and the 2,2′-bipyridine. Again the values are reasonably close those reported for other thiophenol derivatives.[17,18]

The only other tin(IV)-2,2′-bipyridine complex whose structure has been reported[19] is the adduct of $(C_6H_5)_2SnCl_2$, in which the trans-phenyl groups are almost perpendicular to the SnN_2Cl_2 plane. The Sn-N bond length in $Sn(SC_6H_5)_4bpy$ (av 2.331 Å) is close to those in $(C_6H_5)_2SnCl_2{\cdot}bpy$ (2.344 (6) and 2.375 (6) Å) and well within the range of values found in other organotin compounds, as reviewed by Harrison, King, and Richards.[19] The bite of the 2,2′-bipyridine is essentially the same in both compounds, as is the twist of the bipyridine rings.

Finally we note that the C-C bond lengths in the phenyl rings (not shown in Table V) lie in the range 1.35-1.45 (1) Å, and the C-C-C angles are in the range 117.5-123.2 (7)°. These call for no comment, being entirely compatible with accepted values.

Structure of $Pb(SC_6H_5)_2$. In the course of characterizing $Pb(SC_6H_5)_2$, we recorded both NMR and infrared spectra. The ^1H NMR spectrum (in dimethyl-d_6 sulfoxide) shows a broad absorption centered at 7.1 ppm from Me_4Si; the parent C_6H_5SH has a much sharper resonance at 6.5 ppm. The infrared spectrum has no unexpected features above 500 cm^{-1}; the far-infrared spectrum has absorptions at 474 s, 416 m, 145 m, br and 120 w cm^{-1}, similar to the far-infrared spectra of $M(SC_6H_5)_2$ (M = Zn, Cd, Hg), reported elsewhere,[6] and especially to that of the cadmium compound. The bands at 474, 416, and 174 cm^{-} are tentatively identified as modes of the ligand, leaving absorptions at 338, 319, 252, and 220 cm^{-1} as modes of the metal-sulfur kernel. It has been suggested elsewhere[6] that the benzenethiolate derivatives of group 2B are polymeric in the solid state, and the far-infrared spectrum implies a similar conclusion for $Pb(SC_6H_5)_2$.

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Registry No. $Sn(SC_6H_5)_2$, 22881-46-5; Sn(S-*m*-$CH_3C_6H_4)_2$, 81616-24-2; $Sn(SC_6H_5)_4bpy$, 12119-13-0; $Sn(SC_6H_5)_4phen$, 81616-65-1; Sn(S-*o*-$CH_3C_6H_4)_4bpy$, 81616-66-2; Sn(S-*o*-$CH_3C_6H_4)_4phen$, 81616-67-3; Sn(S-*m*-$CH_3C_6H_4)_4bpy$, 81616-68-4; Sn(S-*m*-$CH_3C_6H_4)_4phen$, 81616-69-5; $Pb(SC_6H_5)_2$, 32812-89-8.

Supplementary Material Available: Tables of thermal parameters, least-squares planes, and observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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X-ray Photoelectron Spectra of Inorganic Molecules. 31.[1] Satellite Structure Associated with the Core-Electron Binding Energies of Alkyl and Aryl Isocyanide Complexes of the Transition Metals

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The observation of shake-up satellite structure associated with the N 1s and C 1s binding energies in the X-ray photoelectron spectra (XPS) of a range of six- and seven-coordinate alkyl and aryl isocyanide complexes of zerovalent and divalent chromium, molybdenum, and tungsten and the complexes $[Re(CNCMe_3)_6]PF_6$ and $[Rh(CNCMe_3)_4]PF_6$ expands considerably the occurrence of this phenomenon within compounds of the second and third transition series. By comparison with literature data for mononuclear and polynuclear metal carbonyls it is concluded that these satellites most probably arise from M(d) → π^*(CNR) and M(d) → π^*(CNAr) excitations accompanying the primary photoemission processes.

Introduction

The similarities between the photoelectron spectra of transition-metal carbonyl complexes and the corresponding spectra of metal surfaces containing adsorbed CO[2,3] have led to detailed experimental[2-4] and theoretical[5] studies of the X-ray photoelectron spectra (XPS) of mononuclear and polynuclear cluster metal carbonyls. The focus of much of the recent interest has been the measurement and assignment of the shake-up satellite structure associated with the metal, the C 1s, and the O 1s primary photolines.[2-5] The interpretation of these satellites is particularly important in the modeling of the electronic structure of discrete molecular transition-metal carbonyl species to that of metal surfaces containing adsorbed CO. In addition to this application of XPS to the characterization of catalytically important surfaces, shake-up satellites are of interest from another point of view. While a common feature in the XPS of salts and complexes of many first-row transition metal ions, they are rarely encountered in the spectra of complexes of the second- and third-row transition elements.[6,7] The one major exception to this experimental observation is the shake-up satellites that are observed in the XPS of carbonyls of the second and third transition series.[2,4,8]

