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**Supplementary Material Available:** Table I, observed rate constants for the decomposition reaction (1 page). Ordering information is given on any current masthead page.

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## Comparison of Thionitrosyl and Nitrosyl Bonding in Dicarbonyl( $\eta^5$ -cyclopentadienyl)chromium Complexes by Gas-Phase Ultraviolet and X-ray Photoelectron Spectroscopy

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The gas-phase He I/He II UPS and Mg K $\alpha$  XPS data for the compounds  $(\eta^5-C_5H_5)Cr(CO)_2NO$  and  $(\eta^5-C_5H_5)Cr(CO)_2NS$  are reported. The first ionization potentials for the two complexes are nearly the same (nitrosyl 7.56 eV; thionitrosyl 7.47 eV), contrary to indications from mass spectrometry appearance potentials. A short C–O stretching progression (ca. 2000  $cm^{-1}$ ) in the first ionization band of the nitrosyl compound shows that it is predominantly associated with metal d character and is symmetrically  $\pi$  delocalized into the carbonyls. This orbital is primarily of  $\delta$  symmetry with respect to the NO or NS ligand. The next two ionizations for both complexes, which complete the formal  $d^6$  configuration at the metal, are sensitive to the  $\pi$  symmetry interaction with the NO or NS group. These ionizations are approximately degenerate for the NO complex and are stabilized by nearly 1 eV relative to the first band as a consequence of the stronger Cr–NO  $\pi$ -back-bonding relative to Cr–CO back-bonding. These ionizations are slightly destabilized and are sharper for the NS complex relative to the NO complex, showing stronger metal  $\pi$  interaction with both the NS  $\pi$  bond and  $\pi^*$  orbitals. The dramatic loss of intensity of these ionizations in the He II spectrum of the thionitrosyl complex experimentally demonstrates significant delocalization with both the NS  $\pi$ -donor and  $\pi$ -acceptor levels to give large NS (sulfur) character for these ionizations. The nitrogen 1s binding energy for the NS complex is almost 2 eV lower than that for the NO complex, suggesting a much more negative charge on the NS nitrogen. In contrast, the chromium, carbon, and oxygen core binding energies do not differ significantly between the two complexes. A formal potential model analysis of the (Cr–N–O) and (Cr–N–S) XPS shifts indicates a slightly more positive metal in the NS complex. These results are in agreement with Fenske–Hall approximate calculations and with other physical properties of the two compounds.

### Introduction

The discovery by Legzdins and co-workers<sup>1</sup> of the volatile thionitrosyl complex  $(\eta^5-C_5H_5)Cr(CO)_2NS$  has provided an excellent opportunity to compare the ligating and other physical-chemical properties of NS with those of NO in its isoelectronic and nearly isostructural analogue,  $(\eta^5-C_5H_5)Cr(CO)_2NO$ . The IR, mass spectral, and certain NMR properties have been examined by Legzdins and co-workers, and the results apparently present an "interesting dichotomy" between the ligating abilities of NO and NS in these molecules.<sup>1</sup> Although the mass spectral fragmentation data and the infrared data suggested that the NS ligand is more strongly bound to the metal and is a better remover of metal electron density than NO, their appearance potential data and NMR shifts suggested on first principles that the metal is more electron rich in the thionitrosyl complex. We have reported the results of a valence He I study of the nitrosyl and thionitrosyl complexes<sup>2</sup> and subsequently discussed the counterintuitive aspects of CS and NS coordination, which arises from their ability to act as both strong  $\pi$  donors and  $\pi$  acceptors to the metal.<sup>3</sup> More recently we have provided a complete heteronuclear NMR study of pairs of nitrosyl/thionitrosyl complexes of chromium, molybdenum, and tungsten.<sup>4,5</sup>

The previous ionization studies of these complexes were limited to valence He I photoelectron spectroscopy and comparison with approximate molecular orbital calculations. A clear and more complete understanding of these systems is available from a combination of gas-phase He I/He II UPS valence ionization information and gas-phase Mg K $\alpha$  XPS core ionization data. As opposed to core-only or valence-only studies, the combined valence/core ionization analysis allows an effective separation of effects of charge distribution from the effects of bonding and/or electron relaxation.<sup>6</sup> This is particularly important in the com-

parison of NS with NO. Of special interest is the relationship between specific  $\sigma$  and  $\pi$  interactions and the charge distribution around the metal. When oxygen is replaced by a less electronegative sulfur atom the increase in negative charge at nitrogen will effectively increase the  $\sigma$ -donor ability of the ligand. Therefore, the change of charge on the nitrogen atom, and consequently on the metal atom, is of special importance. Also, like CS, the NS ligand is expected to be a considerable  $\pi$  donor to the metal as well as a good  $\pi$  acceptor.<sup>7</sup> The XPS analysis allows us to assess the net effect of these bonding interactions on the distribution of charge in the molecule.

Comparison of the ionizations of the  $CpCr(CO)_2NO$  complex ( $Cp = \eta^5-C_5H_5$ ) with those of  $CpMn(CO)_3$  also allows measurement of the electronic effects of formally moving a proton from the metal to one of the carbonyls, i.e. transforming a  $(Mn-CO)^+$  unit to a  $(Cr-NO)^+$  unit while leaving the rest of the coordination environment essentially unchanged. Compared to that in the  $CpMn(CO)_3$  and  $CpMn(CO)_2CS$  complexes, where the metal  $d^6$  ionizations (arising from a perturbed  $t_{2g}$  set in strict octahedral symmetry) were closely overlapping, this "proton" perturbation distorts the pseudo-octahedral electronic symmetry around the metal to pseudo- $C_{4v}$  symmetry, thus separating the metal orbital with  $\delta$  symmetry from the metal orbitals with  $\pi$  symmetry to the NO or NS group. This convenient  $\delta$ - $\pi$  separation allows observation of the difference between Cr–NO and Cr–NS  $\pi$  mixing by the measurement of the He I/He II cross section

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Table I. He I and He II Valence Band Analysis Results for CpCr(CO)<sub>2</sub>NO and CpCr(CO)<sub>2</sub>NS (eV)<sup>a</sup>

peak	IE	width(h)	width(l)	rel area	
				He I	He II
CpCr(CO) <sub>2</sub> NO					
A	7.56	0.25	0.25	1.00	1.00
A'	7.80	0.25	0.25		
B	8.35	0.59	0.42	2.41	2.68
C	9.68	0.47	0.33		
C'	10.05	0.47	0.33	3.42	1.92
CpCr(CO) <sub>2</sub> NS					
A	7.47	0.40	0.29	1.00	1.00
B	7.76	0.37	0.20		
B'	7.96	0.37	0.20	3.80	1.92
C	9.51	0.57	0.33		
C'	9.93	0.57	0.33	3.89	1.94
D	11.13	0.52	0.37		
D'	11.42	0.52	0.37	2.19	1.15

<sup>a</sup> See Experimental Section for an explanation of the table.

changes in these predominantly "metal d" ionizations.

