ESCA Studies on the Charge Distribution in Some Dinitrogen Complexes of Rhenium, Iridium, Ruthenium, and Osmium

BÖRJE FOLKESSON

Division of Inorganic Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

Nitrogen $1s$ electron spectra have been recorded on the following rhenium dinitrogen complexes, *viz.* $ReClN_2(Ph_2PCH_2PPh_2)_2$, $ReClN_2$-$[Ph_2P(CH_2)_2PPh_2]_2$, $ReClN_2(Ph_2PCH=CHPPh_2)_2$, $ReClN_2(PMe_2Ph)_4$ and $ReClN_2(PPh_2Me)_4$ and on $IrClN_2(PPh_3)_2$. Two peaks in the $N1s$ electron spectra show that the dinitrogen ligand has an appreciable polarity. It has been found that both the nitrogen atoms in the complexes carry a negative charge. The total charge on the dinitrogen group was found to be about $0.7 - 0.9$ a.u. A connection between the magnitude of the shift in nitrogen $1s$ binding energy and the $N-N$ stretching frequency has been found, *viz.* the lower the $N-N$ stretching frequency the larger the chemical shift in binding energy. This means that the more disturbed the dinitrogen molecule is, indicated by a low $N-N$ stretching frequency, the larger is the charge separation on the nitrogen atoms.

Nitrogen $1s$ electron spectra have also been recorded on dinitrogen complexes of ruthenium and osmium, *viz.* $Ru(NH_3)_5N_2X_2$ and $Os(NH_3)_5N_2X_2$, where $X = Cl$, Br, I. As these complexes also contain ammonia, the $N1s$ electron spectra were found to be broad and of high intensity. So far, no resolution of the spectra into components has been successful, and consequently no information about the charge distribution on the dinitrogen ligand in the ruthenium and the osmium complexes is yet available. Work on this subject is in progress.

Besides nitrogen $1s$ electron spectra, some metal electron spectra have also been recorded on the dinitrogen complexes and on some other compounds of various formal oxidation states of the metal. Thereby, it was possible to get an idea about the charge on the metal atom in the dinitrogen complexes. Thus, it was found that the metal atom in the dinitrogen complexes of rhenium and iridium carries a small positive charge only, while the metal atom in the dinitrogen complexes of ruthenium and osmium was considerably more positive.

The binding energies of the atomic core electrons depend on the chemical surroundings of the atom. Recent developments in photoelectron spectroscopy (ESCA) have made possible the measurements of chemical shifts of inner-electron binding energies.[1] Correlations have been established between measured electron binding energies and formal oxidation state in sulphur [1,2]

and chlorine [1,3] compounds and with fractional atomic charges (calculated by a modification of Pauling's method [4]) in sulphur,[1] nitrogen,[5] and carbon [6] compounds. Also, more elaborate theoretical calculations, *e.g.* CNDO calculations,[7] of the charge distribution in molecules have been performed and correlated with ESCA data.[8-11] Atomic charges from extended Hückel calculations [12] have also been correlated with electron binding energies in nitrogen [13] and phosphorus [14] compounds.

Recently, Leigh *et al.*[15] reported nitrogen $1s$ electron spectra on two rhenium dinitrogen complexes. In one of these complexes, a chemical shift in the nitrogen $1s$ binding energy of about 2 eV was found. This shift was found to correspond to a difference in charge on the two nitrogen atoms of 0.4 a.u. based on Pauling charges from the correlation diagram given by Nordberg *et al.*[5] It was thus shown that the $N-N$ bond has an appreciable polarity.

Earlier, infrared spectroscopic investigations by the present author [16,17] on metal dinitrogen complexes have given approximate information about the polarity of the $N-N$ bond. Increased information about the charge distribution in the dinitrogen complexes is to be expected by applying the ESCA method on these complexes. Nitrogen $1s$ electron spectra have therefore been recorded on the following metal dinitrogen complexes: $Ru(NH_3)_5N_2X_2$, $Os(NH_3)_5N_2X_2$, where $X = Cl$, Br and I; $IrClN_2(PPh_3)_2$ and some rhenium dinitrogen phosphino complexes. The $N-N$ stretching frequency in the above mentioned complexes varies between 1900 cm^{-1} and 2100 cm^{-1}, and perhaps there is a connection between the magnitude of the ESCA shift in binding energy and the $N-N$ stretching frequency. Nitrogen $1s$ electron spectra have also been redetermined for a number of ionic nitrogen compounds. The measured nitrogen $1s$ binding energies have been plotted against calculated charges on nitrogen atoms given in the literature. The correlation diagrams thus obtained have been used in the determination of the charges on the nitrogen atoms in the dinitrogen complexes.

Electron spectra have also been recorded on pure metals of ruthenium, osmium, iridium, and rhenium and on some oxides and chlorides of the metals to compare the binding energies of some of the metal core electrons with the corresponding binding energies for the dinitrogen complexes. Thereby, some information about the charge on the metal atom in the dinitrogen complexes is to be expected.

EXPERIMENTAL

Chemicals. The same preparations of the dinitrogen complexes as those used in the earlier work [16,17] were used in this investigation. The ionic nitrogen compounds used to construct the correlation diagrams were of analytical grade. The metals, the metal oxides, and the metal chlorides were of lower purity.