Our recent discovery of satellite structure in the XPS of the homoleptic alkyl isocyanide complexes of molybdenum(II) of the type $[Mo(CNR)_7](PF_6)_2$, where R = CH_3, CMe_3, or C_6H_{11},[9] was the first instance where this phenomenon has been reported in complexes containing these ligands. Furthermore, studies on the XPS of metal isocyanide complexes provide the opportunity to gather the necessary experimental XPS data with which to model the binding of isocyanide ligands to metal

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Table I. Core-Electron Binding Energies of Isocyanide Complexes of the Transition Metals[a]

compd	cyano C 1s	N 1s	P 2p		metal[b]
			PF_6^-	phosphine	
$Cr(CNPh)_6$		399.2 (1.8)			Cr $2p_{3/2}$ 574.5 (1.2)
$[Cr(CNPh)_6]PF_6$		399.9 (1.9)	136.3		Cr $2p_{3/2}$ 575.3 (2.0)
$[Cr(CNCMe_3)_6](PF_6)_2$[c]	~286.5	400.3 (2.2)	135.9		Cr $2p_{3/2}$ 576.7 (2.1)
$[Cr(CNC_6H_{11})_6](PF_6)_2$[c]	~286.6	400.4 (2.1)	136.1		Cr $2p_{3/2}$ 576.7 (2.0)
$[Cr(CNCMe_3)_7](PF_6)_2$[c]	~286.6	399.7 (1.8)	135.8		Cr $2p_{3/2}$ 576.4 (2.0)
$[Cr(CNC_6H_{11})_7](PF_6)_2$	~286.4	400.4 (1.8)	136.1		Cr $2p_{3/2}$ 576.5 (2.2)
$Mo(CNPh)_6$[d]	~286.1	399.2 (1.8)			Mo $3d_{5/2}$ 227.5 (1.0)
$[Mo(CNCH_3)_7](PF_6)_2$	286.7	400.2 (1.6)	136.1		Mo $3d_{5/2}$ 229.2 (1.4)
$[Mo(CNCMe_3)_7](PF_6)_2$	286.6	399.7 (1.6)	135.9		Mo $3d_{5/2}$ 228.9 (1.3)
$[Mo(CNC_6H_{11})_7](PF_6)_2$	286.5	400.0 (1.6)	136.0		Mo $3d_{5/2}$ 229.2 (1.2)
$[Mo(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$	~286.6	399.8 (1.7)	135.9	130.8	Mo $3d_{5/2}$ 228.8 (1.2)
$[Mo(CNCH_3)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	~286.3	400.0 (1.6)	136.3	131.0	Mo $3d_{5/2}$ 228.8 (1.3)
$[Mo(CNC_6H_{11})_5(PEtPh_2)_2](PF_6)_2$		399.9 (1.9)	136.4	131.3	Mo $3d_{5/2}$ 228.9 (1.6)
$[Mo(CNCMe_3)_5(dppe)](PF_6)_2$	286.6	399.7 (2.0)	136.1	131.3	Mo $3d_{5/2}$ 228.9 (1.3)
$[Mo(CNC_6H_{11})_5(dppm)](PF_6)_2$		399.8 (2.0)	136.2	131.4	Mo $3d_{5/2}$ 229.0 (1.3)
$[Mo(CNC_6H_{11})_5(dppe)](PF_6)_2$		399.8 (2.0)	136.1	131.3	Mo $3d_{5/2}$ 228.8 (1.5)
$W(CNPh)_6$		398.7 (2.4)			W $4f_{7/2}$ 31.0 (1.8)
$[W(CNCH_3)_7](PF_6)_2$	286.4	399.8 (1.7)	136.2		W $4f_{7/2}$ 32.2 (1.2)
$[W(CNCMe_3)_7](PF_6)_2$	286.8	399.5 (1.9)	135.9		W $4f_{7/2}$ 32.1 (1.4)
$[W(CNC_6H_{11})_7](PF_6)_2$	286.4	399.9 (1.6)	136.0		W $4f_{7/2}$ 32.1 (1.4)
$[W(CNCMe_3)_6I]I$[e]	~286.5	399.4 (2.0)			W $4f_{7/2}$ 31.9 (1.6)
$[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$	~286.8	399.5 (1.8)	135.9	130.9	W $4f_{7/2}$ 31.9 (1.3)
$[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$	~286.8	399.7 (1.7)	136.1	131.0	W $4f_{7/2}$ 32.0 (1.5)
$[W(CNCMe_3)_5(dppe)](PF_6)_2$	~286.7	399.5 (1.8)	136.3	131.4	W $4f_{7/2}$ 32.2 (1.5)
$[Re(CNCMe_3)_6]PF_6$	286.6	399.1 (1.7)	135.9		Re $4f_{7/2}$ 40.2 (1.4)
$[Rh(CNCMe_3)_4]PF_6$	~286.5	400.0 (1.6)	136.0		Rh $3d_{5/2}$ 308.4 (1.5)
$[Rh(CNCMe_3)_3(PPh_3)_2]PF_6$		400.1 (2.0)	136.2	131.4	Rh $3d_{5/2}$ 308.6 (2.0)

