energy to the *d* levels of the metal [11-13], the extent of back bonding and consequently the charge distribution varies considerably with respect to the energy difference between the metal *d* orbitals and $\pi^{\star}$(NO). Sufficient back bonding in (a) therefore, could result in enough electron transfer from the metal to produce a formally negative nitrogen atom. π Interactions also allow for modification of the charge on the bent NO [13,14]. A complete molecular orbital calculation is necessary to follow the charge flow as the M—N—O bond angle is bent and (a) converted to (b). Nevertheless, some insight can be gained by consideration of one of the principal interactions, overlap of the d_{z^2} metal orbital with $\pi^{\star}$ (NO), in a C_{4v} complex [13]. In the linear system there is zero overlap due to symmetry restrictions, whereas in the bent system there may be considerable interaction. If the d_{z^2} orbital is filled and $\pi^{\star}$(NO) unfilled in a linear case, then bending will mix the orbitals and allow delocalization of the electrons in the d_{z^2} into the $\pi^{\star}$ (NO) orbital. Thus, electrons would flow from the metal to the nitrosyl on bending, which would produce a more negative bent than straight nitrosyl. Conversely, if the $\pi^{\star}$(NO) was filled and d_{z^2} unfilled (i.e., the energy of $\pi^{\star}(NO) < d_{z^2}$), bending would allow charge delocalization onto the metal. This would result in a situation in which a bent NO would be more positive than a straight NO. A complete description of MO parameters is not appropriate here; suffice it to say that in certain circumstances, consideration of all of the bonding interactions would imply that the nitrogen atom in a bent nitrosyl could be more positive than in a straight nitrosyl.

The relative energies of the N 2*p* and O 2*p* orbitals would imply that the charge distribution in the $\pi^{\star}$ orbital would be weighted toward the nitrogen atom. Consequently, if d—$\pi^{\star}$ interactions predominate, the nitrogen atom should





show the largest influence on angle. R. Hoffmann et al. have calculated the differences in charge, which might be expected in a hypothetical situation, in which energies of the d_{z^2} and $\pi^{\star}$(NO) orbitals were inverted by raising the metal coulomb integrals by 1.5 eV in $IrCl_4NO$ [13] (Table 2). Only trends would be expected to be significant. These results indicate that: *i*) the nitrogen 1*s*

TABLE 2

CALCULATED CHARGES ON A MODEL COMPLEX (eV)

	180°		120°	
	N	O	N	O
$d > \pi^*(NO)$	+0.60	−0.09	+0.31	−0.34
$d < \pi^*(NO)$	−0.78	−0.83	−0.42	−0.73

binding energies should vary more than those of oxygen; *ii*) bending of a nitrosyl may produce a more positive nitrogen atom; *iii*) if N 1*s* and O 1*s* binding energy differences are used to characterize bent and linear systems, a large scatter in results can be anticipated.

The previous discussion has focused on five coordinate complexes and it is obvious that the orbital interactions which control the charge distribution will vary with the complexes studied here. The points outlined above, however, will apply with modifications to all of the complexes. Consequently, it appears that preconceived viewpoints of charge distributions may not prove to be adequate for the correct assignment of observed binding energies in cases where ambiguities exist; i.e., $Ru(PPh_3)_2Cl(NO)_2^+$ or $CoL_2Cl_2NO^+$.

The validity of the relative shift method for assigning observed binding energies depends on the accuracy of our data and comparison of model compounds. Although detailed consideration of the bonding in each compound is outside the scope of this article, some commentary and correlation with previous work is appropriate.

Pentacyanonitrosyls

The N 1*s* binding energies observed in the three pentacyanonitrosyls are lower than those reported by Finn and Jolly [5]; however, this may be ascribed to the different reference energies employed. Thus, the difference between N 1*s* binding energies in $Fe(CN)_5(NO)^{2-}$ and $Cr(CN)_5(NO)^{3-}$ is 2.7 in Table 1 compared to Finn and Jolly's value of 2.6 eV. Since an absolute value of binding energy has little meaning in this study, these differences are unimportant for the discussions which follow.