Experimental techniques. The measurements were performed with an AEI ES 100 electron spectrometer. This is equipped with a hemispherical electrostatic analyzer and uses a preretardation field. Oil diffusion pumps fitted with cold traps produce a vacuum of 10^{-7} torr during the measurements. All spectra were obtained with AlKα-radiation (1486.6 eV). The instrumental resolution for gold $4f_{7/2}$ electrons is 1.30 eV under the experimental conditions in this work. The electron binding energy E_b can be obtained [1] from the following expression:

$$E_b = h\nu - E_{kin} - \phi_{spec} \qquad (1)$$

where $h\nu$ is the quantum energy of the characteristic X-rays used to eject the electrons and E_{kin} is the measured kinetic energy of the electrons. ϕ_{spec} is a constant including the work function of the spectrometer. According to the calibration,[18] it has been found that electron binding energies can be obtained from the following equation, when AlKα-radiation is used, viz.

$$E_b = 1476.9 - E_{kin} \tag{2}$$

As ESCA is a surface method, it is of importance how the surface is constituted during the measurements. Therefore, the following preparation procedure was used. The dinitrogen complexes were dissolved in a suitable solvent; the iridium and rhenium dinitrogen complexes were dissolved in chloroform, the other dinitrogen complexes in water. The ionic nitrogen compounds were partly dissolved in water-ethanol. One or two drops of the solution or suspension were immediately placed on a platinum foil. A thin film of the compound was obtained on the foil after evaporation of the solvent. Through this preparation procedure no surface charging effects were obtained during the measurements. Charging effects depending on sample thickness have recently been investigated by Johansson et al.[19] Their results are in agreement with our findings. If the film was not too thick, it was possible to register platinum signals and thus refer measured binding energies to a fixed platinum peak. As reference peak, that of $Pt4f_{7/2}$ electrons has been chosen, which was found to have $E_{kin} = 1405.8$ eV. The binding energy of $Pt4f_{7/2}$ electrons is thus from eqn. (2) 71.1 eV, a value in good agreement with the literature.[20] Two or sometimes three measurements were made on each sample except for the dinitrogen complexes, for which nitrogen $1s$ electron spectra were recorded at least five times. After each recording, the $Pt4f_{7/2}$ electron peak from the backing platinum foil was also recorded. All reported binding energy values are consequently referred to the binding energy of $Pt4f_{7/2}$ electrons. The reproducibility of the photoelectron peaks was within 0.1 eV.

RESULTS AND DISCUSSION

Rhenium and iridium dinitrogen complexes. Nitrogen $1s$ electron spectra have been recorded on five rhenium dinitrogen complexes, viz. the complexes I – V in Table 1. Fig. 1 shows the nitrogen $1s$ electron spectrum of $ReClN_2$-$(Ph_2PCH_2PPh_2)_2$. It is evident that the $1s$ electrons of coordinated dinitrogen give rise to two peaks separated by 1.9 eV. The $1s$ electrons of the two nitrogen atoms have thus different binding energies, which indicates [1] different effective charges on the nitrogen atoms. Compound II gave an identical nitrogen $1s$ electron spectrum, but the intensity of the N$1s$ electron peaks was smaller, probably depending on lower crystallinity of this complex. Compound III, on the other hand, gave also the same nitrogen $1s$ electron spectrum as compounds I and II, but the N$1s$ electron peaks were not at the same binding energy between different recordings. This fact can indicate surface charging or decomposition effects. It was found previously [17] that complex III was probably not quite pure. Surface charging or decomposition effects can probably occur as a result of the impurity of complex III. Even the positions of the C$1s$ and Re electron peaks were found to change with time. The shift in binding energy of the N$1s$ electrons was, however, constant and equal to that found for complexes I and II. The first recorded spectrum of complex III gave the same N$1s$ binding energies as complexes I and II. In Fig. 2, the nitrogen $1s$ electron spectrum of complex IV is shown. It can be seen that the difference in N$1s$ binding energy for the two nitrogen atoms is somewhat larger (about 2.1 eV) than for complex I (cf. Fig. 1). This fact indicates a larger charge separation on the nitrogen atoms. Complex V, viz. $ReClN_2(PPh_2Me)_4$, gave

Table 1. Measured nitrogen $1s$ binding energies (E_b) and obtained charges on the nitrogen atoms ($M-N_1-N_2$) in the dinitrogen complexes of rhenium and iridium.

Metal complex	E_b eV $N_1 1s$	$N_2 1s$	Shift eV	Extended Hückel $-q_{N_1}$ a.u.	$-q_{N_2}$ a.u.	CNDO $-q_{N_1}$ a.u.	$-q_{N_2}$ a.u.	Ab initio SCF MO $-q_{N_1}$ a.u.	$-q_{N_2}$ a.u.	$\nu_{NN}(CHCl_3)$ cm^{-1}
I. ReClN$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$	398.5	400.4	1.9±0.1	1.20	0.25	0.47	0.24	0.56	0.28	1993
II. ReClN$_2$[Ph$_2$P(CH$_2$)$_2$PPh$_2$]$_2$	398.5	400.4	1.9±0.1	1.20	0.25	0.47	0.24	0.56	0.28	1975
III. ReClN$_2$(Ph$_2$PCH=CHPPh$_2$)$_2$	398.5	400.4	1.9±0.1	1.20	0.25	0.47	0.24	0.56	0.28	1970
IV. ReClN$_2$(PMe$_2$Ph)$_4$	398.2	400.3	2.1±0.1	1.30	0.30	0.50	0.25	0.60	0.30	1924
V. ReClN$_2$(PPh$_2$Me)$_4$	—	—	2.1±0.1	1.30	0.30	0.50	0.25	0.60	0.30	1922
IrClN$_2$(PPh$_3$)$_2$	399.1	400.5	1.4±0.2	0.90	0.20	0.40	0.23	0.47	0.27	2105
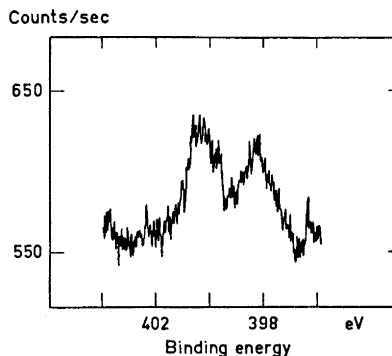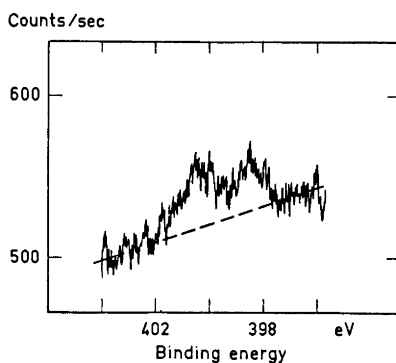
Fig. 1. Nitrogen 1s electron spectrum of ReClN$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$.