[a] All values are in eV; spectra were recorded with a 1-kW beam power and a probe temperature of 35 °C unless noted otherwise; full width at half-maximum (fwhm) values are given in parentheses. [b] The Cr $2p_{1/2}$, Mo $3d_{3/2}$, W $4f_{5/2}$, Re $4f_{5/2}$, and Rh $3d_{3/2}$ spin-orbit components are located to higher binding energies of the more intense Cr $2p_{3/2}$, Mo $3d_{5/2}$, W $4f_{7/2}$, Re $4f_{7/2}$, and Rh 3d $_{5/2}$ peaks. Their positions are not reported here, but details can be obtained from R.A.W. upon request. [c] Spectra recorded with a probe temperature of 250 K. [d] Spectra recorded with a probe temperature of ca. 200 K. [e] Inner- and outer-sphere iodines were characterized by I $3d_{5/2}$ binding energies of 619.2 and 618.2 eV, respectively.

surfaces and small metal particles. Recent work on the chemisorption of methyl isocyanide on the Ni(111) surface[10] and Al_2O_3-supported rhodium[11] points up the growing interest in such systems.

In the present report we describe the XPS of a range of mononuclear alkyl and aryl isocyanide complexes of the transition elements with particular emphasis upon those of Cr, Mo, and W. This choice permits a comparison with the related spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$,[2-5] molecules that are isoelectronic with many of the isocyanide complexes we have studied.

Experimental Section

The X-ray photoelectron spectra were recorded with a Hewlett-Packard Model 5950A ESCA spectrometer. Monochromatic aluminum $K\alpha_{1,2}$ radiation (1486.6 eV) was used as the X-ray excitation source. An electron "floodgun" was used in conjunction with the instrument to reduce to a minimum surface-charging effects. A Du Pont 310 curve resolver was used for peak deconvolutions using Gaussian peak shapes. Samples were prepared by burnishing the powdered material into a gold-plated copper planchet or by dissolving the sample in an appropriate solvent, applying a drop of the solution to the plate, and allowing it to evaporate to dryness.

Most of the complexes used in this study were available from synthetic procedures developed in this laboratory. Samples of the following complexes were obtained in this way: $W(CNPh)_6$,[12] $[Cr(CNR)_6](PF_6)_2$ (R = CMe_3 or C_6H_{11}),[13,14] $[M(CNR)_7](PF_6)_2$ (M = Cr, Mo, or W; R = CH_3, CMe_3, or C_6H_{11}),[13-16] $[M(CNR)_{7-x}(PR_3)_x](PF_6)_2$ (M = Mo or W; R = CH_3, CMe_3, or C_6H_{11}; x = 1 or 2),[16,17] $[M(CNR)_5(Ph_2P(CH_2)_nPPh_2)](PF_6)_2$ (M = Mo or W; n = 1 or 2),[16,17] $[W(CNCMe_3)_6I]I$,[16] and $[Re(CNCMe_3)_6]PF_6$.[18] The complexes $Cr(CNPh)_6$,[19] $[Cr(CNPh)_6]PF_6$,[20] $Mo(CNPh)_6$,[21] and $[Rh(CNCMe_3)_3(PPh_3)_2]PF_6$[22] were prepared by literature methods. A sample of $[Rh(CNCMe_3)_4]PF_6$ was prepared by refluxing a methanol solution of $Rh_2(O_2CCH_3)_4{\cdot}2CH_3OH$ with an excess of *tert*-butyl isocyanide for 2 h and adding KPF_6 to the cooled reaction solution. The ^1H NMR and IR spectral properties of this product were in agreement with those cited in the literature for an authentic sample of the complex.[23]

Results

The appropriate core-electron binding energies of the 27 alkyl and aryl isocyanide complexes that were the subject of the present investigation are presented in Table I. The details of the satellite structure associated with the C 1s and N 1s binding energies of the isocyanide ligands are given in Table II. The binding energies listed in Table I have been referenced when possible to a C 1s energy of 285.0 eV for the maximum of the band envelope associated with the aliphatic or aromatic carbon atoms of the isocyanide and phosphine ligands. Such a procedure has been advocated in the past[24-29] and is that

