smaller than the perturbation of the d_σ orbitals, shows that the isocyanide ligand is a relatively stronger π acceptor than the arsine ligand, as expected.

The electronic modifications of the isocyanide ligand, as seen in the variations in the C–N bond, are strongly related to the possibility of π-electron transfer from osmium to the isocyanide ligand. In isomers I and III, in which the isocyanide ligands are cis, the overlap $d_\pi-\pi^*$ is too small for the influence of the different electronic distributions to be transferred from the metal atom to the C–N group; in isomer II the two trans isocyanide ligands are clearly distinguishable.

Acknowledgment. Thanks are due to Dr. Carlo Busetto and to L. S. R. Snam Progetti (S. Donato Milanese) for helpful contributions.

Registry No. Isomer I, 61491-27-8; isomer II, 61521-48-0; isomer III, 61521-49-1; *mer*-$[O_5Cl_3(AsPh_3)_3$, 61491-28-9; $[O_5Cl_2(AsPh_3)_2(p\text{-}CH_3C_6H_4NC)_2]$, 61491-29-0.

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Contribution from the Departments of Chemistry, University of Durham,
Durham, England, and King's College, London WC2R 2LS, England

Complexes of the Platinum Metals. 8.[1a] Electron Spectroscopy for Chemical Analysis Studies of Some Nitrosyl, Aryldiazo, and Aryldiimine Derivatives of Ruthenium, Osmium, Rhodium, and Iridium†

D. T. CLARK,*[1b] I. S. WOOLSEY,[1b] S. D. ROBINSON,*[1c] K. R. LAING,[1c] and J. N. WINGFIELD[1c]

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ESCA spectra have been obtained for nitrosyl, aryldiazo, and aryldiimine complexes of ruthenium, osmium, rhodium, and iridium. The observed binding energies have been used, in conjunction with spectroscopic and structural data, to discuss the structures and electronic properties of the complexes investigated. A good correlation between the N 1s binding energies of the nitrosyl complexes and those of their aryldiazo analogues is found and lends further support to the view that nitrosyl and aryldiazo ligands possess similar coordination characteristics. The variation of metal binding energies with ligand substituents taken together with N 1s binding energies allows more reliable evaluation of ligand–metal bonding than N 1s binding energies alone. The values of the binding energies and the chemical shift difference for the N 1s electrons of the aryldiazo and aryldiimine ligands suggest that these moieties possess low overall charges and are appreciably less polar than dinitrogen ligands coordinated under similar circumstances.

Introduction

Extensive studies of the structural and electronic properties of transition metal nitrosyl complexes have led to the recognition of two limiting bonding modes involving linearly coordinated (NO^+) or angularly bound (NO^-) ligands.[2-5] Experimentally observed systems approximate to one or the other of these two formal extremes. More recently, aryldiazo (N_2Ar) complexes have been tentatively assigned analogous structures containing linearly coordinated (N_2Ar^+) or angularly bound (N_2Ar^-) ligands, either on the basis of infrared data or by analogy with the corresponding nitrosyl derivatives.[6] Partial confirmation of these assignments has been provided by x-ray diffraction studies on selected aryldiazo complexes[6] including $[RuCl_3(N_2Ar)(PPh_3)_2]$solv (Ar = *p*-tolyl; solv = CH_2Cl_2[7] or Me_2CO[8]) and $[RhCl(N_2Ph)\{PhP(CH_2CH_2CH_2PPh_2)_2\}][PF_6]$[9,10] which reveal the presence of linearly coordinated (N_2Ar^+) and angularly coordinated (N_2Ar^-) ligands, respectively. Previous infrared[7,11,12] and ESCA[13-15] studies of metal nitrosyl complexes have shown that assignment of linear (NO^+) or angular (NO^-) geometries on the basis of nitrosyl infrared stretching frequencies [ν(NO)] and N 1s binding energies is not a valid procedure. The lack of a simple correlation between metal nitrosyl bonding modes and spectroscopic parameters has been attributed to the fact that the energies of the metal d orbitals and the π^* orbitals of the NO ligand are similar. Under these circumstances the relative distribution of electrons between the metal and the nitrosyl ligand in the 2e molecular orbital can vary markedly within an isoelectronic series of complexes and relatively minor changes in the metal atom and/or other coordinated ligands may result in substantial differences in spectroscopic properties.[16] Recently, however, an attempt has been made to establish a correlation between nitrosyl binding modes and ESCA data by employing the (O 1s–N 1s) binding energy difference as the ESCA parameter.[17]

In the present study nitrogen (N 1s) binding energies supplemented by metal binding energies have been employed to explore the formal analogy between nitrosyl and aryldiazo ligands and to seek a reliable correlation between ESCA data and NO or N_2Ar ligand bonding modes. Attempts to develop model systems for nitrogenase based on the reduction of coordinated dinitrogen or aryldiazo ligands has stimulated interest in the overall electronic charge and the polarity of these moieties and their reduction products.[18,19] We have therefore measured N 1s electron binding energies for coordinated aryldiazo and aryldiimine ligands and compared our results with similar data previously reported for coordinated dinitrogen ligands.[20-23] Finally, rather than use the NO^+/NO^- notation

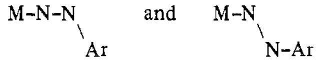
† No reprints of this paper are available from the authors.