Fig. 2. Nitrogen 1s electron spectrum of ReClN$_2$(PMe$_2$Ph)$_4$.

also two N1s electron peaks, but the position of the peaks in the spectrum was found to be different between different recordings. The difference in N1s binding energy for the two nitrogen atoms was, however, the same as for complex IV. Complex V has earlier[17] been found to be impure and infrared intensity measurements could not be performed on this complex. As suggested above, surface charging or decomposition is probably related to the impurity of the compounds. The measurements on complex V have been omitted, as accurate N1s binding energy values could not be determined and the infrared intensity value (A_{NN}) was not available. Nitrogen 1s electron spectra have also been recorded on IrClN$_2$(PPh$_3$)$_2$. The intensity of the two N1s electron peaks was, however, small and therefore it was more difficult to determine the exact position of the two peaks. The magnitude of the shift in N1s binding energy was, however, found to be smaller than the corresponding shift for the rhenium dinitrogen complexes. The error in the measured binding energy is as mentioned above ± 0.1 eV, but for IrClN$_2$(PPh$_3$)$_2$ the error in the measured N1s binding energy was found to be ± 0.2 eV. The measured nitrogen 1s binding energies for the complexes described so far are given in Table 1.

To obtain the charges on the nitrogen atoms in the dinitrogen complexes, the measured binding energies can be compared with correlation diagrams given in the literature.[5,13] Because of various preparation techniques and different ways of referring measured binding energies (e.g. with the C1s electron peak as a reference [1]), a direct comparison with earlier measurements seems to be uncertain. Therefore, nitrogen 1s electron spectra have been recorded on a number of ionic nitrogen compounds, i.e. such compounds which have been measured before [13] and for which the charge on the nitrogen atoms has been calculated. The N1s binding energies measured by the present author are given in Table 2 together with the effective charge on the nitrogen atoms calculated by Hendrickson et al.[13] Recently, Wyatt et al.[21] have presented charges on the nitrogen atoms in the salts KN$_3$, KNO$_2$, and KNO$_3$ from ab initio SCF

Table 2. Nitrogen $1s$ binding energies and calculated charges.

Com-pound No.	Compound	Half-width eV	Nitrogen $1s$ binding energy	Calculated nitrogen atom charge a.u.		
				Extended Hückel [13]	CNDO [13]	*Ab initio* SCF MO [21]
1	$NaNO_3$	1.7	407.3	$+2.557$	$+0.429$	$+0.66$
2	$NaNO_2$	1.7	403.3	$+1.273$	$+0.100$	$+0.20$
3	NaN_3	1.8	403.0	$+1.066$	$+0.096$	$+0.14$
3	NaN_3	1.9	398.6	-1.033	-0.548	-0.57
4	$N_2H_6SO_4$	2.0	401.7	$+0.184$	$+0.094$	
5	KCN	1.9	398.1	-1.181	-0.518	
6	$KOCN$	2.2	397.9	-1.572	-0.550	
7	$NaSCN$	1.6	397.8	-1.672		
8	NH_4NO_3	1.8	406.0	$+2.557$	$+0.429$	
8	NH_4NO_3	2.1	400.9	-0.145	$+0.039$	
9	$NH_2OH.HCl$	2.7	401.4	$+0.612$	$+0.219$	

MO calculations and these charges are also included in Table 2. On comparison between the binding energies measured by the present author and those measured by Hendrickson *et al.*[13] and by Wyatt *et al.*[21], a fairly good agreement is obtained. The binding energies are then plotted against calculated charge. In this way, three different correlation diagrams are obtained (Figs. 3 – 5). The correlation between nitrogen $1s$ binding energy and calculated charge seems to be linear in all diagrams. This was also the case from the
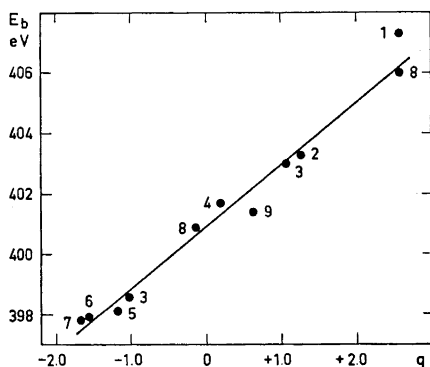