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Table II. Satellite Features in the XPS of Isocyanide Complexes of the Transition Metals

compd	ΔE_{sat}(N 1s),[a] eV	$(I_s/I_p)_{N1s}$[b]	ΔE_{sat}(C 1s),[a] eV	$(I_s/I_p)_{C1s}$[b]
$Cr(CNPh)_6$	3.4	0.18		
$[Cr(CNPh)_6]PF_6$	3.3	0.10		
$[Cr(CNCMe_3)_6](PF_6)_2$	3.5	0.18		
$[Cr(CNC_6H_{11})_6](PF_6)_2$	3.4	0.16		
$[Cr(CNCMe_3)_7](PF_6)_2$	3.2	0.22	~2.1	0.15
$[Cr(CNC_6H_{11})_7](PF_6)_2$	3.1	0.18		
$Mo(CNPh)_6$	3.6	0.18		
$[Mo(CNCH_3)_7](PF_6)_2$	3.6	0.22	2.4	0.27
$[Mo(CNCMe_3)_7](PF_6)_2$	3.7	0.18	2.3	0.22
$[Mo(CNC_6H_{11})_7](PF_6)_2$	3.5	0.20	2.6	0.15
$[Mo(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$	3.6	0.12	1.9	0.20
$[Mo(CNCH_3)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	3.8	0.13	2.0	0.20
$[Mo(CNC_6H_{11})_5(PEtPh_2)_2](PF_6)_2$	3.6	0.16		
$[Mo(CNCMe_3)_5(dppe)](PF_6)_2$	3.6	0.19		
$[Mo(CNC_6H_{11})_5(dppm)](PF_6)_2$	3.7	0.12		
$[Mo(CNC_6H_{11})_5(dppe)](PF_6)_2$	3.8	0.17		
$W(CNPh)_6$	3.8	0.27		
$[W(CNCH_3)_7](PF_6)_2$	3.9	0.27	2.8	0.27
$[W(CNCMe_3)_7](PF_6)_2$	3.9	0.23	2.5	0.31
$[W(CNC_6H_{11})_7](PF_6)_2$	3.8	0.24	2.9	0.30
$[W(CNCMe_3)_6I]I$	3.8	0.19	~2.5[d]	
$[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$	3.9	0.21	~2.0[d]	
$[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$	3.7	0.22	~2.0[d]	
$[W(CNCMe_3)_5(dppe)](PF_6)_2$	3.7	0.22		
$[Re(CNCMe_3)_6]PF_6$	4.7	0.14	2.9	0.23
$[Rh(CNCMe_3)_4]PF_6$	~5[c]	~0.09		
$[Rh(CNCMe_3)_3(PPh_3)_2]PF_6$	*e*			

[a] ΔE_{sat} is defined as the position of the satellite relative to that of the primary photoline with which it is associated. [b] I_s/I_p is the ratio of satellite intensity to that of the primary photoline. [c] This satellite is very broad and weak. [d] This satellite is seen as a poorly defined shoulder on the broad high-energy tail associated with the cyano C 1s peak, which is itself a shoulder on the more intense C 1s peak due to the aliphatic carbon atoms of the isocyanide and phosphine ligands. [e] No satellite observed.

which we have used previously in our studies on the XPS of molybdenum and tungsten organometallics.[1,30] The one exception to this referencing procedure was in the case of the homoleptic methyl isocyanide complexes $[M(CNCH_3)_7](PF_6)_2$ (M = Mo or W) for which the C 1s energies of the methyl and cyano carbon atoms were coincident at ~286.5 eV and well separated from the C 1s line of adventitious carbon at ~285 eV. Accordingly, in these two cases a C 1s energy of 285.0 eV for the carbon contaminant[31] was used as the binding energy reference. The internal consistency of our results (vide infra) indicates that our choice of referencing procedure is a satisfactory one.

Metal and Phosphorus 2p Core Binding Energies. The Cr 2p binding energy spectra were of acceptable quality with fwhm values ranging from 1.2 to 2.0 eV, the diamagnetic $Cr(CNPh)_6$ possessing the narrowest peaks. The Cr $2p_{3/2}$ binding energies for all the chromium(II) complexes were 576.5 ± 0.2 eV, values which compare favorably with that of 576.7 eV reported for $(\eta^5\text{-}C_5H_5)_2Cr$.[32] The values for $[Cr(CNPh)_6](PF_6)_n$, where n = 0 or 1, were substantially lower than that reported for $Cr(CO)_6$.[32] This is consistent with CO being a significantly better π acceptor than phenyl isocyanide.

The Mo $3d_{5/2}$ binding energy spectra of the molybdenum complexes (229.0 ± 0.2 eV for the molybdenum(II) species and 227.5 eV for $Mo(CNPh)_6$) were of a quality comparable to that reported[23] for gas-phase $Mo(CO)_6$, with fwhm values of 1.0–1.6 eV. These binding energies are in close agreement with values previously reported[30] for molybdenum(II) and molybdenun(0) complexes containing the dicarbonylmolybdenum moiety.