The results of this study emphasize that the observed physical properties of CpCr(CO)<sub>2</sub>NO and CpCr(CO)<sub>2</sub>NS fall into a coherent pattern when all the relevant orbital interactions are carefully considered.

### Experimental Section

( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>NO and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>NS were prepared by published methods.<sup>1,8</sup> Purification of the crude material in both cases was accomplished by elution through a hexane/alumina column (activity III). The hexane eluent was collected, hexane was removed in vacuo, and the final product was obtained by vacuum sublimation (0.01 torr) to a dry-ice-cooled probe: CpCr(CO)<sub>2</sub>NO, 25 °C; CpCr(CO)<sub>2</sub>NS, 45 °C.

The photoelectron spectra were obtained with a photoelectron spectrometer utilizing a 36-cm radius hemispherical analyzer. The instrument was modified by the addition of temperature-controlled gas-phase UPS and XPS sample cells as well as the addition of an oscillating discharge-type He II lamp based on the design of Rabalais.<sup>9</sup> The operating temperatures for the thionitrosyl and nitrosyl complexes were 45 and 25 °C, respectively. The operating resolution for the argon <sup>2</sup>P<sub>3/2</sub> ionization (15.76 eV) was maintained at 0.016–0.020 eV throughout the He I data collections. This argon ionization was used as an "internal lock" during the high-resolution He I signal-averaging process (7–12-eV collections) in order to prevent any significant drift of the absolute kinetic energy scale (drift <0.005 eV). All UPS data were intensity corrected for the experimentally known analyzer transmission function of our spectrometer. The He II data were corrected for the He II  $\beta$  excitation line (48.4 eV; 12% of the He II  $\alpha$  intensity). The linearity of the kinetic energy scale was periodically checked with a CH<sub>3</sub>I/Ar mixture (9.55 eV/15.76 eV, respectively, for valence measurements. For XPS, the kinetic energy linearity was checked against the core ionizations of CO<sub>2</sub>: C 1s, 297.69 eV; O 1s, 541.28 eV.<sup>10</sup> Each core binding energy was measured five or more times in a series of experiments that included monitoring the position of the internal standard. Slow drifts of the spectrometer due to changing sample pressures, temperatures, and surface conditions were corrected, and the standard deviations of the core binding energy determinations are reported in the table.

An analytical representation of the ionizations was determined by the program GFIT.<sup>11</sup> The functional form is

$$C(E) = A \exp[-k[(E - P)/W]^2]$$

where  $C(E)$  is the electron counts at binding energy  $E$ ,  $A$  is the peak amplitude,  $P$  is the peak position (vertical IP),  $W = W_h$ , the half-width when  $E > P$  (on the high binding energy side of the peak), or  $W = W_l$ , the half-width when  $E < P$  (on the low binding energy side of the peak), and  $k = 4 \ln 2$ . For XPS the peaks were constrained to be symmetric.

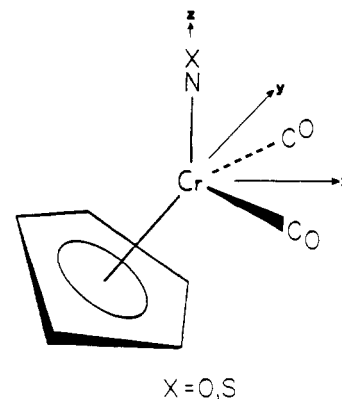


Figure 1. Coordinate system for the CpCr(CO)<sub>2</sub>NX molecules. The CO, NO, and NS ligands are positioned at right angles to one another.

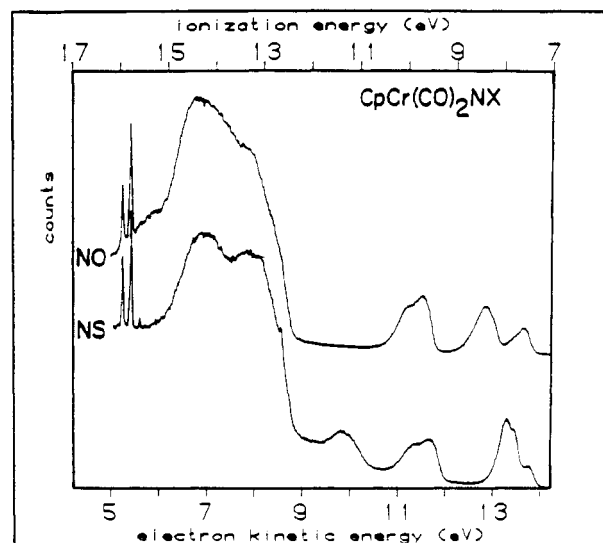


Figure 2. Valence He I photoelectron spectra for CpCr(CO)<sub>2</sub>NO and CpCr(CO)<sub>2</sub>NS. The sharp ionization features near 16-eV ionization energy are from argon.

Table I lists the fit parameters to two figures past the decimal place to give an accurate analytical representation of the overall valence ionization band contours. The reproducibility of the vertical ionization energies by these techniques usually is about  $\pm 0.02$  eV. The relative integrated peak areas are reproducible to about 5% in He I and about 10% in He II for individual peaks. If two peaks are overlapping such that there is not a clear inflection between their maxima, the peaks are constrained to have the same shape. These situations can be identified in the tables when two peaks have the same high-energy widths  $W_h$  and also the same low-energy widths  $W_l$ . Overlapping peaks are included in the fit of a band only if they are needed for a statistically significant representation of the band contour with experimentally reasonable band shapes. Because of the correlation between peak parameters in an overlapping band, there is greater uncertainty in the true vertical ionization energy for each peak (about  $\pm 0.1$  eV in the worst cases).