Table I. Binding Energies (eV) for Nitrosyl, Aryldiazo, and Aryldiimine Complexes of Ru, Rh, Os, and Ir

$RuCl_3L(PPh_3)_2$	L = NO	$L = NO_2C_6H_4N_2$	$L = ClC_6H_4N_2$	$L = CH_3C_6H_4N_2$
N 1s[a]	403.2	401.5 (N_2) (401.8, 400.7) 406.7 (NO_2)	401.4 (402.1, 400.7)	401.5 (401.9, 401.0)
O 1s	534.8			
P 2p	131.1	130.9	131.0	130.9
Cl $2p_{3/2}$	198.1	197.9	198.1	197.9
Ru $3p_{3/2}$	464.7	464.1	463.8	463.6
Ru $3d_{5/2}$	283.1	282.7	282.5	282.2
$RhCl_2L(PPh_3)_2$	L = NO	$L = NO_2C_6H_4N_2$	$L = CH_3OC_6H_4N_2$	$L = CH_3C_6H_4N_2$
N 1s[a]	401.9	400.7 (N_2) (401.1, 400.3) 406.7 (NO_2)	400.5 (400.9, 399.9)	400.5 (400.7, 400)
O 1s	534.1			
P 2p	131.0	131.1	131.0	131.1
Cl $2p_{3/2}$	198.1	198.2	198.1	198.2
Rh $3d_{5/2,3/2}$	309.5, 314.2	309.4, 314.1	309.2, 313.9	309.4, 314.1
$OsBr_3L(PPh_3)_2$	L = NO	$L = CH_3C_6H_4N_2$		
N 1s[a]	403.2	401.3 (401.6, 401.0)		
P 2p	131.2	131.2		
Br 3d	68.2	68.2		
Os $4f_{7/2,5/2}$	52.1, 54.6	51.6, 54.1		
$[RuClL_2(PPh_3)_2]^+BF_4^-$	L = NO	$L = CH_3C_6H_4N_2$		
N 1s[a]	403.1 (402.6, 403.7)	401.0 (401.8, 401.0, 400.8, 399.9)		
O 1s	534.9			
P 2p	131.1	131.3		
Cl $2p_{3/2}$	198.3	198.2		
Ru $3p_{3/2}$	464.7	463.5		
Ru $3d_{5/2}$	283.1	282.5		
F 1s	686.6	686.9		
	$RhCl_3(HN_2C_6H_4\text{-}CH_3)(PPh_3)_2$	$IrCl_3(HN_2C_6H_4\text{-}CH_3)(PPh_3)_2$	$RuCl_2CO(HN_2C_6H_4\text{-}OCH_3)(PPh_3)_2$	
N 1s[a]	401.0 (401.5, 400.3)	401.0 (401.4, 400.5)	400.6 (401.2, 400.2)	
P 2p	131.0	131.2	130.8	
Cl $2p_{3/2}$	197.9	198.1	197.8	
Rh $3d_{5/2,3/2}$	309.4, 314.0			
Ir $4f_{7/2,5/2}$		61.7, 64.6		
Ru $3p_{3/2}$			463.5	
$Ru(NO)_2(PPh_3)_2$				
N 1s	400.8			
O 1s	532.8			
P 2p	130.9			
Ru $3p_{3/2}$	463.4			
Ru $3d_{5/2}$	281.3			

[a] Values in parentheses are binding energies obtained by deconvolution of the composite peak.

with its implication of unrealistic charge distribution, we follow the advice of a referee and refer to "linear" and "nonlinear" MNO moieties. In order to preserve the analogy between nitrosyl and aryldiazo (N_2Ar) ligands we refer to the moieties



as "linear" and "nonlinear", respectively.

Experimental Section

The nitrosyl,[24,25] aryldiazo,[26,27] and aryldiimine[26] complexes employed in this work were prepared by literature methods; their purity was checked by spectroscopic and chemical analysis. The ESCA spectra were recorded at room temperature on an AEI ES100 electron spectrometer using Mg $K\alpha_{12}$ radiation. The samples were examined as powders pressed onto double-sided scotch tape, and the binding energies were referred to the C 1s level of the triphenylphosphine groups present in all of the compounds studied, which was taken to have a constant binding energy of 285.0 eV. The use of the triphenylphosphine as an internal calibrant is well established and compensates for the effects of differential sample charging.[15,20] This is confirmed by the constancy of the P 2p and Cl $2p_{3/2}$ binding energies in the series of complexes studied. Each compound was measured several times and the reproducibility of the binding energies measured in this way was ±0.1 eV. No changes in the ESCA spectra with time were observed, indicating little or no sample decomposition during irradiation. As a further check the relative intensities of the Ru, Cl, N, and P peaks of the nitrosyl, aryldiazo, dinitrosyl and bis(aryldiazo) complexes of ruthenium were measured and compared within the series. The peak area ratios for the series were in agreement with those predicted from the stoichiometry of the compounds, confirming that no significant sample decomposition had occurred. This approach has also been used recently by Brant and Feltham.[28] In addition the two N 1s peaks observed for the $N_2C_6H_4NO_2$ derivatives of ruthenium and rhodium had the expected area ratio of 2:1.