The W $4f_{7/2}$ binding energies were also consistent with data from a recent study of low-valent organometallic complexes of tungsten,[1] with $W(CNPh)_6$ having a W $4f_{7/2}$ value of 31.0 eV and W $4f_{7/2}$ values for the various tungsten(II) complexes being 32.0 ± 0.2 eV. The corresponding fwhm values for all the tungsten compounds ranged from 1.8 eV for $W(CNPh)_6$ to 1.2 eV for $[W(CNCH_3)_7](PF_6)_2$. The higher value for $W(CNPh)_6$ may reflect the difficulty of ensuring that this complex does not react with adventitious oxygen to give some surface oxidation. It is much more susceptible to oxidation than its molybdenum analogue $Mo(CNPh)_6$.

The small number of rhenium and rhodium complexes studied in the present work does not justify a detailed comparison with literature data other than noting that the Re 4f and Rh 3d binding energies are in accord with the isocyanide complexes, being low-valent derivatives of these metals.[33,34]

The P 2p values for the PF_6^- phosphorus atoms ranged from 135.6 to 136.4 eV and those for phosphine phosphorus from 130.8 to 131.4 eV. In all instances, the PF_6^-/PR_3 P 2p intensity ratio was consistent with the known stoichiometry of the complexes.

Nitrogen 1s and Carbon 1s Core Binding Energies. While the N 1s binding energies (Table I) varied over quite a wide range (399.6 ± 0.9 eV), several trends are apparent. The N

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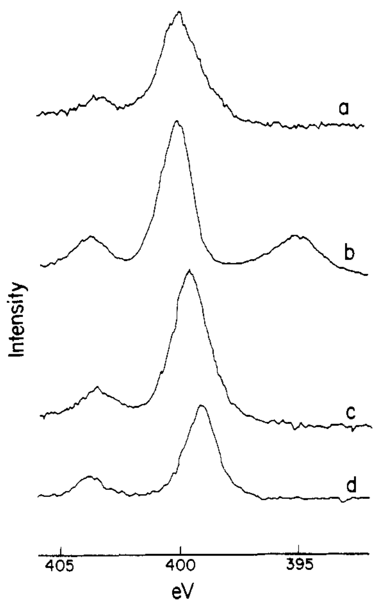

Figure 1. N 1s binding energy spectra of (a) $[Cr(CNPh)_6]PF_6$, (b) $[Mo(CNCH_3)_7](PF_6)_2$ (the Mo $3p_{3/2}$ peak is at 395 eV), (c) $[W(CNCMe_3)_7](PF_6)_2$, and (d) $[Re(CNCMe_3)_6]PF_6$.

1s binding energies for zerovalent complexes were typically 0.5–1.0 eV lower than the corresponding energies in the XPS of the higher oxidation state complexes. This observation is in accord with the π-acceptor ability of isocyanides. In zerovalent complexes, more electron density is available for π back-bonding. This increases the electron density on the isocyanide nitrogen and results in a shift to lower binding energy of the N 1s peak.

The N 1s spectra of all the complexes except $[Rh(CNCMe_3)_3(PPh_3)_2]PF_6$ exhibited a broad satellite feature at $\Delta E_{sat} = 3.1$–3.9 eV for the chromium, molybdenum, and tungsten complexes and $\simeq$4.8 eV for the rhenium and rhodium complexes (Table II). Representative spectra are shown in Figure 1. The energies of these satellite peaks were found to be invariant with respect to changes in X-ray flux and irradiation times. When different preparative batches of the same complex were studied, the intensity ratio I_s/I_p remained constant.

A number of different observations can be made with regard to the N 1s satellites. There is a consistency in the ΔE_{sat} values and intensities within the sets of complexes of the types $[Cr(CNR)_6](PF_6)_2$, $[Cr(CNR)_7](PF_6)_2$, $[Mo(CNR)_7](PF_6)_2$, and $[W(CNR)_7](PF_6)_2$. The satellite separations from the main N 1s photolines only vary by ±0.2 eV, and the I_s/I_p ratios change by no more than ±0.04 (Table II). This adds credibility to the contention that these peaks are genuine satellite structure rather than arising from the formation of a high oxidation state nitrogen-containing contaminant (such as nitrite) on the sample surface.