The molecular orbital calculations were performed by the Fenske–Hall method<sup>12</sup> on a CDC-CYBER 175 computer. The usual chromium functions were used with 4s and 4p exponents of 2.0 and 2.1, respectively. The molecular geometries were idealized from the X-ray crystallographic data and are described in Figure 1.<sup>1,13</sup> The same geometry for the CpCr(CO)<sub>2</sub> fragment was used in both calculations. The bond distances are C–C(ring) = 1.43 Å, Cr–C(O) = 1.883 Å, C–O = 1.15 Å, Cr–N(O) = 1.687 Å, N–O = 1.169 Å, Cr–N(S) = 1.694 Å, and N–S = 1.551 Å.

### Results

The 7–17-eV He I spectra for CpCr(CO)<sub>2</sub>NO and CpCr(CO)<sub>2</sub>NS are presented in Figure 2. The spectra show a general resemblance to the valence ionizations of the CpMn(CO)<sub>3</sub> mol-

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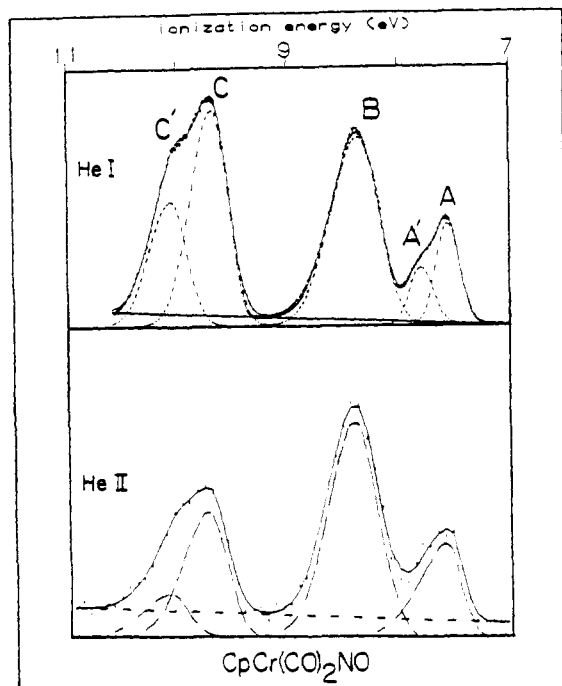


Figure 3. High-resolution He I spectrum and comparative He II spectrum for CpCr(CO)<sub>2</sub>NO.

ecules, which we have previously reported in detail.<sup>14</sup> Specifically, the broad overlapping ionizations above 12 eV are associated with the CO and NO 5 $\sigma$  and 1 $\pi$  ionizations and certain ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) ionizations. In analogy to the CS complexes studied by He I UPS<sup>12</sup> (and one CSe complex<sup>15</sup>) the NS 7 $\sigma$  (donor) and 2 $\pi$  (NS  $\pi$  bonds) ionizations are expected to appear at lower ionization energies than the corresponding NO 5 $\sigma$  and 1 $\pi$  levels. The spectrum of the thionitrosyl complex shows only one additional band near 11.3 eV. In the region below 11 eV several discrete ionization bands appear for both complexes.

The bands below 9 eV are typical of ionizations from the predominantly metal 3d orbitals. On inspection of these ionizations it can be seen that the first ionization potential for the nitrosyl and thionitrosyl are at nearly the same energy. The ionization potentials determined by mass spectrometry<sup>1</sup> are seen to correlate to the most intense He I bands in the metal region (bands labeled B in Figures 3 and 4). We have noted a similar situation in the case of W(CO)<sub>6</sub>,<sup>16</sup> where only the most intense He I metal ionization is detected by the appearance potential technique.<sup>17</sup>

The ionization band near 10 eV in each case shows a high binding energy shoulder and energy characteristic of the predominantly Cp e<sub>1</sub>' donor orbital. In order to gain a clearer picture of these low-energy ionizations (especially their behavior in both He I and He II radiation) close-up data collections for the low-energy ionization regions were obtained.

**The 7-11-eV Region for CpCr(CO)<sub>2</sub>NO.** Figure 3 shows the He I/He II ionization profiles for the NO complex. Table I lists the ionizations in analytical form. The separate ionization bands are labeled A, B, and C, starting with the first ionization band. The He I spectrum clearly shows a shoulder on band A, which is labeled A'. The position and intensity of peak A' relative to peak A suggests that it is an element of a short C-O vibrational progression and not a separate electronic ion state. We have often observed similar vibrational fine structure in metal carbonyl ionization bands where the metal orbital is symmetrically delocalized into a group of carbonyl  $\pi^*$  ligand orbitals.<sup>16,18,19</sup>

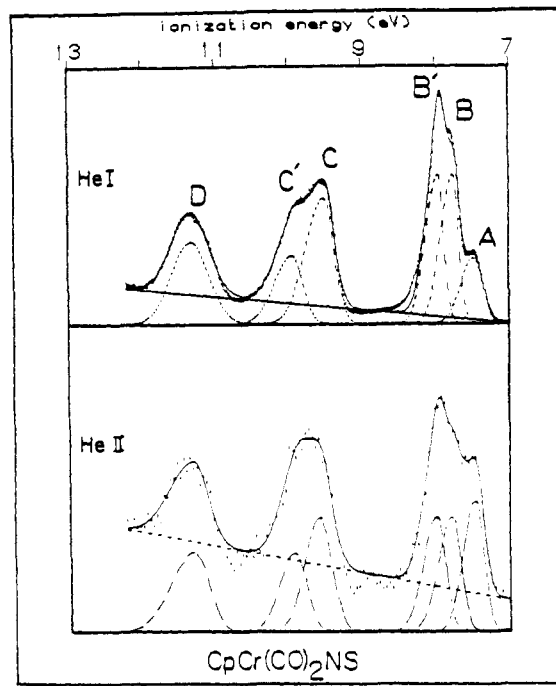


Figure 4. High-resolution He I spectrum and comparative He II spectrum for CpCr(CO)<sub>2</sub>NS.

