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Publication Date

1980-08-01

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August 1980

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AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY
OF ORGANOMETALLIC NITROSYL COMPOUNDS
OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

H. W. Chen,^{1a} W. L. Jolly,^{*1a} S.-F. Xiang,^{1a} and
P. Legzdins^{1b}

ABSTRACT:

Gas-phase core electron binding energies of organometallic nitrosyl complexes of chromium, molybdenum and tungsten are reported. On going from Cr to W in the series $\text{CpM}(\text{NO})_2\text{Cl}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), back-bonding to the NO groups increases and electron density is withdrawn from the Cl atoms. The data for $\text{CpM}(\text{NO})_2\text{Cl}$ and $\text{CpM}(\text{CO})_2\text{NO}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) indicate that the back-bonding in the Mo and W compounds is significantly different from that in first-row transition metal nitrosyls. Electron density is mainly transferred to the nitrosyl oxygen atom, whereas in first-row nitrosyls, approximately equal amounts of electron density are transferred to the oxygen and nitrogen atoms.

Previous x-ray photoelectron spectroscopic (XPS) studies of transition metal nitrosyls and carbonyls in the gas phase have established that NO groups are stronger π -acceptors than CO groups², and that the 1s binding energies of the atoms of these ligands are linearly related to the corresponding N-O or C-O stretching force constants.³⁻⁵ We now report the results of a gas-phase XPS study of a series of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten. The measured core binding energies, listed in Table I, allow us to compare the π -donor and σ -acceptor properties of the group VI transition metal atoms. The data also allow us to compare the donor and acceptor properties of the nitrosyl group with those of other groups, such as the carbonyl group, the cyclopentadienyl group, and the chloro group.

Spectra

The carbon 1s spectrum of $\text{CpCr(CO)}_2\text{NO}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) is shown in Fig. 1. The spectrum is readily deconvoluted into two peaks, separated by 1.7 eV. An unrestricted least-squares fit of the spectrum yields an intensity ratio of 3.8:1, although the ratio of Cp to CO carbon atoms in the compound is 2.5:1. This result is not unexpected; the C 1s and O 1s peaks of carbonyl groups usually lose considerable intensity to shake-up peaks at higher binding energy.

The nitrogen 1s spectrum of $\text{CpCr(NO)}_2\text{NO}_2$ (Fig. 2) shows, on the high binding energy side, a strong band due to free nitric oxide from decomposition of the sample. A peak at approximately 407.6 eV due to $\text{CpCr(NO)}_2\text{NO}_2$ can be clearly resolved. Because there are twice as

many NO groups as NO₂ groups, and because the nitrogen binding energy of the analogous compound, CpCr(NO)₂Cl, is fairly close to 407.6 eV, we believe that the binding energy of the NO groups in CpCr(NO)₂NO₂ is approximately 407.6 eV. The nitrogen of the NO₂ group either has about the same binding energy as the nitrogen of the NO group or, more likely, has a higher binding energy. Indeed it is possible to fit the spectrum quite well with peaks at 407.5 and 408.5 eV, having an intensity ratio of 2:1, respectively. However, because of the interference of the nitric oxide band, we have little faith in this deconvolution and prefer simply to conclude that the binding energy of the NO₂ group is probably greater than 407.6 eV.

The oxygen 1s spectrum of CpCr(NO)₂NO₂ (Fig. 3) also shows a peak due to free nitric oxide; however in this case the nitric oxide peak is well separated from the peaks due to the coordinated NO₂ and NO groups at 537.7 and 539.3 eV. By comparison with the oxygen binding energy of CpCr(NO)₂Cl, the peak at 539.3 eV is readily assigned to the NO group.

Binding Energy Trends

Consider the binding energies of the mononuclear chromium compounds. On going from CpCr(CO)₂NO to CpCr(NO)₂NO₂, the chromium, cyclopentadienyl carbon, nitrosyl nitrogen, and nitrosyl oxygen binding energies all increase, indicating that the combined electron withdrawing ability of one NO group and one NO₂ group is greater

than that of the two CO groups that they replace. This result is not surprising in view of the great electron withdrawing ability of the NO₂ group and the fact that the nitrosyl group is a better π-acceptor than the carbonyl group. On going from CpCr(NO)₂NO₂ to CpCr(NO)₂Cl, similar but smaller binding energy increases occur, except in the case of the nitrosyl nitrogen binding energy (which has an uncertainty of ~ 0.3 eV in the former compound), indicating that the Cl group is slightly more electron-withdrawing than the NO₂ group.