The NO stretching frequencies of these compounds have been correlated with the degree of π back-bonding from the metals[*] and with the bond order of N—O according to molecular orbital calculations [1d,11,12]. The trends in the binding energies are consistent with the implied increase in back-bonding associated with lowering of the NO stretching frequency. Nevertheless, the possibility of significant contributions from the Madelung potential of the gegenions in these ionic complexes should not be overlooked. It is striking that Δ(O 1*s* — N 1*s*) is not affected significantly by the formal charge difference on the metal in these complexes, as was observed in the study of sulfoxide complexes [9].

The assignment of O 1*s* binding energies of NO in $Na_2Fe(CN)_5(NO) \cdot 2H_2O$

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[*] This correlation is in agreement with the NO bond lengths; however, the M—N bond lengths show an opposite trend despite the purported increase in π back-bonding revealed by NO stretching frequencies.

was based on the observation that the 534.4 eV peak was not affected by the presence of different amounts of water in the sample examined. This serves to indicate the absence of significant interaction between anions and water as suggested from infrared [15] and X-ray studies [16]. An O 1*s* binding energy of 532.1 eV was assigned to water in a sample prepared in absolute methanol. This peak was broader than the O 1*s* of NO and becomes broader and shifts to lower values by one eV when the sample was prepared from water.

The N 1*s* and O 1*s* peak positions for the manganese and chromium salts are critically affected by the presence of water. Increasing the water content produces a decrease in Δ(O 1*s* — N 1*s*) by approximately one eV. We believe that this effect may be due to hydrogen bonding between NO and H_2O as shown by infrared [15] and X-ray studies [16,17]. Obviously, further studies would be necessary to understand these smaller effects.

Linear nitrosyls in neutral complexes

The data for five neutral linear complexes is shown in Table 1 and show (O 1*s* — N 1*s*) values between 130.9 and 132.6 eV. These data combined with the pentacyanonitrosyl results tend to establish the 132 ± 1 range for linear nitrosyls. Deviations are expected to be less in neutral complexes due to the absence of a Madelung contribution from gegenions, but interactions with adjacent molecules may occur (i.e., NO oxygen interaction with other ligands) [19, 20].

Bent nitrosyls in neutral complexes

Two complexes, $Rh(PPh_3)_2Cl_2(NO)$ and $Ir(PPh_3)_2(CH_3)I(NO)$ provide especially reliable data which suggest a lower value for (O 1*s* — N 1*s*) of ~128 eV characteristic of bent nitrosyls. These values tend to be corroborated by cobalt complexes listed toward the end of Table 1, but the ease of decomposition of the cobalt complexes makes the data less reliable.

Bent nitrosyls in ionic complexes

The assignment of O 1*s* binding energies in $Ir(PPh_3)_2Cl(CO)(NO)^+$ is ambiguous. The O 1*s* binding energy of Vaska's compound at 531.3 eV lies in between the values found for its $NOBF_4$ adduct, but the effects of the Madelung potential make any extrapolation unreliable.

The $Co(NCS)(dias)_2NO^+$ ion shows a peculiarly low (O 1*s* — N 1*s*) value but tends to support the assignment of bent nitrosyls to relative shifts less than 130 eV.

The N 1*s* binding energies of $Ru(PPh_3)_2Cl(NO)_2^+$ observed in this study are lower than those previously reported by Finn and Jolly [5]. Furthermore, the separation of the N 1*s* peaks is 3.7 in our data, but only 2.6 eV in the published work [5]. These differences are not particularly important and may be attributed to choice of reference and the higher resolution attainable with our imstrumentation. Only one O 1*s* peak (FWHM = 1.8 eV) is observed indicating the overlap of the O 1*s* binding energies of the bent and linear NO. The relative differences between O 1*s* and N 1*s* are 132.7 and 129.0 eV, which from the previous correlations should be assigned to linear and bent nitrosyls respectively. This leads to the assignment of lower N 1*s* binding energy to the linear NO and the higher N 1*s* binding energy to the bent NO in contrast to the conclusion drawn by Finn and Jolly [5].