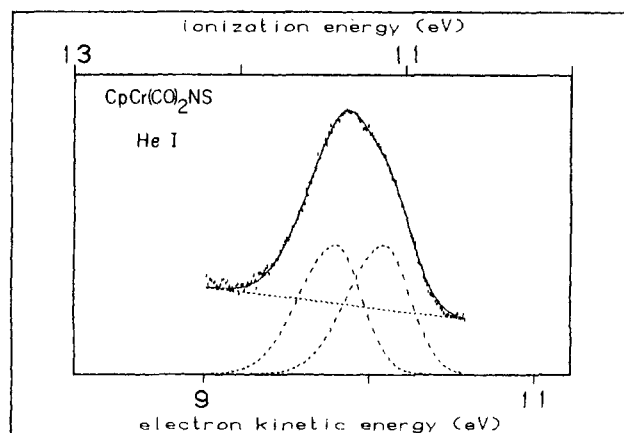


Figure 5. High-resolution He I spectrum of band D for the CpCr(CO)<sub>2</sub>NS complex.

The predominantly metal ionization region shows an approximate 2:1 (B:(A + A')) ratio of bands representative of the pseudo-C<sub>4v</sub> electronic symmetry at the d<sup>6</sup> metal center. This is the expected disruption of the pseudooctahedral t<sub>2g</sub> degeneracy of the d<sup>6</sup> ionizations seen in the CpMn(CO)<sub>3</sub> spectrum.<sup>14</sup> Bands C and C' (predominantly Cp e<sub>1</sub>' ionizations) decrease in relative area in He II spectra compared to bands A and B, consistent with their predominant ligand character.<sup>14</sup>

**The 7-13-eV Region for CpCr(CO)<sub>2</sub>NS.** Figure 4 shows the low ionization energy data for the thionitrosyl complex. The He I spectrum shows a "metal" ionization region below 9 eV (bands A, B, and B') followed by the familiar Cp e<sub>1</sub>' donor orbital ionization band (bands C and C') and a new band not seen for CpCr(CO)<sub>2</sub>NO (band D). From Table I it is apparent that peak A of the nitrosyl complex displays He I/He II behavior similar to that seen for the corresponding peak (A + A') in the thionitrosyl spectrum. For the thionitrosyl, peaks B and B' are partially resolved and, as shown in Figure 4, can be adequately represented as a pair of identical asymmetric Gaussians. The He I area ratio (B + B') : A for CpCr(CO)<sub>2</sub>NS is 3.80, considerably higher than

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Table II. XPS Results for  $\text{CpCr}(\text{CO})_2\text{NO}$  and  $\text{CpCr}(\text{CO})_2\text{NS}$  (eV)

	$\text{CpCr}(\text{CO})_2\text{NO}$		$\text{CpCr}(\text{CO})_2\text{NS}$	
	IE	fwhm	IE	fwhm
Cr $2p_{3/2}$	581.76 (3)	1.34 (9)	581.66 (4)	1.29 (16)
C 1s				
Cp	290.83 (1)	1.43 (5)	290.72 (2)	1.44 (5)
CO	292.62 (1)		292.51 (4)	
O 1s	538.93 (4)	1.80 (10)	539.10 (1)	1.67 (16)
N 1s	406.83 (2)	1.30 (10)	404.89 (5)	1.46 (11)
S $2p_{3/2}$			168.51 (3)	1.63 (27)

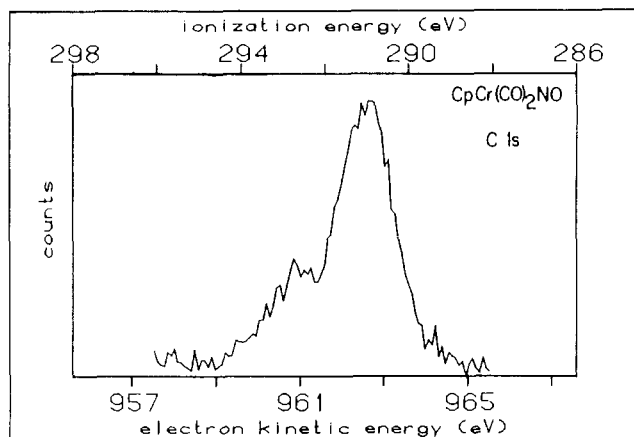


Figure 6. Gas-phase XPS spectrum of the carbon 1s region for  $\text{CpCr}(\text{CO})_2\text{NO}$  showing the resolution of the CO carbon ionization from the Cp carbon ionizations.

the nitrosyl B:(A + A') ratio of 2.41. In He II radiation a reversed order is observed for these area ratios: for the thionitrosyl complex, (B + B') : A = 1.92; for the nitrosyl complex, B : (A + A') = 2.68. The significance of this result will be addressed in the Discussion.

Band D in Figure 4 is shown in better detail in Figure 5. This band in the high-resolution He I spectrum shows evidence that at least two overlapping bands are present. An inflection is observed on the low binding energy side near the band maximum, and an attempt to fit this band with a single asymmetric Gaussian envelope visibly failed to follow this contour and gave an unrealistic broadening on the low binding energy side. The excellent fit of the overall band (including the inflection) by the two identical asymmetric peaks in Figure 5 shows the ionization band can be represented by two components separated by 0.29 eV. The relative area of the bands is seen to decrease in He II radiation, indicating their predominant ligand orbital character. Further assignment of this ionization will be presented in the Discussion.

**XPS Results.** Table II lists the results of the gas-phase XPS analysis for  $\text{CpCr}(\text{CO})_2\text{NO}$  and  $\text{CpCr}(\text{CO})_2\text{NS}$ . These ionization energies are in good agreement with those reported by Jolly and co-workers.<sup>20</sup> As shown in Figure 6 the carbon 1s ionization for the carbonyl carbons is easily distinguished from the carbon 1s ionization of the Cp ring carbons, thus allowing the precise measurement of each type of carbon ionization energy. The nitrosyl oxygen 1s ionization cannot be distinguished from the carbonyl oxygen 1s ionization in the case of  $\text{CpCr}(\text{CO})_2\text{NO}$ , although the peak width of the oxygen 1s ionization is observed to be somewhat broader than that for the thionitrosyl complex.<sup>21</sup> The apparent shift of the oxygen core ionization energy from  $\text{CpCr}(\text{CO})_2\text{NO}$  to  $\text{CpCr}(\text{CO})_2\text{NS}$  cannot be considered significant due to uncertainty from the overlap of NO and CO oxygen ionizations in the case of  $\text{CpCr}(\text{CO})_2\text{NO}$ . The Cp ring, carbonyl, and metal shifts are quite small between the two compounds, but the N 1s ionization shift from the NO complex to the NS complex is a substantial 1.94 eV to lower binding energy.