Deconvolutions of composite peaks were performed using a Du Pont 310 curve resolver employing a Gaussian line shape. The measured binding energies are given in Table I. The average N 1s binding energies could be measured to ±0.1 eV; however, the binding energies obtained by deconvolution were accurate to only ±0.2 eV. More accurate deconvolutions were precluded due to the low percentage of nitrogen in the samples giving relatively poor counting statistics. Figure 1 shows the N 1s spectrum of $[RuCl(N_2C_6H_4Me)_2(PPh_3)_2][BF_4]$ and the deconvoluted peaks.

The N 1s line widths for the nitrosyl complexes were close to 1.8 eV. This was due partly to the necessity of using larger slit widths to obtain better counting statistics and was also typical of the line widths obtained by deconvolution. No attempt was made to fix the relative intensities of the component peaks obtained by deconvolution,

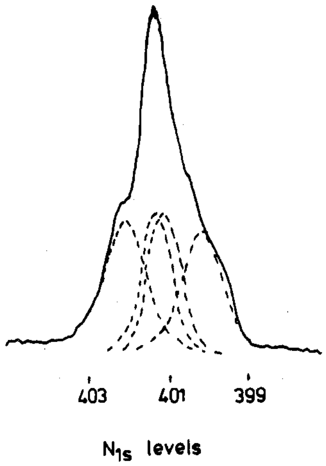


Figure 1. N 1s spectrum of $[RuCl(N_2C_6H_4Me)_2(PPh_3)_2][BF_4]$ and the deconvoluted peaks.

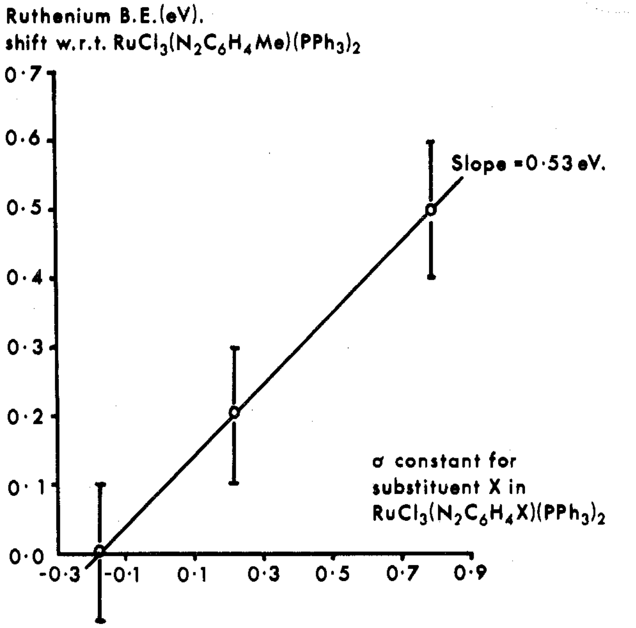
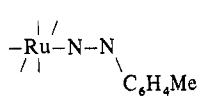


Figure 2. Plot of Ru $3p_{3/2}$ binding energy shifts for $RuCl_3(N_2C_6H_4X)(PPh_3)_2$ vs. the Hammett σ_p constant of X.



$$-\overset{|\ /}{\underset{/\ |}{Ru}}-N-N\backslash C_6H_4Me$$

I

but they appeared to be in good agreement with those expected.

Results and Discussion

The ruthenium and osmium nitrosyl complexes $MX_3(NO)(PPh_3)_2$ (M = Ru, X = Cl; M = Os, X = Br) show N 1s binding energies 1.3 eV higher than that of the rhodium nitrosyl $RhCl_2(NO)(PPh_3)_2$, and the O 1s binding energy of the ruthenium complex is 0.7 eV higher than that of the rhodium compound. This behavior is also observed for the ruthenium and osmium aryldiazo complexes, which show average N 1s binding energies 0.9 ± 0.1 eV higher than those of the analogous rhodium complexes. This indicates a more positively charged nitrosyl or aryldiazo N_2 group in the ruthenium and osmium complexes than in the rhodium species and, in accord with previous conclusions based on infrared and structural evidence, suggests parallel coordination behavior for nitrosyl and aryldiazo ligands in complexes of this type.[5,6] These results are consistent with the formulation of the ruthenium and osmium complexes as "linear" MNO (or MN_2Ar) species and the rhodium complexes as "nonlinear" MNO (or MN_2Ar) species. However, in metal nitrosyl complexes the electron density on "linear" NO is not necessarily less than that on "nonlinear" NO[14-17] and for this reason attempts to assign geometry on the basis of N 1s binding energies alone are not reliable. Therefore we have examined metal 3p and 3d binding energies in search of corroborative evidence. The ruthenium aryldiazo complexes display a distinct correlation between the ruthenium $3p_{3/2}$ or $3d_{5/2}$ binding energies and the Hammett σ_p constant of the para substituent on the aryldiazo group as shown in Figure 2.