The assignment of binding energies to bent and linear nitrosyls

As with the ruthenium dinitrosyl derivative discussed above, the correlation of relative differences with bond angle should resolve certain aspects of the "paradox" associated with the two nitrosyl stretching frequencies observed in CoL_2Cl_2NO complexes [7]. For $Co(PPh_2Me)_2Cl_2NO$, a "linear" (M—N—O angle = 165°) nitrosyl is found in the solid. However, it appeats that in solution and on the surface of the solid an equilibrium with a bent nitrosyl exits [7]. We have noted two N 1*s* peaks comparable to other reported values [5.7]. Larger areas were associated with the lower N 1*s* and the higher O 1*s* peaks; thus ascribing the Δ(O 1*s* — N 1*s*) of 132.1 for the species in higher concentration at the surface and 129.4 eV for the species in lower concentration. Hence, we would assign the greater intensity, higher binding energy peak to the bent species and the lower intensity, lower binding energy peak to the linear isomer. in contrast to the assignments of previous reports [5,7]. With these assignments the conflict between the infrared results and ESCA results suggested in previous work [7] does not arise, thus eliminating much of the paradoxical character of the problem.

Assignment of oxidation state

In view of the previous discussion, it must be recognized that the concept of a bent nitrosyl being negative is artificial. Data in Table 1 demonstrate that the electron density on a bent nitrosyl formally described as NO^- is not necessarily greater than on a straight nitrosyl formally described as NO^+. Holsboer, Beck and Bartunik [8] also reached a similar conclusion on the basis of ^{193}Ir Mössbauer and ESCA studies. In particular, they noted that despite the Ir—N—O angles in $Ir(PPh_3)_2(CO)(NO)Cl^+$ and $Ir(PPh_3)_3NOH^+$ of 124° and 175° respectively, binding energies of 403.4 and 401.1 eV for N 1*s* were observed, which indicated that the straight NO was more negative than the bent NO. Mingos and Ibers [4, 14] anticipated the possibility of a positive bent nitrosyl by proposing that an appropriate valence bond description involved two canonical forms with either an sp^2 hybrid NO^+ accepting a pair of electrons from a low oxidation state metal or an sp^2 hybrid NO^- donating an electron pair to the higher oxidation state metal.

Thus at this juncture, if one wishes to assign a realistic oxidation state to a metal, it is not necessarily appropriate to consider a bent NO as a negatively charged ligand. In addition to measurement of N 1*s* binding energy, measurement of binding energies of the electrons on the metal may provide a justification for a choice; and hence, by a circuitous pathway, require a choice of oxidation state for NO for consistency. These oxidation state assignments must be viewed in the perspective of the reliability of ESCA in determining charge, as discussed earlier. Nevertheless, in the absence of better methods of determining "atomic charge", it provides supplementary evidence from which a rational choice can be made.

Comparing the Ir $4f_{7/2}$ binding energy of $Ir(NO)(CO)Cl(PPh_3)_2^+BF_4^-$ (61.45), $Ir(NO)(CH_3)I(PPh_3)_2$ (60.2), $Ir(CO)Cl(PPh_3)_2$ (59.4) and $IrH(CO)PPh_3)_3$ (59.0 eV), we suggest that the iridium atom in the ionic species is better assigned as Ir^{III}.

Hence in this case, a description as a bent nitrosyl being an sp^2 hybrid NO$^-$ bonded to a higher oxidation state of the metal center is appropriate.

The Ru $3d_{5/2}$ binding energy of Ru(PPh$_3$)$_2$(NO)$_2$Cl$^+$ is similar to that of Ru(PPh$_3$)$_2$(NO)Cl$_3$ and is 2.5 eV higher than that of Ru(PPh$_3$)$_3$H(NO). This implies that the former compounds exhibit a higher oxidation state than the latter. Hence we conclude that the original assignment [21] as Ru^0 to RuL$_2$(NO)$_2$Cl$^+$ is less appropriate than Ru^{II} with NO$^-$ and NO$^+$ ligands.