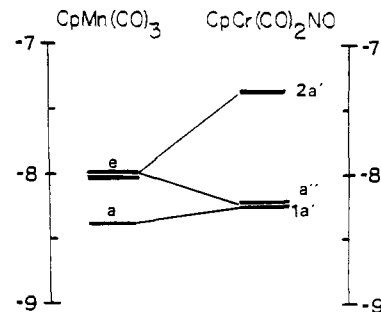


Figure 7. Experimental shifts of the metal ionizations from  $\text{CpMn}(\text{CO})_3$  to  $\text{CpCr}(\text{CO})_2\text{NO}$ .

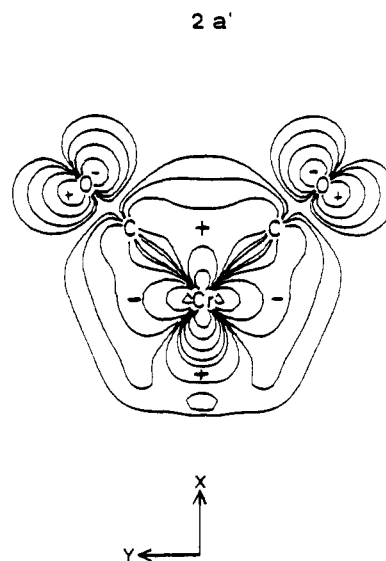


Figure 8. Calculated orbital contour plot (Fenske-Hall method) of the  $2a'$  orbital of the  $\text{CpCr}(\text{CO})_2\text{NX}$  molecules. The lowest contour values are  $+2.44 \times 10^{-4} \text{ e} \text{ \AA}^3$ , with each successive contour being a factor of 2 greater.

## Discussion

A comparison of NO and NS binding as revealed by these experiments is aided by first establishing the relationship between  $\text{CpCr}(\text{CO})_2\text{NO}$  and  $\text{CpMn}(\text{CO})_3$ . As previously mentioned,  $\text{CpCr}(\text{CO})_2\text{NO}$  can be related to  $\text{CpMn}(\text{CO})_3$  by the shift of one proton from the manganese core to one of the carbonyl carbons, thereby changing the metal from  $\text{Mn}^+$  to  $\text{Cr}^0$  and the CO ligand to a  $\text{NO}^+$  ligand and retaining a formal  $d^6$  metal configuration. The different orbital electron densities will respond differently to this proton shift. Previous theoretical work by us on  $d^6 \text{ CpM}(\text{CO})_2\text{L}$  systems helps simplify the orbital relationships in these systems.<sup>22</sup> The perturbation of the  $d^6 \text{ CpMn}(\text{CO})_3$  molecule to a  $\text{CpM}(\text{CO})_2\text{L}$  system (i.e., the loss of a pseudo-3-fold rotation axis) results in the a and the e type metal orbitals of the tricarbonyl complex splitting into the  $2a'$ ,  $a''$ , and  $1a'$  orbitals. When the  $\text{M}(\text{CO})_2\text{L}$  geometry is aligned as shown in Figure 1 the  $2a'$  orbital is largely  $d_{x^2-y^2}$  in composition, with the  $a''$  and  $1a'$  being largely  $d_{yz}$  and  $d_{xz}$ , respectively. The expected consequences on the metal d orbitals on proceeding from  $\text{Mn}(\text{CO})_3$  to  $\text{Cr}(\text{CO})_2\text{NO}$  are primarily 2-fold. First, the electrons in the vicinity of the metal will experience the destabilizing effect of one less proton at the metal center. The  $2a'$  orbital (which is primarily of  $\delta$  symmetry to the ligand on the z axis) will largely reflect this effect. The  $a''$  and  $1a'$  ionizations will also experience this effect but in addition will be strongly influenced by  $\pi$ -overlap interactions with the ligand on the z axis. The shift of the proton to this ligand will make it a stronger  $\pi$  acceptor, and thus stabilize  $a''$  and  $1a'$  relative to  $2a'$ .

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Table III. Fenske-Hall MO Calculation Results for CpCr(CO)<sub>2</sub>NO and CpCr(CO)<sub>2</sub>NS

		Eigenvalues (eV)			
	CpMn(CO) <sub>3</sub>	CpMn(CO) <sub>2</sub> CS	CpCr(CO) <sub>2</sub> NO	CpCr(CO) <sub>2</sub> NS	
metal d	-9.62 (e)	-9.21 (a'')	-8.67 (2a')	-8.82 (2a')	
	-9.79 (a)	-9.40 (1a')	-9.78 (1a')	-9.18 (a'')	
Cp e <sub>1</sub> ''	-12.96 (a'')	-9.52 (2a')	-9.80 (a'')	-9.29 (1a')	
	-13.00 (a')	-12.67 (a')	-12.40 (a'')	-12.30 (a')	
		-12.82 (a'')	-12.44 (a')	-12.45 (a'')	
		-15.41		-16.92	
		CS 7 $\sigma$		NS 7 $\sigma$	
		CS 2 $\pi$		NS 2 $\pi$	
		-15.98 (a'')		-16.48 (a')	
		-16.05 (a')		-16.69 (a'')	
Orbital Populations					
	CpMn(CO) <sub>3</sub>	CpMn(CO) <sub>2</sub> CS	CpCr(CO) <sub>2</sub> NO	CpCr(CO) <sub>2</sub> NS	
CO 5 $\sigma$	1.43	1.44	1.51	1.51	
CO 2 $\pi$	0.62	0.61	0.54	0.52	
		CS 7 $\sigma$	NO 5 $\sigma$	NS 7 $\sigma$	
		CS 2 $\pi$	NO 2 $\pi$	NS 3 $\pi$	
		1.42	1.58	1.61	
		0.72	1.51	1.69	
Atomic Charges					
	CpMn(CO) <sub>3</sub>	CpMn(CO) <sub>2</sub> CS	CpCr(CO) <sub>2</sub> NO	CpCr(CO) <sub>2</sub> NS	
Mn	0.66	Mn 0.72	Cr 0.80	Cr 0.88	
C(CO)	-0.04	-0.04	-0.10	-0.09	
O(NO)	-0.02	-0.02	-0.04	-0.05	
C(Cp)	-0.10	-0.10	-0.15	-0.12	
		C(CS) -0.32	N 0.02	N -0.25	
		S 0.20	O(NO) -0.10	S 0.04	