With the exception of the methyl isocyanide complexes $[M(CNCH_3)_7](PF_6)_2$ (M = Mo or W), all complexes listed in Table I exhibited an intense C 1s binding energy peak close to 285.0 eV, which is a composite of the C 1s energies of the aliphatic and/or aromatic carbon atoms of the isocyanide and phosphine ligands. It is this binding energy of 285.0 eV to which all others given in Table I have been referenced. In the case of the homoleptic methyl isocyanide complexes of molybdenum(II) and tungsten(II), a weak C 1s peak at ~285 eV is due to adventitious carbon "contaminant", while the more intense primary photoline at ~286.5 eV (Figure 2 and Table I) can be assigned[35-37] to an overlap between the C 1s energies of the cyano and methyl carbon atoms. In view of the narrowness of this peak (fwhm ~1.8 eV) and its symmetrical shape, we chose not to deconvolute it. The corresponding cyano C 1s binding energy for certain of the other isocyanide complexes was seen as a shoulder between 287 and 286 eV (on the high binding energy side of the much more intense C 1s peak at 285.0 eV). In other instances while the C 1s envelope centered at 285.0 eV was asymmetric to its high binding energy side, the position of the cyano C 1s binding energy was not well defined. Since the C 1s envelope in these instances contains contributions from carbon contaminant and all the carbon atoms of the isocyanide and/or phosphine ligands, we deemed it inappropriate to deconvolute the complete C 1s envelope in order to estimate these cyano C 1s energies. Accordingly, Table I lists only those C 1s values that could be determined without such a deconvolution procedure.

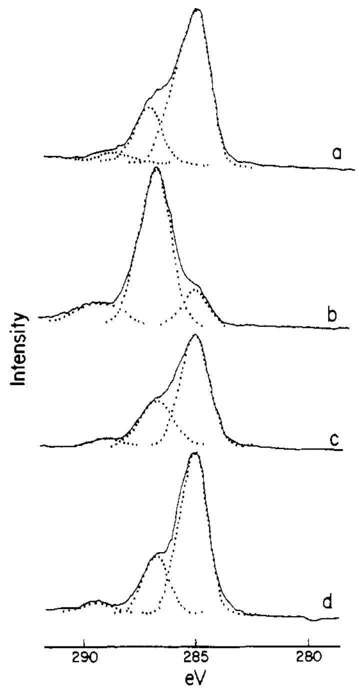

Figure 2. C 1s binding energy spectra of (a) $[Cr(CNCMe_3)_7](PF_6)_2$, (b) $[Mo(CNCH_3)_7](PF_6)_2$, (c) $[W(CNCMe_3)_7](PF_6)_2$, and (d) $[Re(CNCMe_3)_6]PF_6$. Deconvolutions were carried out as described in ref 9.

Approximately 3 eV above the 286.5-eV C 1s peak of $[M(CNCH_3)_7](PF_6)_2$ (M = Mo or W) is a satellite whose intensity relative to that of the primary photoline (I_s/I_p) is 0.10–0.14 (Table II and Figure 2). Actually, its intensity relative to that of the cyano C 1s peak alone will be approximately twice this value since the 286.5-eV peak arises from the overlap of signals due to the cyano and the methyl carbons. This makes the I_s/I_p ratios comparable with those observed for the corresponding N 1s satellites (vide supra). In those instances where the quality of C 1s spectra of the isocyanide complexes was sufficient to permit the location and measurement of C 1s satellites, we have listed the appropriate data in Table II. A selection of spectra is shown in Figure 2.

When the C 1s satellite could be measured, its energy separation from the main photoline was always less than that of the N 1s satellite (Table II). The differences in the values of ΔE_{sat} for the N 1s and C 1s satellites may reflect differences in relaxation energy contributions to the chemical shifts. Ionization of the core electrons results in formation of a positive

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hole, and the electron relaxation will depend on the environment of the atom. This difference in satellite separation has also been observed in metal carbonyls where ΔE_{sat} for the O 1s satellies is ~0.5 eV greater than that for the corresponding C 1s satellite.[4]

Discussion

The values of the metal, C 1s, O 1s, and P 2p binding energies that characterize the alkyl and aryl isocyanide complexes reveal a consistent pattern based upon trends in the different metal oxidation states, e.g., Cr(0), Cr(I), and Cr(II), and differences in the σ-donor and π-acceptor properties of the RNC and ArNC ligands. However, of special note in the present investigation is the observation of the quite intense satellite structure that is associated with the primary C 1s and N 1s photolines (Table II). It is these satellites and their interpretation upon which we will focus our subsequent discussion.