The fact that the oxygen 1s binding energy of the coordinated NO₂ group, the oxygen atoms have a negative formal charge,

whereas in the coordinated NO group, the oxygen atom has a positive formal charge:

Thus we would expect the oxygen atoms of the coordinated NO₂ group to be more negatively charged than that of the coordinated NO group. Although no peak corresponding to the NO₂ nitrogen could be reliably deconvoluted from the N 1s spectrum, the data suggest that the N 1s binding energy of the NO₂ group is greater than that of the NO group. Simple valence bond considerations show that the nitrogen atoms of these groups have the same formal charge. However, the back-bonding to the NO group is probably greater than that to any other ligand

(except perhaps NS and NSe groups), and therefore one would expect the nitrogen atom charge to be more negative in the coordinated NO group than in the coordinated NO₂ group.

The binding energy shifts of the molybdenum and tungsten compounds are similar to those of the chromium compounds. Thus, on going from CpW(CO)₂NO to CpW(NO)₂H, the nitrogen, cyclopentadienyl carbon, and tungsten binding energies increase, indicating that the combination of an NO group and an H group is more electron-withdrawing than two CO groups. Although the hydrogen atom is an electron-withdrawing group,⁶⁻⁸ replacement of the hydrogen atom by a chlorine atom causes all the binding energies to increase further, because of the greater electronegativity of chlorine.

Effect of NO Back-bonding on σ -Donation of Cl. In the series of compounds CpM(NO)₂Cl (M = Cr, Mo, W), the carbon binding energy is essentially constant. However, on going from the chromium compound to the tungsten compound, the oxygen and nitrogen binding energies markedly decrease and the chlorine binding energy increases. We believe these data are consistent with the general observation that, on descending a transition metal family, the π -donor ability of the metal increases. Thus on going from the chromium compound to the tungsten compound, π -donor bonding to the NO groups increases, and to compensate for the increased metal atom charge, σ -donor bonding from the chlorine atoms increases. These bonding changes are also manifest in

the solid-state molecular structures of the chromium and tungsten complexes: the W-Cl bond length is short (relatively strong σ bonding), whereas the Cr-Cl bond length is more characteristic of ionic bonding.⁹ Apparently the σ and π parts of the metal-cyclopentadienyl bonding are of comparable importance, and thus the opposing effects of the changes in σ and π bonding cancel, resulting in essentially no change in the charge on the cyclopentadienyl group.

We have interpreted the increase in chlorine bonding energy in the series $\text{CpM}(\text{NO})_2\text{Cl}$ on going from Cr to W as evidence for a corresponding decrease in negative charge on the chlorine atom. This is an important result, representing direct evidence of ligand charge compensation for back-bonding in a series of compounds. However, it is conceivable that the increase in chlorine binding energy is not due to a decrease in negative charge on the chlorine, but rather to an increase in potential at the chlorine atom due to an increase in positive charge on the metal atom. To eliminate doubt, we have used the binding energy data to calculate the changes in charge on the N, O, Cl, and metal atoms on going from the chromium compound to the molybdenum compound and from the chromium compound to the tungsten compound. In each case we solved four equations in four unknowns. The four unknowns were the changes in the four atomic charges.¹⁰ Three of the equations were potential equations¹¹ of the type

$$\Delta E_B(A) = k\Delta Q_A + \sum_{i \neq A} (14.4\Delta Q_i/r_i)$$

where k is the average value of the reciprocal of the valence electron

radius,^{12,13} Q_i is the charge on atom i , and r_i is the distance between atom i and atom A.¹⁴ One of the equations was $\sum \Delta Q_i = 0$. The results of the calculations, shown in Table II, confirm the fact that the increases in chlorine binding energy do indeed correspond to increases in charge (measured as positive charge) on the chlorine atoms.