Figure 7 presents the experimental results of this "proton shift" between CpMn(CO)<sub>3</sub> and CpCr(CO)<sub>2</sub>NO. The 2a' ionization energy decreases markedly from CpMn(CO)<sub>3</sub> to CpCr(CO)<sub>2</sub>NO, sensing the formal change from Mn<sup>+</sup> to Cr<sup>0</sup>. The observation of a short C-O vibrational progression in the first ionization band of the CpCr(CO)<sub>2</sub>NO spectrum establishes the symmetric alignment of 2a' with the cis carbonyls, as illustrated in Figure 8 by a calculated (Fenske-Hall method) orbital contour plot. The a'' and 1a' levels also feel the destabilizing effect of the loss of metal charge but are stabilized by the strong  $\pi$ -accepting ability of the NO ligand. The a'' and 1a' ionizations are observed to be approximately degenerate and stabilized by nearly 0.8 eV relative to the 2a' level, illustrating that the predominant metal-NO interaction is the stabilizing back-donation from the metal to the ligand  $\pi^*$  levels. The metal  $\pi$ -electron density is able to partially "follow" the shift of nuclear charge to the ligand.

A Fenske-Hall molecular orbital calculation for the nitrosyl is in good agreement with the above interpretation. The results listed in Table III concur with the order of the ionizations and the separation of the 2a' energy from the nearly degenerate a'' and 1a' levels.

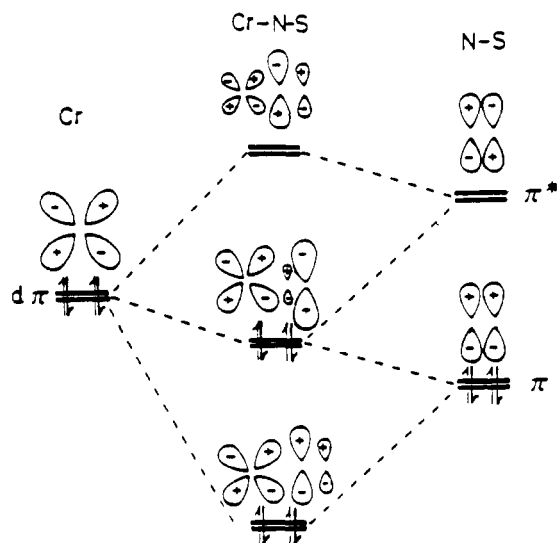
The comparison of NO and NS ligands from a theoretical (and intuitive) perspective leads to a description similar to that for the CO and CS ligands. The replacement of oxygen by sulfur will result in a weakened  $\pi$  bond to nitrogen because of poorer  $\pi$ -orbital overlap. The empty acceptor orbitals for NS will be correspondingly lower in energy than the NO acceptor level and therefore more energetically favorable for metal to ligand  $\pi$  back-donation. Likewise, the NS  $\pi$  bond (the 2 $\pi$  orbital) will be less stable and will also be more energetically favorable for interaction with the metal. The replacement of oxygen by the less electronegative sulfur will also result in a higher negative charge on the nitrogen, reinforcing the  $\sigma$ -donor ability of the ligand. The He I analysis for CpMn(CO)<sub>2</sub>CS<sup>11</sup> showed that these effects are large enough to cause clear resolution of the predominantly CS 7 $\sigma$  and 2 $\pi$  ionizations in the 11-12-eV ionization region. However, the effects of this O-S perturbation may be expected to be somewhat different in the case of the nitrosyl to thionitrosyl change due to the increased nuclear charge on the metal-bound ligand atom (N vs. C).

On comparison of the valence ionizations of the nitrosyl and the thionitrosyl complexes, one first notices the appearance of an ionization band at 11.3 eV for the thionitrosyl complex, which is not present in the nitrosyl spectrum. This new band shows a

reduced relative He II area, indicating predominant ligand character, and has an energy similar to those of the 7 $\sigma$  and 2 $\pi$  CS ionizations of the thiocarbonyl complex. However, only one separate ionization band is observed in the thionitrosyl spectrum. Comparison of the relative band areas of the CS 7 $\sigma$  and 2 $\pi$  bands to the Cp band area reported for the thiocarbonyl complex<sup>11</sup> indicates that the lone band observed in the spectrum of the NS complex is probably not both NS 7 $\sigma$  and 2 $\pi$  ionizations overlapping. Furthermore, close inspection of band D in the thionitrosyl spectrum (Figure 5) shows the band to display an inflection of the low-energy side near the band maximum. Since the band shapes of the CS 7 $\sigma$  and 2 $\pi$  ionizations were considerably different, the fit of band D with two similar components separated by 0.29 eV also does not support the likelihood of the 7 $\sigma$  and 2 $\pi$  overlap in the NS spectrum. This ionization band must be related to a slight symmetry splitting of the NS 2 $\pi$  levels, and the 7 $\sigma$  ionization must then occur at higher energy with the broad group of ionizations beyond 12 eV. This indicates a reversal of the 7 $\sigma$  and 2 $\pi$  levels between the CS and NS complexes, which might be expected because of the greater nuclear charge for nitrogen in place of carbon stabilizing the 7 $\sigma$  (N lone pair) more than the NS  $\pi$  bond. The Fenske-Hall calculations support 7 $\sigma$ /2 $\pi$  crossover between CS and NS complexes, placing the NS 7 $\sigma$  level ca. 0.5 eV below the NS 2 $\pi$  level.