In contrast the rhodium $3d_{5/2,3/2}$ binding energies of the rhodium aryldiazo complexes are scarcely perturbed by changes in the para substituents. Furthermore, the ruthenium nitrosyl shows significantly higher metal binding energies than the corresponding aryldiazo compounds, whereas the rhodium nitrosyl and aryldiazo complexes have the same metal binding energies within experimental error.

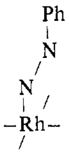
The relatively large aryldiazo para-substituent effect on the metal binding energies in the ruthenium compounds is indicative of the removal of electronic charge from the metal via a conjugated π system, since σ effects at these distances should be very small indeed. This in turn would imply a substantial ruthenium–aryldiazo dπ–pπ* back-bonding interaction and is consistent with the known strong π-acceptor character of linearly coordinated (N_2Ar) aryldiazo ligands.[29] Confirmation of this geometry has been provided by two recent x-ray diffraction studies[7,8] on solvated crystals of $RuCl_3(N_2Ar)(PPh_3)_2$ (Ar = p-MeC_6H_4) which establish configuration I for the $RuN_2C_6H_4Me$ moiety. The Ru–N–N group is coplanar, though not collinear, with the tolyl group thus providing the conjugated π system necessary for the large para-substituent effect on the ruthenium binding energies. The slope of the correlation between ruthenium $3p_{3/2}$ binding energies and the Hammett σ_p constants shown in Figure 2 is 0.53 eV.

A similar correlation of tungsten $4f_{7/2}$ binding energies with the σ constants of the para substituents X exists for the complexes $W(\eta^5\text{-}C_5H_5)(CO)_2(NC\{C_6H_4X\}_2)$ studied by Briggs et al.,[30] where the methyleneamino ligand is thought to be linearly bonded to the tungsten. In this case the correlation has a slope of 0.99 eV due to the presence of two $-C_6H_4X$ groups per ligand. The change in the $W4f_{7/2}$ binding energy per para substituent X is therefore effectively the same as for the ruthenium $3p_{3/2}$ level of the aryldiazo compounds. The ability of remote ligand substituents to influence the electronic properties of the metal center has recently been convincingly demonstrated by Bowden et al.[31] In a related study of the redox potentials of p-nitrosoarene complexes of ruthenium(II) *cis*-$[Ru(bpy)_2\{p\text{-}N(O)C_6H_4X\}Cl]^+$ these workers observed a remarkably large influence of the substituent X on the redox potential of the complex, reflected in a good linear correlation between the Hammett σ_p values of the substituents X and the Ru(III)–Ru(II) reduction potentials. The effect of the substituent X is thought to be transmitted primarily through the π system of the nitrosoarene ligand.

As noted earlier, the complex $RuCl_3(NO)(PPh_3)_2$ continues the trend observed for the ruthenium $3p_{3/2}$ binding energies of the corresponding aryldiazo complexes, thereby suggesting that in this system the nitrosyl ligand is a strong π acceptor and should accordingly be formulated as linearly bound NO. Structures of this geometry have been established by x-ray diffraction for $RuCl_3(NO)(PPh_3)_2$[29] and the closely related complex $RuCl_3(NO)(PMePh_2)_2$.[32] A similar effect on Fe 2p binding energies has also been observed for $[Fe(NO)(CO)_2(PPh_3)_2][PF_6]$ and $[Fe(p\text{-}N_2C_6H_4Me)(CO)_2(PPh_3)_2][PF_6]$ where the nitrosyl and aryldiazo groups are linearly bonded to the iron atom.[33,34]

The significant increase in ruthenium $3p_{3/2}$ and $3d_{5/2}$ binding energies on moving from the aryldiazo to the nitrosyl complexes supports the intuitive opinion that linearly coordinated nitrosyl ligands are better π acceptors and/or poorer σ donors than linear aryldiazo (N_2Ar^+) ligands in a similar environment,[35] rather than the contrary view expressed elsewhere.[36,67]