Fig. 3. Plot of nitrogen $1s$ binding energies (E_b) against extended Hückel calculated charges (q) on nitrogen atoms. The numerals refer to those used in Table 2.
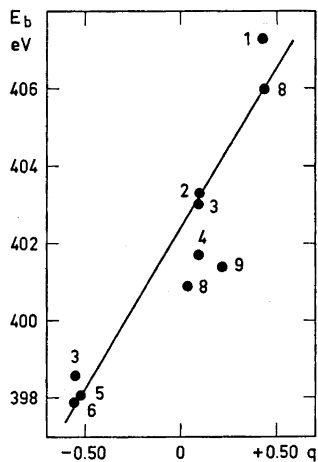

Fig. 4. Plot of nitrogen $1s$ binding energies (E_b) against CNDO calculated charges (q) on nitrogen atoms. The numerals refer to those used in Table 2.
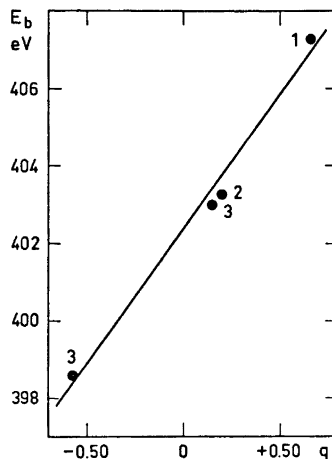
Fig. 5. Plot of nitrogen $1s$ binding energies (E_b) against *ab initio* SCF MO calculated charges (q) on nitrogen atoms. The numerals refer to those used in Table 2.

results of Hendrickson *et al.*[13] It can also be seen from Table 2 that the nitrogen atom charges obtained from extended Hückel calculations range from -1.7 to almost $+2.6$. Much smaller charge variation is obtained from CNDO calculations. It is also of interest to see that the charges obtained from CNDO and *ab initio* SCF MO calculations are almost the same.

The charges on the nitrogen atoms in the dinitrogen complexes can now be estimated by comparison between measured N$1s$ binding energies and the correlation diagrams. The result is given in Table 1. It can be seen that both the nitrogen atoms are found to be negatively charged. This fact indicates an increase of the electron density over the dinitrogen ligand caused by $d\pi - p\pi$ * back donation from filled metal d-orbitals to antibonding π-orbitals of dinitrogen. This result thus confirms and strengthens the earlier results from the infrared intensity measurements.[16,17] The total negative charge on the dinitrogen ligand is found to be greatest for $ReClN_2(PMe_2Ph)_4$ and smallest for $IrClN_2(PPh_3)_2$. This result is completely in accordance with the infrared intensity measurements,[17] for the intensity (A_{NN}) for $ReClN_2$-$(PMe_2Ph)_4$ was found to be larger than the intensity (A_{NN}) for $IrClN_2(PPh_3)_2$. It seems, however, difficult to decide [22] which nitrogen atom should carry which charge. Leigh *et al.*[15] assign the smallest N$1s$ binding energy to the terminal nitrogen atom, which thus gets the largest negative charge. It has been concluded earlier,[17] through a combination of infrared intensity data and the charges on the nitrogen atoms determined in this investigation, that the terminal nitrogen atom is the least negative one. Therefore, the largest nitrogen $1s$ binding energy is assigned to the terminal nitrogen atom. The difference in charge on the two nitrogen atoms is about 1 a.u. from the extended Hückel method. From the CNDO method and the *ab initio* SCF MO method the difference in charge on the nitrogen atoms is about 0.2 to 0.3 a.u., respectively. The charge separation varies, however, from one complex to another. The

greatest difference in charge on the nitrogen atoms is observed for $ReClN_2$-$(PMe_2Ph)_4$ and the smallest for $IrClN_2(PPh_3)_2$. It was mentioned above that surface charging effects probably occur on the measurements on $ReClN_2$-$(PPh_2Me)_4$, which made it impossible to get accurate $N1s$ binding energies. The charges on the nitrogen atoms in this complex are, however, assumed to be the same as those in $ReClN_2(PMe_2Ph)_4$, as the magnitude of the shift in $N1s$ binding energy is the same for both the complexes. Further support for this suggestion is that the $N-N$ stretching frequency is the same in the two complexes (cf. Table 1).

It is of interest to compare the magnitude of the shift in $N1s$ binding energy with the $N-N$ stretching frequency in the dinitrogen complexes (cf. Table 1). The largest shift in $N1s$ binding energy is found for the complexes $ReClN_2$-$(PMe_2Ph)_4$ and $ReClN_2(PPh_2Me)_4$. Thus, the lower the $N-N$ stretching frequency the larger is the shift in binding energy. This means that when the disturbance of the dinitrogen molecule is large, i.e. low ν_{NN}, the charge separation on the nitrogen atoms is large. When the disturbance of the dinitrogen molecule is considerable, there will be a decrease in the $N-N$ bond order. It then follows [16,17] that the $M-N_2$ bond will be stronger. The conclusion above can thus be expressed in another way, viz. the stronger the dinitrogen ligand is bound to the metal, the more pronounced is the charge separation on the nitrogen atoms. The smallest shift in $N1s$ binding energy is found for $IrClN_2$-$(PPh_3)_2$, which complex also shows the highest $N-N$ stretching frequency. The charge separation on the nitrogen atoms in this complex is thus smaller than the charge separation on the nitrogen atoms in the rhenium complexes. The smallest $N1s$ binding energy is found for the inner nitrogen atom in $ReClN_2(PMe_2Ph)_4$, and thus this nitrogen atom is the most negative one. In the other rhenium dinitrogen complexes and in $IrClN_2(PPh_3)_2$, the corresponding binding energy is higher and thereby the inner nitrogen atom is less negative. The difference in $N1s$ binding energy of the terminal nitrogen atom for the various complexes is not so pronounced (cf. Table 1) and consequently, the charges on the terminal nitrogen atoms are more similar than the charges on the inner nitrogen atoms.