The fact that we see C 1s and N 1s satellites but none that are associated with the P 2p core ionization is in accord with the notion that they arise principally from an excitation process associated with the "M–CNR" and "M–CNAr" moieties. In this event, we might also expect to see satellites associated with the metal core levels. Indeed when the Mo 3d spectrum of $[\mathrm{Mo(CNCH_3)_7}](\mathrm{PF_6})_2$ was recorded to very high statistics, a weak feature was observed at ~3.1 eV to the high binding energy side of the primary Mo $3d_{3/2}$ photoline (at 232.4 eV). Its intensity relative to that of the latter was ~0.05. The position of this weak peak ($\Delta E \approx 3$ eV) means that a corresponding "satellite" associated with the Mo $3d_{5/2}$ photoline would be masked by the much more intense Mo $3d_{3/2}$ primary peak since the Mo $3d_{3/2}$–Mo $3d_{5/2}$ spin–orbit separation is 3 eV. The three most reasonable interpretations which might explain this phenomenon are as follows. (1) This is indeed a genuine shake-up satellite which is associated with the same charge-transfer process as that which gives rise to the N 1s and C 1s satellites. (2) It arises from a Mo 3d excitation due to a small amount of high oxidation state molybdenum oxide contaminant. (3) It is the result of a characteristic "plasmon" energy loss. Possibility 3 can be ruled out because of the dramatic intensity difference between the "satellite" associated with the Mo 3d, the N 1s, and the C 1s lines, the difference in the satellite position in the Mo 3d, N 1s, and C 1s spectra, and the absence of such a feature accompanying the P 2p spectra. Attempts to locate "satellites" in the Mo 3d spectra of the other crystalline isocyanide complexes met with limited success. Thus such structure was not observed in the XPS of the *tert*-butyl and cyclohexyl isocyanide complexes of the type $[\mathrm{Mo(CNR)_7}](\mathrm{PF_6})_2$ or with any of the chromium complexes listed in Table I. However, very weak structure was seen in the Mo 3d XPS of $[\mathrm{Mo(CNCH_3)_5(P\text{-}\mathit{n}\text{-}Pr_3)_2}](\mathrm{PF_6})_2$ and $[\mathrm{Mo(CNC_6H_{11})_5(dppm)}](\mathrm{PF_6})_2$ at $\Delta E \approx 3.6$ eV. This erratic behavior could be in accord with point 2, namely, the presence of small and variable amounts of high oxidation state molybdenum surface contaminants. In any event, it is apparent that the intensity of any satellites that might accompany the metal core photolines of these isocyanide complexes is invariably an order of magnitude less than that of the N 1s and C 1s satellites. The fact that XPS measurements on these isocyanide complexes cannot be carried out in the gas phase is unfortunate, since it is likely that only under such experimental conditions[4] will we expect to see, with any confidence, very weak satellite structure on the metal photolines. In this same context we note that the XPS of the hexacarbonyls $\mathrm{M(CO)_6}$ (M = Cr, Mo, or W) in the *solid state* exhibit[38] a single broad satellite associated with both the O 1s and C 1s primary photolines ($\Delta E_{\mathrm{sat}} \approx 5$–6 eV) but at most a very weak satellite on the metal core levels. This observation is in accord with our observations concerning the XPS of the alkyl and aryl isocyanide complexes of Cr, Mo, and W.

The question as to the assignment of the shake-up satellites is perhaps best approached qualitatively by analogy with the corresponding interpretation of the XPS of the "isoelectronic" hexacarbonyls $\mathrm{M(CO)_6}$.[2,4,5,38] The most intense satellites on the C 1s and O 1s levels of gaseous $\mathrm{M(CO)_6}$,[2,4,5] and the broad satellites that are a property of solid samples of these same carbonyls,[38] have been assigned to a transition which is predominantly M(d) → π^*(CO) in character. Although an earlier interpretation using the sudden approximation[4] was subsequently modified by Hall and Sherwood[5] in terms of localized hole states (involving reduction in symmetry to C_{4v}), from the point of view of the present discussion the type of transition giving rise to the C 1s and O 1s satellites remains of the type M(d) → π^*(CO), irrespective of the model used. The similarity in the magnitudes of the I_s/I_p ratios for the N 1s and C 1s spectra of the isocyanide complexes (Table II) and those of the corresponding I_s/I_p ratios for the O 1s and C 1s photoemissions of $\mathrm{M(CO)_6}$ (M = Cr, Mo, or W)[4] supports a similarity in bonding. Plummer et al.[2] have described how, for $\mathrm{M(CO)_6}$ species, an increase in the strength of the M–CO bonding will influence both the satellite position relative to the primary peak and the I_s/I_p ratio. The latter becomes smaller the stronger the M–CO interaction. A similar model may be considered to be pertinent to the isoelectric M–CNR unit. For example, the difference in I_s/I_p in the N 1s spectra of $\mathrm{Cr(CNPh)_6}$ and $[\mathrm{Cr(CNPh)_6}]\mathrm{PF_6}$ (Table II) may reflect a stronger Cr–CNPh interaction for the chromium(I) complex. Since π back-bonding is most likely less in $[\mathrm{Cr(CNPh)_6}]\mathrm{PF_6}$ than in $\mathrm{Cr(CNPh)_6}$, this implies that the σ component increases in strength with increase in oxidation state and is thereby responsible for the stronger Cr–CNPh interaction.