The lack of a similar relationship between constitution of the NO or N_2Ar donor ligand and the rhodium $3d_{5/2,3/2}$ binding energies of the complexes $RhCl_2(NO)(PPh_3)_2$ and $RhCl_2(N_2Ar)(PPh_3)_2$ supports the formulation of these species as formal rhodium(III) derivatives containing nonlinearly bound NO or N_2Ar ligands with relatively small π-acceptor capacity. X-ray diffraction data for $RhCl_2(NO)(PPh_3)_2$, published[38] after completion of this work, establish a nonlinear RhNO linkage with Rh–N–O = 123.8° and thus confirm the conclusion reached on the basis of the ESCA results. The structures of the corresponding aryldiazo complexes $RhCl_2(N_2Ar)(PPh_3)_2$ are unknown. However, x-ray diffraction studies on the closely related aryldiazo salt $[RhCl(N_2Ph)(PhP\{CH_2CH_2CH_2PPh_2\}_2)][PF_6]$[9,10] and its nitrosyl analogue $[RhCl(NO)(PhP\{CH_2CH_2CH_2PPh_2\}_2)][PF_6]$[36] reveal angular Rh–N–NPh and Rh–N–O moieties with values of 125 and 131° for ∠Rh–N–NPh and ∠Rh–N–O respectively. The Rh–N–NPh group has configuration II, with the phenyl ring rotated 9.6° out of plane of the RhN_2 group. The $M-N_2Ar$ and MN_2-Ar bond lengths in $[RhCl(N_2Ph)(PhP\{CH_2CH_2CH_2PPh_2\}_2)][PF_6]$ are greater by 0.18 and 0.07 Å, respectively, than the corresponding bonds in $[RuCl_3(N_2Ar)(PPh_3)_2]\cdot CH_2Cl_2$.[39] These data suggest the presence of reduced metal to ligand $d\pi-p\pi^*$ back-donation in the rhodium complex relative to the ruthenium one and are therefore in accord with current ideas concerning the greater π-acceptor ability of linearly bound N_2Ar and NO ligands relative to their angularly coordinated analogues.



II

The osmium nitrosyl and aryldiazo complexes show variation in metal binding energies similar to, but smaller than, those apparent for the analogous ruthenium species. The differences in the magnitude of the variations may result from a genuine difference in the nature of the two systems (e.g., changing bond angles and electronegativities) or may arise from the choice of the Os 4f level for study. The latter possibility does not influence the comparison of the ruthenium and rhodium complexes, however, as both Ru $3p_{3/2}$ and Ru $3d_{5/2}$ levels show similar binding energy changes. The Ru $3p_{3/2}$ line is preferable for comparison with the Rh $3d_{3/2,5/2}$ lines, however, as the strong C 1s line overlaps somewhat with the Ru $3d_{5/2}$ line, especially for those at higher binding energy, making exact determination of the Ru $3d_{5/2}$ binding energies more difficult.

The single N 1s peak observed at 400.8 eV for $Ru(NO)_2(PPh_3)_2$ and the infrared data [ν(NO) 1619 and 1665 cm^{-1}] recorded for this complex[24] indicate the presence of equivalent nitrosyl ligands. Without other evidence these data would also suggest that the nitrosyl ligands are nonlinearly coordinated. However, an x-ray diffraction study has revealed essentially linear Ru–NO groups.[40] Thus the low N 1s binding energy and ν(NO) stretching frequencies found for $Ru(NO)_2(PPh_3)_2$ presumably reflect an exceptional degree of $d\pi-p\pi^*$ back-donation due to the unusually low formal oxidation state of the ruthenium. This is reflected in the lower binding energies of the Ru $3p_{3/2}$ and $3d_{5/2}$ levels compared with the case of $RuCl_3NO(PPh_3)_2$. It is also in agreement with a recent study of iridium nitrosyls which show a parallel between the binding energies and the formal oxidation state of the iridium, which is in turn reflected in the Ir 4f binding energies.[14]

This clearly illustrates the difficulties in assigning bonding characteristics from N 1s binding energies alone. A more reliable approach must also consider the changes in binding energy of the other atoms in the complex, particularly the central metal atom, due to changes in metal oxidation state and the electronegativities of other ligands. Alternatively one may invoke parallels with related complexes such as the aryldiazo complexes considered here. Unfortunately the bis(aryldiazo) analogues of $Ru(NO)_2(PPh_3)_2$ are unknown and we are therefore unable to examine para-substituent effects in these systems.

However, the dinitrosyl cation $[RuCl(NO)_2(PPh_3)_2]^+$ [41] and the corresponding bis(aryldiazo) cations $[RuCl(N_2Ar)_2(PPh_3)_2]^+$ [27] are known as their hexafluorophosphate or tetrafluoroborate salts. The dinitrosyl complex is known to contain one linear and one nonlinear nitrosyl ligand;[25,41] however, no structural information is available for the corresponding bis(aryldiazo) derivatives.