Bands B and B' of the thionitrosyl, which appear in the metal d ionization region, show very interesting He I/He II behavior. The total B + B' area is nearly four times the area of band A in the He I spectrum but is reduced to roughly half this value in the He II spectrum. This effect indicates large ligand (sulfur) character for the B and B' ionizations, meaning that the NS  $\pi$  levels are mixing heavily with the CpCr(CO)<sub>2</sub> a'' and 1a' levels. The fact that the a'' and 1a' levels are destabilized by 0.6 eV from that seen in the nitrosyl is evidence that a substantial amount of this Cr-NS mixing is due to the interaction of the filled NS 2 $\pi$  level with the filled a'' and 1a' levels of the CpCr(CO)<sub>2</sub> fragment.

The interaction of the NS  $\pi$  levels with the metal  $\pi$  levels can be described as a balance between  $\pi$  donation and  $\pi$  acceptance by the NS ligand and is represented schematically in Figure 9. The filled-ligand-filled-metal interaction alone does nothing to the net electron density or charge at the metal but serves to stabilize a portion of a'' and 1a' metal density in the  $\pi$ -bonding combination (mainly NS  $\pi$  character) and destabilize the remainder in the antibonding combination (mainly metal character). The back-donation interaction from the metal to the  $\pi$ -acceptor



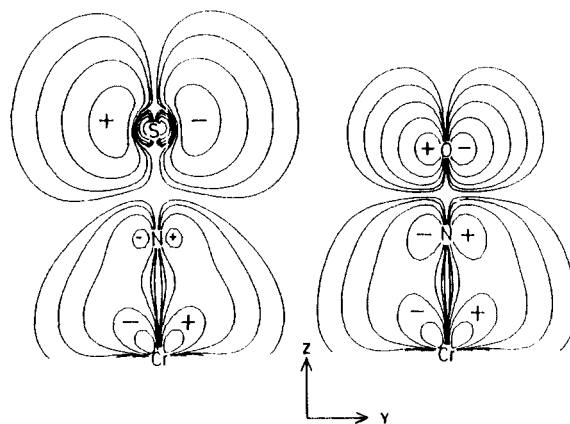
**Figure 9.** Qualitative description of the metal-NS interactions in  $\text{CpCr}(\text{CO})_2\text{NS}$ .

levels on NS further enhances the mixing of the metal-ligand  $\pi$  orbitals as seen in the full 3-center/4-electron description. The narrow ionization band shape which is observed for these upper ionizations shows the "lone-pair" or nonbonding character of these levels, consistent with the small nitrogen character resulting from the nodal position in the center orbital depicted in Figure 9. The narrow shape in combination with the He I/He II intensity comparison indicates that most of the orbital density is on the sulfur, a lesser amount is on the metal, and very little density is on the nitrogen atom. The spectra suggest that the lower combination is largely ligand (NS bonding) character due to the lower He II intensity and broader band shape of the components, which also indicate considerable bonding in this orbital. The observed splitting seen in both the upper and lower  $\pi$  levels (0.20 and 0.29 eV, respectively) is in accord with the metal  $a''$  level being slightly better hybridized toward NS  $\pi$  interaction than the  $1a'$  level.

The Fenske-Hall calculations indicate the NS  $\pi$  donation and  $\pi$  acceptance are roughly equally involved in delocalizing the metal  $d\pi$  density. Figure 10 shows the calculated orbital contour plots for the  $a''$  of the thionitrosyl and nitrosyl. A distinct reduction of nitrogen character is shown from the nitrosyl to the thionitrosyl complex with the node nearer the nitrogen in the latter case. This indicates large sulfur "lone-pair" character in the case of the thionitrosyl, which is also shown by the spectra.

The observed splitting of the NS  $2\pi$  ionizations differs significantly from that of the thiocarbonyl  $2\pi$  ionization. Several elements of a CS stretching progression were observed in the CS  $2\pi$  ionization, showing no simple symmetry splitting of the band. Additionally, there is only a very small change in the metal ionization band shape from the carbonyl to the thiocarbonyl complexes. This can be compared to the 0.6-eV  $1a'$  and  $a''$  destabilization observed from the nitrosyl to thionitrosyl complexes. This evidence indicates more metal-ligand  $\pi$  interaction for a thionitrosyl ligand than for a thiocarbonyl ligand.

Further inspection of the He I/He II data for the NS complex shows two features that are similar to those in the spectra of the NO complex. First, the predominantly Cp  $e_1''$  ionization (band C and C') maintains its familiar band shape but appears at slightly lower BE. The Cp carbon  $1s$  shift of  $-0.11$  eV from the nitrosyl to thionitrosyl complex is similar to the corresponding valence shift of  $-0.17$  eV. Similar shifts are predicted from the calculations and can be correlated with slightly less Cp to metal donation. Second, the energy of band A and its relative behavior in both He I and He II are quite similar to that seen for bands (A + A') for the nitrosyl case. Unlike neighboring bands B and B', band A for the NS complex gains intensity in He II, supportive of negligible NS character mixing into the  $2a'$  level for the thionitrosyl complex. The calculations support this observation, indicating nearly identical  $2a'$  energy and composition for the



**Figure 10.** Calculated orbital contour plots (Fenske-Hall) of the  $a''$  orbital in the  $\text{CpCr}(\text{CO})_2\text{NO}$  and  $\text{CpCr}(\text{CO})_2\text{NS}$  molecules. Contour values and wave function signs are the same as in Figure 8.

thionitrosyl and the nitrosyl complexes (Figure 8).

The nitrosyl to thionitrosyl shift of the Cr  $2p_{3/2}$  ionization is similar to the corresponding  $2a'$  valence shift for the two compounds. This is consistent with the observation that metal core levels will generally shift about the same as a metal valence level that is  $\delta$  symmetry (i.e. nonbonding) to the ligand substitution site.<sup>18,23</sup> Both the Cr  $2p_{3/2}$  core ionization and the  $2a'$  ionization are equally sensitive to the electron charge environment at the metal atom. The fact that these levels are destabilized by only 0.1 eV from the NO complex to the NS complex is somewhat surprising in view of the analogous 1.94-eV destabilization of the nearby nitrogen  $1s$  core ionization. Qualitatively, this large negative shift of the nitrogen  $1s$  is an indication of an increase of negative charge resulting from substitution of oxygen with a less electronegative sulfur atom, and the increased  $\pi$  donation from the metal center. According to the point-charge model the larger negative charge on the N of the thionitrosyl will translate to the Cr atom by a  $1/R$  term, where  $R$  is the Cr to N distance. In view of the apparently large increase in the charge on nitrogen, this two-center effect cannot be considered negligible. Therefore, a charge analysis of the observed XPS shifts from the NO complex to the NS complex must specifically include both one- and two-center terms.