To get an idea about the charge on the metal atom in the complexes some metal core electron spectra have also been recorded. Table 3 shows the binding energies of $Re4f_{5/2}$ and $Re4f_{7/2}$ electrons in the dinitrogen complexes together with the corresponding binding energies for Re metal and $ReOCl_3(PPh_3)_2$. A representative example of a $Re4f$ electron spectrum of a rhenium dinitrogen complex is given in Fig. 6. For $IrClN_2(PPh_3)_2$, the $Ir4f_{5/2}$ and $Ir4f_{7/2}$ electron peaks have been registered and the binding energies are compared with the corresponding binding energies for Ir metal and $IrCl_3$. These binding energies are included in Table 3. It is evident that the $Re4f_{5/2}$ and $Re4f_{7/2}$ electron binding energies are practically constant from one rhenium dinitrogen complex to another. These binding energies are also about the same as those measured for Re metal. This indicates a low positive charge on the metal atom. On the other hand, it is expected that the π^*-acceptor ability of the dinitrogen ligand should cause a lower electron density around the metal atom and consequently a higher binding energy and thereby a positive charge on the rhenium atom. Probably the increased positive charge is partly reduced by the σ-bond from
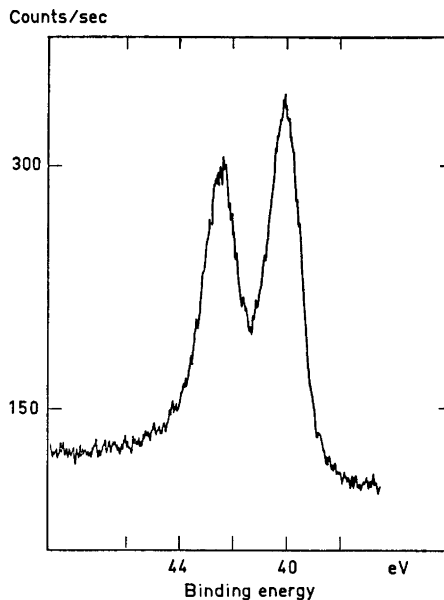
Fig. 6. Rhenium $4f$ electron spectrum of
$ReClN_2(Ph_2PCH_2PPh_2)_2$.

the dinitrogen ligand to the metal. Depending on the various degree of π-backbonding in the different complexes, there should be a slight difference in electron density around the metal atom and consequently a difference in binding energy. This has, however, not been found. It must be pointed out that also the σ-donor and π-acceptor ability of the phosphine ligands can influence the charge on the metal atom and certainly do so, but this effect has not been investigated. Probably this balance of σ- and π-bonding can serve to keep the electron density around the rhenium atom fairly constant, as observed. It is, however, evident that the σ-donor ability of the phosphine ligands can be the most pronounced, and thus cause an increase of the electron

Table 3. The binding energies of $M4f_{5/2}$ and $M4f_{7/2}$ electrons in the dinitrogen complexes of rhenium and iridium and in some other rhenium and iridium compounds. M stands for Re and Ir.

Compound	E_b eV	
	$M4f_{5/2}$	$M4f_{7/2}$
Re metal	42.5	40.1
$ReClN_2(Ph_2PCH_2PPh_2)_2$	42.5	40.1
$ReClN_2[Ph_2P(CH_2)_2PPh_2]_2$	42.4	40.1
$ReClN_2(PMe_2Ph)_4$	42.6	40.2
$ReOCl_3(PPh_3)_2$	46.2	43.7
Ir metal	63.2	60.3
$IrClN_2(PPh_3)_2$	63.5	60.7
$IrCl_3$	65.4	62.7

density around the metal atom and thereby reduce the positive charge caused by π-backbonding to the dinitrogen ligand. The suggestions above can thus explain the low and equal Re$4f$ electron binding energies measured for the rhenium dinitrogen complexes. The effect of σ-donor and π-acceptor ability of phosphine ligands has been discussed in connection with ESCA measurements by Blackburn et al.[23] on some metal phosphine complexes and by Cook et al.[24] on some platinum phosphine complexes. These authors[23,24] find that the P$2p$ electron binding energies are practically constant from one complex to another, which indicates that there might be a balance between the P$\rightarrow$M σ-bonding and the M$\rightarrow$P π-bonding. The effect of σ- and π-bonding in some palladium phosphine complexes has recently been discussed by Kumar et al.,[25] supporting the suggestions above on the rhenium dinitrogen phosphino complexes.

In the compound ReOCl$_3$(PPh$_3$)$_2$, the Re$4f_{5/2}$ and Re$4f_{7/2}$ electron binding energies are higher than the corresponding binding energies in the rhenium dinitrogen complexes, which is also to be expected, as the formal oxidation state on the rhenium atom is greater. It must, however, be pointed out that the Re$4f$ electron binding energies measured in this investigation are about 5 eV lower than those given by Siegbahn et al.[1] In the electron spectrum of Re metal, small peaks were obtained at binding energies about 5 eV higher than the main peaks, so the binding energies given by Siegbahn et al.[1] probably are assigned to Re of a higher formal oxidation state. Recently, Nefedow[26] reported binding energies of Re in good agreement with those measured in this work.