The salt $[RuCl(NO)_2(PPh_3)_2][BF_4]$ displayed only a single N 1s peak, slightly broadened relative to that of $RuCl_3(NO)(PPh_3)_2$. Deconvolution of this peak gave N 1s binding energies of 403.6 and 402.5 eV, and hence a peak separation of 1.1 eV. This separation is considerably less than the values of 2.4[13] and 3.7 eV[17] recorded by other workers for the hexafluorophosphate derivative of the same cation. Careful measurement of the relative intensities of the Ru, Cl, N, and P peaks of our compounds confirmed the stoichiometry of $[RuCl(NO)_2(PPh_3)_2]^+$ [and also the bis(aryldiazo)complex] so that there was no decomposition or loss of NO during x irradiation in our experiments. At present, therefore, it is not possible to explain the discrepancies between the three different results. We would note, however, that our results for the binding energy difference are more consistent with those of the mononitrosyl complexes studied, and also the bis(aryldiazo) complex discussed below.

The complex $[RuCl(N_2C_6H_4Me)_2(PPh_3)_2][BF_4]$ also displayed only a single N 1s peak but with shoulders to both higher and lower binding energy (Figure 1) which could be readily interpreted in terms of inequivalent aryldiazo groups. A better deconvolution of this peak, though not necessarily a unique one, indicated the presence of two pairs of component peaks centered at 401.3 and 400.5 eV with splittings of 1.0 and 1.1 eV, respectively. This interpretation is in agreement with our data for the corresponding dinitrosyl cation and those for the complexes containing a single aryldiazo group. Thus although not unambiguous, it favors description of the complex in terms of a linear and a bent aryldiazo group. This view is supported by the difference of 1.2 eV between the Ru $3p_{3/2}$ binding energies of the dinitrosyl and bis(aryldiazo) compounds, which is the same (within experimental error) as for the ruthenium mononitrosyl and mono(aryldiazo) complexes.

While this paper was in preparation, Su and Faller reported[17] an empirical ESCA relationship for distinguishing linear and nonlinear nitrosyl ligands. They reported the O 1s–N 1s binding energy difference to be in the range 132 ± 1 eV for linear nitrosyls and 128 ± 2 eV for nonlinear nitrosyls. Our values for the linear nitrosyls are in accord with theirs and with the data of Folkesson.[43] However, our only nonlinear nitrosyl $RhCl_2NO(PPh_3)_2$ showed an O 1s–N 1s energy of 132.2 eV in contradiction of Su and Faller's hypothesis and their results. While this is only one point of disagreement, and their result for the O 1s binding energy of this compound is evidently subject to some doubt,[17] we have some reservations about the generality of their conclusions for bent nitrosyls.

Folkesson[43] has pointed out that surface oxygen impurities commonly appear at about 532 eV, and we have also observed this phenomenon. Most of the bent nitrosyls studied by Su and Faller show O 1s binding energies close to this value when the differences in energy scale are allowed for, and surface oxygen impurities would almost certainly have been present on their samples, especially as they were frequently deposited from oxygen-containing solvents such as water and methanol. It seems likely therefore that impurity oxygen lines may have been assigned as nitrosyl oxygen in some cases, particularly for the bent nitrosyls. It may also be noted that while Su and Faller rationalized their findings on the basis of calculations by Hoffman et al.,[44] they had to choose the less likely of two parameterization schemes in order to do so. The more normal scheme would predict an almost constant O 1s–N 1s energy with bending of the nitrosyl, which would be consistent with our observations.

In view of current interest in the reduction of coordinated dinitrogen and related nitrogen donor ligands[18,19] we have investigated charge levels and distribution in the aryldiazo and aryldiimine ligands and have compared these with similar results for dinitrogen complexes.[20-23] ESCA studies of substituted diazobenzenes[20] have revealed large para-substituent effects of the N 1s binding energies of the N_2^+ group, although the difference between the two nitrogen 1s levels remained almost constant at ca. 1.4 eV. The correlation of N 1s binding energies with Hammett σ_p constants has a slope of about 2.1 eV. In contrast the correlation of the Ru $3p_{3/2}$ binding energies of the aryldiazo compounds with Hammett σ_p constants has a much smaller slope (0.53 eV) and the average N 1s binding energies of these complexes are almost constant. This suggests that electronic charge back-donated from ruthenium to the $-N_2-$ moiety by $d\pi-p\pi^*$ bonding is compensated by that removed by the para-substituted aryl group.

The absence of any significant para-substituent effect on the N 1s binding energies of the rhodium aryldiazo complexes is rather surprising and must reflect, in part at least, the reduced conjugation of the aryl group and the $-N_2-$ moiety noted earlier.