Change in Nature of Back-bonding in Molybdenum and Tungsten.

Evidence for an increase in back-bonding on going from a chromium compound to a corresponding tungsten compound is also apparent from the decrease in oxygen binding energy on descending the series $\text{CpM}(\text{CO})_2\text{NO}$ ($M = \text{Cr, Mo, W}$). However it is significant that the carbonyl carbon and nitrosyl nitrogen binding energies are essentially constant in this series. This sort of result was also observed in the $\text{CpM}(\text{NO})_2\text{Cl}$ series; from Table II it can be seen that the changes in the nitrogen atom charge are much lower than the changes in the oxygen atom charge. The data indicate that, at least for nitrosyl groups, the oxygen atom receives most of the electron density when back-bonding increases by descending the Cr, Mo, W family. Previous work⁵ has shown that the nitrogen and oxygen atoms receive comparable amounts of electron density when back-bonding increases in nitrosyls of the first-row transition metals. Thus the present data suggest that back-bonding of second- and third-row transition metals is different in character from that of first-row transition metals. Some data⁵ for carbonyls support this idea. On going from $\text{CH}_3\text{Mn}(\text{CO})_5$ to $\text{CH}_3\text{Re}(\text{CO})_5$, $E_B(\text{C } 1s)$ is unchanged, whereas $E_B(\text{O } 1a)$ decreases by

0.27 eV. However, in the cases of $M(CO)_5PF_3$ ($M = Cr, Mo$), $M(CO)_5CS$ ($M = Cr, W$), and $M(CO)_6$ ($M = Cr, Mo, W$), the changes in both $E_B(C\ 1s)$ and $E_B(O\ 1s)$ are very small, indicating no significant change in back-bonding.

The effect which we have observed in the case of nitrosyl compounds may be rationalized by assuming that, on descending a transition metal family, σ -donation by the NO group increases because of the large increase in nuclear charge of the metal, and the resultant improved $d\pi-\pi^*$ overlap causes an increase in back-bonding. The stronger σ bonding between the nitrogen and metal atom causes a shift of electron density from nitrogen to metal which compensates for the increase in π^* electron density due to increased back-bonding. Thus the nitrogen atom charge is almost unchanged although the oxygen atom becomes more negative.

Experimental Section

The spectra were obtained using procedures described previously.⁶ Some of the C 1s, N 1s, and O 1s binding energies have been reported previously.⁵ The $CpM(CO)_2NO$ complexes and $CpW(NO)_2H$ are volatile enough that we were able to obtain their spectra at room temperature. However, it was necessary to hold $CpCr(NO)_2NO_2$ at 50°, and the $CpM(NO)_2Cl$ complexes at 80°, in order to obtain satisfactory spectra. In the elevated-temperature runs, the entire spectrometer (except for the pumps, the detector preamplifier, and a few control valves) was enclosed in a thermostatted oven. This technique prevents condensa-

tion of sample in the analyzer chamber, and thus possible deterioration of electron focussing is avoided. Most of the binding energies are based on spectrometer calibrations with the N_2 1s, Ne 1s, and Ne 2s lines. However, in the case of the O 1s and N 1s spectra of $CpCr(NO)_2NO_2$, it was possible to measure the binding energies relative to the decomposition product nitric oxide, NO. In a separate run, we determined the binding energies of a commercial sample of nitric oxide (Matheson) as follows: $E_B(O\ 1s) = 543.46(4)$ eV, $FWHM(O\ 1s) = 1.39(11)$ eV; $E_B(N\ 1s, \text{ deconvoluted strong line}) = 410.34(5)$ eV, $FWHM(N\ 1s, \text{ deconvoluted strong line}) = 1.29(15)$ eV; $E_B(N\ 1s, \text{ deconvoluted weak line}) = 411.57(19)$ eV, $FWHM(N\ 1s, \text{ deconvoluted weak line}) = 1.35(39)$ eV.

The $CpCr(NO)_2NO_2$,¹⁵ $CpW(NO)_2H$,⁸ $CpM(CO)_2NO$,¹⁶ and $CpM(NO)_2Cl$ ¹⁶ (M = Cr, Mo, W) were prepared according to published procedures.