The degree of $d\pi - p\pi^*$ back donation from metal d-orbitals to π-orbitals of dinitrogen has earlier[17] been found to be smaller in the iridium dinitrogen complex, IrClN$_2$(PPh$_3$)$_2$, than in the rhenium dinitrogen complexes. It is thus to be expected that the iridium atom is less positive than the rhenium atom in the dinitrogen complexes. But the Ir$4f_{5/2}$ and Ir$4f_{7/2}$ electron binding energies in IrClN$_2$(PPh$_3$)$_2$ are somewhat higher than the corresponding binding energies in Ir metal, which indicates a small positive charge on the iridium atom. This is to be compared with the rhenium complexes above, where the Re$4f_{5/2}$ and Re$4f_{7/2}$ electron binding energies were found to be equal to those measured for Re metal. The influence of the phosphine ligands on the charge of the iridium atom has not been investigated. In an investigation by Chatt et al.[27] on iridium dinitrogen complexes containing various phosphine ligands, it was found that the more aliphatic phosphine complexes tend to have slightly lower N – N stretching frequencies. The more aliphatic phosphines are the more basic ones and so they should consequently increase the electron density around the metal atom. It is thus quite reasonable that the σ-bond from the phosphorus in triphenylphosphine to the metal is weaker in the iridium complex than in the more aliphatic phosphino rhenium complexes above. Consequently, the iridium atom can be more positive than the rhenium atom in the dinitrogen complexes, which is shown by the results reported here.

The Ir$4f_{5/2}$ and Ir$4f_{7/2}$ electron binding energies in IrClN$_2$(PPh$_3$)$_2$ are, however, found to be smaller than the corresponding binding energies in IrCl$_3$, which also is to be expected, as the formal oxidation state on the metal atom is smaller in IrClN$_2$(PPh$_3$)$_2$ than in IrCl$_3$.

Table 4. Measured nitrogen $1s$ binding energies (E_b) and half-widths of the N$1s$ electron peaks in the dinitrogen complexes of ruthenium and osmium.

Metal complex	E_b eV	Half-width eV
$Ru(NH_3)_5N_2Cl_2$	399.6	2.0
$Ru(NH_3)_5N_2Br_2$	399.4	2.2
$Ru(NH_3)_5N_2I_2$	399.6	1.8
$Os(NH_3)_5N_2Cl_2$	399.5	2.2
$Os(NH_3)_5N_2Br_2$	399.7	2.0
$Os(NH_3)_5N_2I_2$	399.6	1.9

Ruthenium and osmium dinitrogen complexes. Nitrogen $1s$ electron spectra have also been recorded on the ruthenium and osmium dinitrogen complexes, which were investigated earlier [16] by infrared spectroscopy. As these complexes also contain ammonia, the nitrogen $1s$ electron spectrum shows a quite symmetrical N$1s$ electron peak arising from the nitrogen in ammonia and the nitrogen in the dinitrogen ligand. The expected two N$1s$ electron peaks from coordinated dinitrogen are overlapped by the peak from nitrogen in ammonia. A typical nitrogen $1s$ electron spectrum for this kind of dinitrogen complex is given in Fig. 7. In Table 4, measured N$1s$ binding energies of the ammonia nitrogen in the various dinitrogen complexes of ruthenium and osmium are given together with the half-widths of the N$1s$ electron peaks. The half-widths of the peaks are about the same as those found for the ionic nitrogen compounds (*cf.* Table 2), and consequently no indication that the peaks can consist of several components is observed. It is evident from the correlation diagrams (Figs. 3 − 5) that the ammonia nitrogen in the dinitrogen complexes carries a negative charge. The negative charge on the ammonia nitrogen is about the same for all the complexes. The N$1s$ binding energies measured for the ammonia nitrogen lie between those measured for the two nitrogen atoms in the rhenium and iridium dinitrogen complexes (*cf.* Table 1). It is thus reasonable that the N$1s$ electron peaks corresponding to coordinated dinitrogen are located on either side of the maximum of the large N$1s$ electron peak. This conclusion is also supported by the connection between the magnitude of the shift in N$1s$ binding energy and the N−N stretching frequency, which has been found for Re and Ir complexes, and also applied to these complexes. Work is in progress to resolve the N$1s$ electron peaks into components, but as the peaks are quite symmetrical, it is uncertain if this will be successful. The N$1s$ electron spectra of the osmium dinitrogen complexes are particularly complicated to analyse, as these compounds also contain a bisdinitrogen complex.[16] N$1s$ electron spectra on which resolution calculations are in progress have been obtained through measurements with better statistics. If it is possible to resolve the N$1s$ electron spectra of these dinitrogen complexes, the results will be presented later.

To get some information about the charge on the metal atom in the dinitrogen complexes, some metal core electron spectra have also been recorded. It has been found that the $Ru3p_{3/2}$ and $Ru3d_{5/2}$ electron levels give the highest
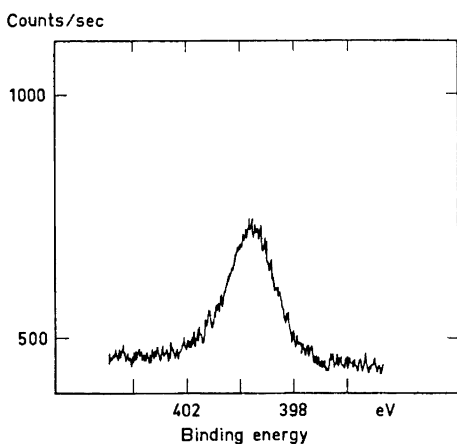
Counts/sec

Fig. 7. Nitrogen $1s$ electron spectrum of $Os(NH_3)_5N_2I_2$.