It is useful to consider what the approximate charges on the nitrogens of the aryldiazo groups might be and how they compare with those of molecular N_2 complexes formed by transition metals. It is most appropriate to consider charges calculated with the CNDO molecular orbital method, as this gives more realistic values than extended Hückel or Pauling electronegativity calculations. Hendrickson et al.[42] have observed that the N 1s binding energies of a variety of nitrogen-containing molecules vary in an approximately linear manner with CNDO charge, with a slope of 10.8 eV/unit charge. This would indicate the $-N_2-$ group of the ruthenium and osmium aryldiazo compounds to be about 0.2 electron more positive than that of the rhodium complexes. The charges of the N_2 groups are predicted to be close to zero and thus differ considerably from the formal ones of 1+ and 1–, respectively. This conclusion is not unexpected; recent studies suggest[14,15] that relative charges on coordinated nitrosyl ligands may be the reverse of those implied by the NO^+/NO^- formalism. However, the average N 1s binding energies observed for the aryldiimine complexes suggest that the aryldiazo N_2 groups in the ruthenium and rhodium complexes may in fact be positively and negatively charged respectively. The binding energy for the rhodium aryldiimine complex is 0.5 eV greater than for the aryldiazo compound but 0.9 eV less in the case of the ruthenium complex. This would be expected if the ligand modification could be formally described as

$$(N_2\text{-}Ar)^- \xrightarrow{H^+} (HN_2\text{-}Ar)$$

and

$$(N_2\text{-}Ar)^+ \xrightarrow{H^-} (NH_2\text{-}Ar)$$

respectively. The higher N 1s binding energy of the rhodium aryldiimine complex compared with that of the ruthenium aryldiimine is also consistent with the higher formal oxidation state of the central metal ion (Rh^{III} and Ru^{II}). As might be expected for isoelectronic systems, the iridium complex appears to be very similar to the rhodium complex.

Finally, the N 1s splitting of 0.9 ± 0.3 eV for the $-N_2-$ group of the aryldiazo and aryldiimine complexes studied here is appreciably less than that of the free benzenediazonium cation[20] (1.4 eV) and markedly less than that of N_2 complexes, where splittings of up to 2 eV have been observed. It may be concluded therefore that the $-N_2-$ groups of the aryldiazo and aryldiimine complexes have relatively low polarity, with a charge difference between the nitrogens of about 0.1 on the CNDO charge scale.

Registry No. $RuCl_3(NO)(PPh_3)_2$, 29826-79-7; $RuCl_3(NO_2C_6H_4N_2)(PPh_3)_2$, 52620-30-1; $RuCl_3(ClC_6H_4N_2)(PPh_3)_2$, 52620-29-8; $RuCl_3(CH_3C_6H_4N_2)(PPh_3)_2$, 39556-32-6; $RhCl_2(NO)(PPh_3)_2$, 40231-80-9; $RhCl_2(NO_2C_6H_4N_2)(PPh_3)_2$, 36581-24-5; $RhCl_2(CH_3OC_6H_4N_2)(PPh_3)_2$, 36581-28-9; $RhCl_2(CH_3C_6H_4N_2)(PPh_3)_2$, 52620-36-7; $OsBr_3(NO)(PPh_3)_2$, 29292-11-3; $OsBr_3(CH_3C_6H_4N_2)(PPh_3)_2$, 52620-35-6; $[RuCl(NO)_2(PPh_3)_2]^+BF_4^-$, 54890-53-8; $[RuCl(CH_3C_6H_4N_2)_2(PPh_3)_2]^+BF_4^-$, 34247-63-7; $RhCl_3(HN_2C_6H_4CH_3)(PPh_3)_2$, 52620-39-0; $IrCl_3(HN_2C_6H_4CH_3)(PPh_3)_2$, 52620-41-4; $RuCl_2CO(HN_2C_6H_4OCH_3)(PPh_3)_2$, 61446-31-9; $Ru(NO)_2(PPh_3)_2$, 50442-24-5.

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Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

A Normal-Coordinate Analysis of Bis(*O,O'*-dialkyldithiophosphato)nickel(II) Complexes

WALTER RUDZINSKI, GEORGE T. BEHNKE, and QUINTUS FERNANDO*

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The infrared spectra of $Ni[S_2P(OCH_3)_2]_2$, $Ni[S_2P(OCD_3)_2]_2$, and $Ni[S_2P(OC_2H_5)_2]_2$ have been recorded in the range 4000–50 cm^{-1} and interpreted on the basis of a 1:1 metal ligand, molecular model of $Ni[S_2P(OCH_3)_2]_2$. A normal-coordinate analysis using a Urey–Bradley force field was carried out to assign infrared vibrational frequencies over a broad spectral range. The infrared band assignments for the metal complexes have been compared with those of analogous molecules. A good correlation was found between the results of the normal-coordinate analysis and previous assignments based on empirical evidence.

Introduction

Structural and spectral studies have shown that the four-membered chelate rings formed by the interaction of metal ions with dithiophosphates have significant differences that can be attributed to either electronic or steric effects that arise from the substituents on the phosphorus atom.[1-4] Variation of the alkyl or alkoxy substituent on the phosphorus atom affects the character of the phosphorus hybrid orbitals and causes marked changes in the phosphorus–sulfur bond distance and the sulfur–phosphorus–sulfur angle in the chelate ring. The phosphorus–sulfur bond order as well as the extent of charge localization on the metal atom and the sulfur donor atoms have been inferred from these investigations.[5] It has been presumed that the participation of phosphorus d orbitals in the bonding in the chelate ring is the primary reason for the differences in the geometry and the charge distribution in the chelate ring, but there are no experimental results that can substantiate this statement. A normal-coordinate analysis of the model compound, bis(*O,O'*-dimethyldithiophosphato)nickel(II), of known structure, was undertaken to establish a firm basis for understanding the factors that influence the stability and configuration of the metal complexes of the dithiophosphates.