Acknowledgments

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under contract No. W-7405-Eng-48, the National Science Foundation, and Grant A5885 from the Natural Sciences and Engineering Research Council of Canada to P.L. We have benefitted by discussion of our data with Prof. William C. Trogler.

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- (12) Values of $\langle 1/r \rangle$ were calculated from data in ref. 13. The k values, in units of electronic charge per eV, were 27.9 for nitrogen (assuming 25% s character), 32.5 for oxygen (20% s character), and 21.7 for chlorine (10% s character).

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Table I. Core Binding Energies and Full Widths at Half Maximum for Nitrosyl Complexes, in eV

Compound	O 1s		N 1s		C 1s		Cl 2p _{3/2}		Metal Core Level ^a	
	E _B	FWHM	E _B	FWHM	E _B	FWHM	E _B	FWHM	E _B	FWHM
CpCr(CO) ₂ NO	538.91(4) ^b	1.59(9)	406.84(7)	1.26(17)	290.82(4) ^c 292.51(12) ^c	1.27(7) 1.47(17)			581.77(5)	1.30(10)
CpCr(NO) ₂ NO ₂	537.7(2) ^d 539.3(2) ^e	1.4(5) 1.4(5)	407.6(3) ^e	1.6(2)	291.08(12)	1.53(33)			582.57(9)	1.34(16)
CpCr(NO) ₂ Cl	539.45(6)	1.39(17)	407.47(9)	1.35(37)	291.25(7)	1.47(17)	203.38(8)	1.21(24)	582.67(7)	1.30(20)
CpMo(CO) ₂ NO	538.77(3)	1.70(13)	406.93(9)	1.23(22)	290.77(3) ^c 292.52(10) ^c	1.26(7) 1.58(18)			234.91(4)	1.34(10)
CpMo(NO) ₂ Cl	538.98(8)	1.50(32)	407.35(8)	1.26(20)	291.31(6)	1.50(17)	203.82(13)	1.35(42)	236.26(9)	1.25(24)
CpW(CO) ₂ NO	538.57(5)	1.80(14)	406.85(8)	1.40(18)	290.98(10) ^c 292.52(17) ^c	1.35(11) 1.64(27)			38.22(12)	1.88(22)
CpW(NO) ₂ H	538.33(15)	1.50(30)	407.05(9)	1.35(20)	291.14(9)	1.44(14)			38.79(11)	1.20(20)
CpW(NO) ₂ Cl	538.67(7)	1.47(21)	407.23(10)	1.38(31)	291.30(5)	1.16(20)	204.08(7)	1.07(23)	39.53(7)	1.22(18)

^aCr 2p_{3/2}, Mo 3d_{5/2}, or W 4f_{7/2}^bUncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. ^cThe lower E_B due to Cp carbons; the higher E_B due to CO carbons.^dNO₂ group. ^eNO group.

Table II. Calculated Changes in Atomic
Charge in $\text{CpM}(\text{NO})_2\text{Cl}$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$.

	Cr $\rightarrow$ Mo	Cr $\rightarrow$ W
ΔQ_{N}	-0.0019	-0.0060
ΔQ_{O}	-0.016	-0.026
ΔQ_{Cl}	0.022	0.034
ΔQ_{M}	0.014	0.030

Figure Captions

Figure 1. Carbon 1s spectrum of $\text{CpCr}(\text{CO})_2\text{NO}$. The more intense peak, at 290.82 eV, corresponds to the cyclopentadienyl group; the weaker peak, at 292.51 eV, corresponds to the CO groups.

Figure 2. Nitrogen 1s spectrum of $\text{CpCr}(\text{NO})_2\text{NO}_2$. The peaks at higher binding energy correspond to free NO from partial decomposition of the sample; the unresolved band at lower binding energy corresponds to the NO and NO_2 groups of the complex.

Figure 3. Oxygen 1s spectrum of $\text{CpCr}(\text{NO})_2\text{NO}_2$. The intense peak at high binding energy corresponds to free NO from partial decomposition of the sample; the peaks at low binding energy correspond to the NO and NO_2 groups of the complex.

Fig. 1

Figure 1

Fig. 2

Figure 2

Fig. 3

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