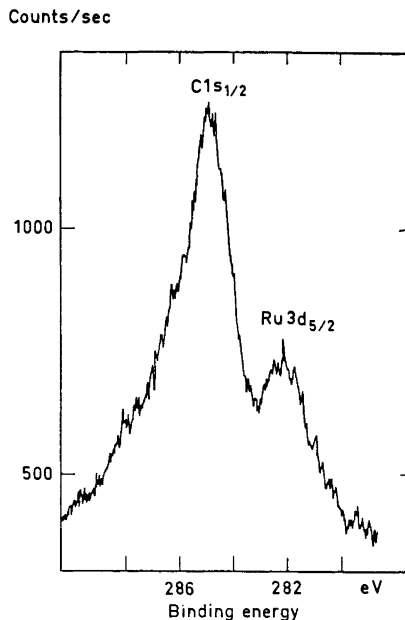*Fig. 8.* Electron spectrum of $Ru(NH_3)_5N_2I_2$ in the carbon $1s$ region.

intensity of the peaks. The $Ru3d_{3/2}$ electrons have about the same binding energy as $C1s$ electrons and, as a carbon peak arising from the pump oil contamination is always obtained, it is difficult to separate the $Ru3d_{3/2}$ electron peak from the carbon $1s$ electron peak. This is demonstrated in Fig. 8, which shows the electron spectrum of $Ru(NH_3)_5N_2I_2$ in the carbon $1s$ region. Therefore, the $Ru3p_{3/2}$ electron peak has been studied instead of the $Ru3d_{3/2}$ electron peak. Electron spectra have also been recorded on Ru metal, $RuCl_3$, and RuO_2 and the binding energies of the $Ru3p_{3/2}$ and $Ru3d_{5/2}$ electron levels determined. The results are given in Table 5. The binding energies measured for

Table 5. Binding energies (E_b) of $Ru3p_{3/2}$ and $Ru3d_{5/2}$ electrons in the ruthenium dinitrogen complexes and in some other ruthenium compounds.

Compound	E_b eV	
	$Ru3p_{3/2}$	$Ru3d_{5/2}$
Ru metal	462.2	279.9
$Ru(NH_3)_5N_2Cl_2$	463.3	282.5
$Ru(NH_3)_5N_2Br_2$	462.2	280.5
$Ru(NH_3)_5N_2I_2$	463.5	282.2
$RuCl_3$	463.3	281.8
RuO_2	463.2	282.1

Ru metal are about 1 eV higher than those given by Siegbahn $et\ al.$[1] It is evident that the binding energies measured for the dinitrogen complexes are close to those for $RuCl_3$ and RuO_2. The binding energies are also higher than the corresponding binding energies for Ru metal. The only exception is the ruthenium bromide. The high binding energy values indicate a high positive charge on the metal atom in the dinitrogen complexes. This result can be compared with the results for the rhenium and iridium dinitrogen complexes, where the binding energies of the metal electrons were close to those of the pure metals, indicating a low positive charge on the metal atom. The reason for the high positive charge on the metal atom in the dinitrogen complexes of ruthenium is, besides the $d\pi - p\pi^*$ back donation from metal to the dinitrogen ligand, that the metal atoms are surrounded by strongly electronegative halide ions.

The ruthenium bromide, on the other hand, shows $Ru3p_{3/2}$ and $Ru3d_{5/2}$ electron binding energies which are considerably smaller than the corresponding binding energies for the chloride and iodide. This fact could indicate a low positive charge on the metal atom in the bromide complex. But a more reasonable explanation of the low binding energies of this complex is that the bromide complex contains an impurity. During the preparation procedure [16] of the dinitrogen complex, the initial azide complex $Ru(NH_3)_5N_3^{2+}$ decomposes to $Ru(NH_3)_5N_2^{2+}$. The infrared $N-N$ stretching vibration band of the ruthenium bromide in the solid state showed a small shoulder at the low frequency side of the spectrum, indicating [28] an azide impurity. The N1s electron peak is somewhat broader in the bromide complex than in the chloride and iodide complexes ($cf.$ Table 4). It can also be mentioned that the $Ru3p_{3/2}$ electron peak of the bromide complex is broader than the corresponding peak for the other complexes. The same is also the case for the $Ru3d_{5/2}$ electron peak. It is evident that there is probably an impurity in the bromide complex, and in such a case the measured binding energy values are uncertain ($cf.$ the rhenium dinitrogen complexes above).