Experimental Section

Synthesis of Bis(*O,O'*-dimethyldithiophosphato)nickel(II), Ni(DMP)$_2$.[6] Methanol (100 mL) was added slowly over a period of 1.5 h to 110 g of finely powdered P_2S_5 (Eastman Chemical Co.). The reaction mixture was heated under reflux for 3 h and the H_2S gas that was evolved was passed through scrubbers containing H_2O_2 and NaOH. The reaction product which consisted of a black oily liquid was filtered and the filtrate was extracted with three 50-mL portions of water. Finely powdered $NiSO_4 \cdot 6H_2O$ was added to the aqueous extract containing the *O,O'*-dimethyldithiophosphonic acid. Violet crystals of the nickel complex which formed on standing were filtered, dried, and dissolved in hot ethanol. The unreacted nickel sulfate precipitated as green crystals and was separated by filtration. When the filtrate was cooled to −15 °C, violet crystals of the pure nickel complex were obtained.

Bis(*O,O'*-diethyldithiophosphato)nickel(II), Ni(DEP)$_2$, was synthesized in the same manner as above by using ethanol instead of methanol.

Synthesis of Bis(*O,O'*-dimethyldithiophosphato-d_6)nickel(II), Ni(DMP-d_6)$_2$. The method used for the synthesis of the deuterio analogue of Ni(DMP)$_2$ was essentially that described by Nyquist.[7] CD_3OD (5 mL) (Aldrich Chemical Co.) was dissolved in 10 mL of toluene and added dropwise over a period of 1.5 h to a stirred mixture of 6.5 g of P_2S_5 in 20 mL of toluene. The toluene was dried over sodium metal and freshly distilled before use. The reaction mixture was maintained at 85 °C for 4.5 h in an atmosphere of nitrogen, cooled to room temperature, filtered to remove the sulfur precipitate, and distilled under reduced pressure to remove the toluene. The viscous liquid that remained was extracted with three 2-mL portions of D_2O (Stohler Isotope Chemicals). Finely powdered $NiSO_4 \cdot 6H_2O$ was added to the D_2O extract and allowed to stand. The violet crystals that formed were separated, dried under reduced pressure, and dissolved in hot ethanol. The unreacted $NiSO_4$ was separated by filtration and the filtrate was cooled to −15 °C for about 2 h. The violet crystals that formed were filtered, dried under vacuum, and stored in a desiccator over molecular sieves (3 Å).

Synthesis of Bis(*O,O'*-diethyldithiophosphato)platinum(II), Pt(DEP)$_2$.[8] $PtCl_2$ (133 mg) was digested in 10 mL of aqua regia, and KCl (320 mg) was added to the solution followed by 10 mL of concentrated HCl. The mixture was heated for 1.5 h and 10 mL of water was added. The resultant solution was red brown and contained $PtCl_4^{2-}$. The addition of an excess of the ammonium salt of *O,O'*-diethyldithiophosphonic acid to the solution containing $PtCl_4^{2-}$ produced a lemon yellow precipitate which was separated, recrystallized from hot acetone, and stored in a desiccator.

Spectral Measurements. The infrared spectra from 4000 to 200 cm^{-1} were obtained with a Beckman IR-12 double-beam spectrophotometer. The KBr disk method was used between 4000 and 600 cm^{-1}; the Nujol mull technique and polyethylene pellets were used to record the spectra from 600 to 200 cm^{-1}.

The far-infrared spectra from 300 to 50 cm^{-1} were obtained in polyethylene pellets and carbon disulfide solutions with a Beckman IR-11 spectrophotometer equipped with a bolometer detector cooled by liquid helium. Wavelength calibrations were made with polystyrene film and water vapor.

Calculations

The calculations were simplified by treating the planar Ni(DMP)$_2$ complex as a 1:1 metal–ligand system conforming to the molecular model shown in Figure 1. The two methoxy groups bonded to the phosphorus atom were treated as single atoms X_1 and X_2 having an effective mass of 15.994 amu. This six-atom model contains 15 internal coordinates having the following molecular parameters obtained from a single crystal x-ray structure determination:[9] $r_1 = r_2 = 2.22$ Å, $r_3 = r_4 = 1.98$ Å, $r_5 = r_6 = 1.565$ Å, $\alpha = 88°$, $\beta_1 = \beta_2 = 84.5°$, $\nu = 103°$, $\delta_1 = \delta_2 = \theta_1 = \theta_2 = 115°$, $\epsilon = 96°$. Since the model has C_{2v} symmetry, its 12 normal vibrations may be classified into four