Scheidt and Hoard [22] have recently challenged the Co^{III} — NO$^-$ description of the bonding in Co(tpp)NO and suggest that a d^7 Co^{II} — NO is more appropriate. ESCA should provide a method of distinguishing these alternatives. Unfortunately, cobalt nitrosyls tend to decompose readily under X-rays. Hence, comparisions with Co(dmtc)$_2$NO, [Co(en)$_2$Cl(NO)]Cl and [Co(NH$_3$)$_5$(NO)]Cl$_2$ were difficult due to uncertainty in the data. We anticipate that future studies with more stable model compounds and better sampling procedures may resolve this problem.

Conclusions

ESCA and the comparison of relative shifts of O 1*s* and N 1*s* binding energies provides a complementary method to infrared spectroscopy for distinguishing bent and linear nitrosyls. We anticipate that there will be exceptions to the generalizations that have been drawn from the limited number of complexes which have been studied. Nevertheless, we believe that the technique offers a reasonably reliable alternative for assessing bending in nitrosyls. The shifts observed for N 1*s* binding energies lend additional support to arguments [4, 8] that the actual electron density on a bent nitrosyl in some complexes may be less than that on a linear nitrosyl.

Experimental

All of the compounds were prepared as described in the references in Table 1. Na$_2$[Fe(CN)$_5$(NO)] · 2H$_2$O was recrystallized from water. Co(tpp)NO was obtained through the courtesy of L. Olson and B.B. Wayland. A Perkin—Elmer 421 infrared spectrophotometer was used to check the spectra of the compounds to assure their identity and purity.

The binding energies were recorded using a Hewlett—Packard 5950A spectrometer equipped with a monochromatized Al—K_α X-ray source, a variable temperature probe and an electron flood gun. Thin layers of samples were prepared by evaporation of solutions of compounds in appropriate solvents, such as methylene chloride, methanol, acetone, benzene, or water, onto a gold-plated sample holder. Direct pressing of powdered solids onto the sample holder proved useful for less stable compounds and appeared to minimize decomposition. Air-sensitive samples were placed in the spectrometer with the aid of a nitrogen-filled glove bag. Some improvement in signal was observed using thicker samples; however, Au $4f_{7/2}$ signals were then no longer available for calibration*. In these

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* For thick samples, Au $4f_{7/2}$ = 83.0 eV (if it can be observed) is less reliable as a reference. This problem appears to arise from different degrees of charging.

situations the reference was taken at 283.0 eV for C 1*s* of triphenylphosphine, rather than the Au $4f_{7/2}$ = 83.0 eV used for thin samples. The flood gun was operated at 0.6 mA to compensate for charging effects. Compounds with bent nitrosyls generally showed slow accumulation of N 1*s* signals. Particular care was exercised to avoid ascribing binding energies to decomposition products. Thus, data were recorded at initial and final stages of X-ray exposure separately (see footnote *g*, Table 1). All of the binding energies reported were recorded with at least two separate samples.

The precision of the instrumentation allows the determination of a binding energy within a given sample with narrow peaks (Au $4f_{7/2}$, FWHM < 0.8 eV) with standard deviations of approximately 0.005 eV. Broader peaks (in these complexes N 1*s* and O 1*s* generally showed FWHM = 1.5—2.0 eV) give rise to greater uncertainty. The range of values for several samples of a given complex was generally less than ± 0.2 eV. Since the deviations are mostly attributable to charging, the observed position of two peaks in the same sample are correlated rather than random. Consequently, the Δ(O 1*s* — N 1*s*) values reported in Table 1 are believed to be accurate to within a range of ± 0.2 eV of the value tabulated. Lower quality data are indicated by parentheses in Table 1.

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