Metal core electron spectra have also been recorded for the osmium dinitrogen complexes and compared with the corresponding spectra of some other osmium compounds. The $Os4f_{5/2}$ and $Os4f_{7/2}$ electron peaks were chosen as suitable electron peaks. Fig. 9 shows the $Os4f$ electron spectrum of $Os(NH_3)_5$-N_2Br_2. The measured binding energy values are collected in Table 6. Like the binding energies of Ru metal, the binding energies for Os metal are found to be 1 eV higher than those given by Siegbahn $et\ al.$[1] It can be seen from Table 6 that the binding energies measured for the osmium dinitrogen complexes are higher than those measured for Os metal. The metal atom in the complexes thus carries a positive charge, which is expected for the same reasons as were mentioned for the ruthenium complexes above. The difference in binding energy between the $Os4f_{5/2}$ and $Os4f_{7/2}$ electron levels is found to be $2.0-2.4$ eV for the dinitrogen complexes with the exception of $Os(NH_3)_5N_2I_2$. In this latter complex, the difference is 3.0 eV. The reason for this is that the $Os4f_{7/2}$ electron binding energy value is somewhat uncertain, as the $Os4f_{7/2}$ electron peak is overlapped by the I4d electron peak. The $Os4f_{5/2}$ and $Os4f_{7/2}$ electron binding energies for OsO_2 and K_2OsCl_6 are somewhat greater than the corresponding binding energies in the dinitrogen complexes. Consequently, the
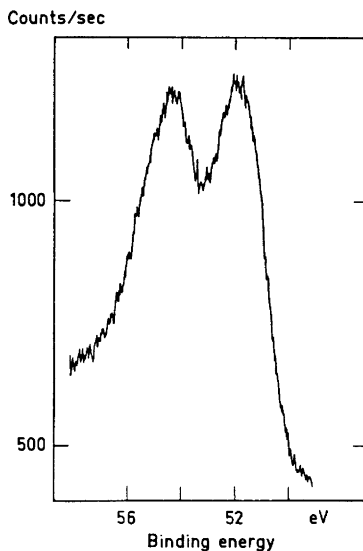
Counts/sec

Fig. 9. Osmium $4f$ electron spectrum of $Os(NH_3)_5N_2Br_2$

positive charge on the osmium atom is greater in OsO_2 and K_2OsCl_6 than in the osmium dinitrogen complexes.

It was suggested before,[16] that a reasonable explanation of the different influence of dimethyl sulfoxide on the mono- and bisdinitrogen osmium complexes could be that the charge on the metal ion was smaller in the bisdinitrogen complex than in the monodinitrogen complex. The same suggestion was used to explain the stability of the bisdinitrogen complex in alkaline solution.[29] This suggestion can easily be checked with the ESCA method. As only one preparation of the pure bisdinitrogen complex, *viz.* $Os(NH_3)_4(N_2)_2Br_2$, was available, the binding energies could be measured only for this complex. It can be seen from Table 6 that the $Os4f_{5/2}$ and $Os4f_{7/2}$ electron binding energies of the bisdinitrogen complex are about 0.5 eV smaller than the corresponding

Table 6. Binding energies (E_b) of $Os4f_{5/2}$ and $Os4f_{7/2}$ electrons in the osmium dinitrogen complexes and some other osmium compounds.

| Compound | E_b eV | |
	$Os4f_{5/2}$	$Os4f_{7/2}$
Os metal	53.3	50.6
$Os(NH_3)_5N_2Cl_2$	54.2	52.2
$Os(NH_3)_5N_2Br_2$	54.4	52.0
$Os(NH_3)_5N_2I_2$	53.9	50.9
$Os(NH_3)_4(N_2)_2Br_2$	53.9	51.6
OsO_2	55.0	52.7
K_2OsCl_6	55.7	53.0

binding energies for the monodinitrogen complex. This fact indicates that the positive charge on the metal ion is smaller in the bisdinitrogen complex than in the monodinitrogen complex and the suggestion presented before [16],[29] is thus well supported.

CONCLUSIONS

The results of the ESCA measurements for the rhenium and the iridium dinitrogen complexes give direct evidence of the charge carried by a dinitrogen molecule in the complexes. Furthermore, from the recorded metal core electron spectra for the dinitrogen complexes and the other metal compounds, it has been possible to get an idea about the charge on the metal atom in the dinitrogen complexes. ESCA spectra thus seem to be capable of providing some information on bonding between the atoms in the dinitrogen complexes. Thus it is possible to get more detailed information from ESCA data about the charge distribution in the dinitrogen complexes than from infrared intensity measurements (cf. Refs. 16 and 17). The combination of infrared intensity data with ESCA data seems to be able to provide increased knowledge about the electronic structure of molecules (cf. Ref. 17).

The question of homolytic and heterolytic splitting of a diatomic molecule is of major interest when considering the activation of the dinitrogen molecule. On homolytic splitting of a diatomic molecule, the electronic structure around each atom will be the same, while on heterolytic splitting the electronic structure will be different. From the present investigation it is evident that the electronic structure around the two nitrogen atoms is different, as the difference in $N1s$ binding energy of the two nitrogen atoms corresponds to different effective charges on the nitrogen atoms. If the charge separation on the nitrogen atoms is considered as a splitting, this is both homolytic and heterolytic; homolytic, since both the nitrogen atoms are negatively charged and heterolytic since there is a small difference in charge on the two nitrogen atoms. This fact is of importance when contemplating the choice of suitable reagents capable of reducing the dinitrogen group.

Ever since the dinitrogen complexes have been known, they have been considered as possible models for nitrogen-fixing enzymes or as models for surface adsorption complexes, which are intermediates in the technical catalytic production of ammonia. For a complete model system one must be able to show the possibility of reduction of the dinitrogen ligand to ammonia. This subject has been attacked earlier,[30]–[32] unsuccessfully. Now, since the charge distribution on the dinitrogen ligand is known, the problem of reducing the dinitrogen group probably can be resolved. Recently, Vol'pin et al.[33] have shown that it is possible to reduce dinitrogen in $CoHN_2(PPh_3)_3$ under mild conditions in the presence of compounds of transition metals of Groups IV — VI of the periodic system. Such work is also planned at this laboratory.

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