Our analysis of the XPS shifts follows from several published methods employing the "potential model".<sup>24,25</sup> Since the only major XPS shift observed from the nitrosyl to the thionitrosyl is on the N atom, we consider in a first approximation only the (Cr-N-O) and (Cr-N-S) species. In the potential model the binding energy of a particular atom in a molecule is expressed as

$$E_i = k_i Q_i + 14.4 Q_j / R_{ij} + l_i$$

where  $E_i$  is the binding energy for the atom in electronvolts,  $k_i$  is the linear coefficient for atom  $i$ ,  $Q_i$  is the charge on atom  $i$ ,  $Q_j$  are the charges on neighboring atoms  $j$  at a distance  $R_{ij}$  in Ångstroms from atom  $i$ , and  $l_i$  is a constant for atom  $i$ . The application of the above equation using the experimental geometries for the (Cr-N-O) and (Cr-N-S) species and the coefficients and constants of Jolly and Perry<sup>25</sup> results in a set of three equations and three unknowns for these complexes; solution of these equations yields the charges within this model for the atoms of the triatomic species. The results of this analysis, presented in Table IV, show the Cr atom to be more positive in the thionitrosyl complex by ca. 0.03 charge unit, while the N atom of the thionitrosyl is more negative by ca. 0.12 charge unit. Of course, there are many approximations in this model and one must not place too much significance on the absolute value of atomic changes.

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**Table IV.** Potential Model Calculation Results for Cr-N-O and Cr-N-S

trial	term	atom			
		Cr	N	O	S
I	$k, eV/Q$	10.95	30.69	25.50	18.63
	$l, eV$	585.43	5.46	2.21	172.30
	$Q_{NO}$	-0.123	-0.185	-0.150	...
	$Q_{NS}$	-0.095	-0.306	...	-0.028
	$\Delta Q$	0.028	-0.121	...	...
	$OC^a$	0.303	-3.72	...	...
	$TC^b$	-0.403	1.76	...	...
II	$k, eV/Q$	10.95	30.69	25.50	18.63
	$l, eV$	580.00	5.46	2.21	172.30
	$Q_{NO}$	0.519	-0.343	-0.199	...
	$Q_{NS}$	0.554	-0.463	...	-0.105
	$\Delta Q$	0.035	-0.120	...	...
	$OC^a$	0.383	-3.683	...	...
	$TC^b$	-0.403	1.723	...	...
III	$k, eV/Q$	15.00	20.00	25.50	18.63
	$l, eV$	585.43	5.46	2.21	172.30
	$Q_{NO}$	-0.003	-0.393	-0.073	...
	$Q_{NS}$	0.057	-0.581	...	0.073
	$\Delta Q$	0.060	-0.188	...	...
	$OC^a$	0.900	-3.760	...	...
	$TC^b$	-1.000	1.800	...	...

<sup>a</sup>One center. <sup>b</sup>Two center.

The calculated charges can be adjusted by the choice of coefficients and constants from literature sources,<sup>23,24</sup> as shown by the different trials in Table IV. However, we found that no reasonable adjustment of these parameters resulted in a more negative metal for the thionitrosyl complex. It should be noted that the particular choice for any value made little difference on the calculated change in charge; hence, a choice of  $l = 580.0$  eV for Cr results in a more reasonable absolute charge on Cr for the NO and NS complexes (i.e., positive), but has little effect on the calculated change in charge between the NO and NS complexes. The results of the Fenske-Hall calculations for the NS and NO complexes similarly predict a change of Cr charge of 0.08 charge units from the nitrosyl complex to thionitrosyl complex (Table III). Thus, the XPS analysis results, nonempirical MO calculations, and the observed

IR shifts all indicate slightly less available electron density for the metal of CpCr(CO)<sub>2</sub>NS than for CpCr(CO)<sub>2</sub>NO.

### Summary

The present study has compared the binding of the CO, CS, NO<sup>+</sup>, and NS<sup>+</sup> ligands to the isoelectronic and essentially isostructural CpMn(CO)<sub>2</sub> and CpCr(CO)<sub>2</sub> fragments. In this type of piano stool system the various binding properties of the L ligand can be conveniently monitored by the gas-phase core and valence orbital ionizations. Specifically, the strong stabilizing influence of NO vs. CO on available metal d  $\pi$  levels can be seen from the valence ionizations of CpMn(CO)<sub>3</sub> and CpCr(CO)<sub>2</sub>NO. In this case, the two metal d levels that interact primarily with the NO  $\pi$  orbitals are stabilized by nearly 0.8 eV relative to the one metal orbital that is largely delocalized into the cis carbonyls. A carbon-oxygen stretching mode resolved in this latter band provides further information for this assignment. The comparison of the valence ionizations of CpCr(CO)<sub>2</sub>NO to those of CpCr(CO)<sub>2</sub>NS shows a similar separation of the metal-NS  $\pi$  orbitals from the metal-(CO)<sub>2</sub>  $\pi$  orbital and clearly shows the increase in these  $\pi$  interactions for the NS complex. The increased interaction between Cr and NS is observed to be balanced between increased NS to Cr  $\pi$  donation and Cr to NS  $\pi$  back-donation. The XPS data show the result of this enhanced  $\pi$  interaction in the NS complex is slightly less available electron density on the metal atom.

Finally, the ionization energy order CS  $2\pi > CS 7\sigma$  seen in the CpMn(CO)<sub>2</sub>CS complex is apparently reversed for the corresponding NS  $2\pi$  and  $7\sigma$  ionizations of the CpCr(CO)<sub>2</sub>NS complex. The reversal of these levels is consistent with the greater nuclear charge on nitrogen (NS<sup>+</sup> vs. CS), stabilizing the  $7\sigma$  orbital more than the  $2\pi$  orbital in the NS case. The spectral observations show that NO to NS substitution will cause a substantially greater effect on available metal  $\pi$  levels than will an analogous CO to CS substitution.

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**Registry No.** ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>NO, 36312-04-6; ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>2</sub>NS, 66539-91-1; SN, 12033-56-6; ON, 10102-43-9; Cr, 7440-47-3.