The idea that satellites are due to M(d) → π^*(CNR) excitation is consistent with intensity differences between the C 1s, N 1s, and metal satellites. In order to have appreciable intensity, the satellites should be associated with the acceptor species in the shake-up process.[6] Therefore, for the isocyanide complexes the C 1s and N 1s satellites should possess the greater intensity since it is the C≡N moiety that is the acceptor species in the shake-up process. The extreme weakness of any metal satellites supports this assignment, paralleling the experimentally observed intensity differences that are seen in the gas-phase XPS of metal carbonyls.[4]

Intense charge-transfer bands have been observed in the region between 4 and 5 eV in the electronic absorption spectra of the chromium, molybdenum, and tungsten complexes listed in Table I.[14,16-18,21,39,40] In some instances, these have been assigned specifically to M(d) → π^*(CNR) electronic transitions[17,21,39,40] and it seems reasonable that such transitions will occur in this region for all the complexes under consideration. The formation of a positive hole upon photoionization lowers the orbital energy of most valence and virtual orbitals,[41,42] and as a consequence the energies of shake-up satellites are usually smaller than those anticipated on the basis of electronic absorption spectral data. The positions of the N 1s and C 1s satellites in the XPS of the isocyanide complexes conform to this expectation, the values of ΔE_{sat} being less than the M(d) → π^*(CNR) transition energies in the electronic absorption spectra.

For the three complexes of the type $\mathrm{M(CNPh)_6}$, where M = Cr, Mo, and W, there is a gradual increase from chromium

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to tungsten in the N 1s satellite separation (ΔE_{sat}), i.e., 3.4 eV for Cr, 3.6 eV for Mo, and 3.8 eV for W. This trend is consistent with the theoretical models,[2,43] which predict that, as the size of the metal ion increases, the separation between the main core level peaks and the satellite should increase. Such a trend is also consistent with the observation[4] that for $M(CO)_6$ (M = Cr, Mo, W) ΔE_{sat} for the O 1s satellite increases from 6.0 eV (Cr) to $\simeq$7.0 eV (Mo or W).

The increase in ΔE_{sat} for the N 1s satellite of $M(CNPh)_6$ as M changes from Cr to Mo to W is also seen in the series $[M(CNCMe_3)_7](PF_6)_2$ (M = Cr, Mo, and W), where the values are 3.2 eV (Cr) and 3.8 eV (Mo or W). Similar behavior is observed within the pairs of complexes $[M(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$ and $[M(CNCMe_3)_5(dppe)](PF_6)_2$, where M = Mo or W.

One additional trend observed in the ΔE_{sat} values for the N 1s spectra, is a decrease for $[Cr(CNR)_n]^{2+}$ as n increases from 6 to 7 ($3.5 \rightarrow 3.2$ eV as $n = 6 \rightarrow 7$ when R = CMe_3 and $3.4 \rightarrow 3.1$ eV as $n = 6 \rightarrow 7$ when R = C_6H_{11}). The electronic absorption spectra of these sets of complexes differ. Thus the absorptions which occur close to 4.0 eV in the six-coordinate complexes shift to 3.5 eV in the seven-coordinate complexes. The decrease in energy of 0.5 eV in the electronic absorption spectra upon change in coordination number from 6 to 7 is reflected by a decrease of 0.3 eV in the value of ΔE_{sat}. This lends further support to the assignment of these satellite peaks as being due to the same type of transition as that responsible for the electronic absorption bands that are located at $\simeq$0.5 eV higher energy.

Although trends in ΔE_{sat} for the N 1s satellite have been observed within several series of complexes (vide supra), there are no clear differences between different classes of compounds. For example, $M(CNPh)_6$ do not have appreciably different ΔE_{sat} values from those for the series of complexes $[M(CNR)_7](PF_6)_2$. The only conclusion that can be drawn at this time is that, in general, ΔE_{sat} is lower for chromium complexes than for molybdenum and tungsten.

The value of ΔE_{sat} in the N 1s spectrum of the rhenium(I) complex $[Re(CNCMe_3)_6]PF_6$ is greater than ΔE_{sat} for any of the isoelectronic group 6 isocyanide complexes (Table II and Figure 1). This may reflect a shift to higher energy of the appropriate Re(d) $\rightarrow \pi^*$(CNR) transition relative to the corresponding M(d) $\rightarrow \pi^*$(CNR) transitions, which characterize the group 6 complexes. As with all other isocyanide complexes, correlations of the N 1s and C 1s satellites with a particular absorption peak in the electronic absorption spectra must await MO calculations on these six and seven-coordinate species. However, in accord with our observation concerning the position of the N 1s satellite for $[Re(CNCMe_3)_6]PF_6$, we note that ΔE_{sat} for the O 1s and C 1s satellites of $Re_2(CO)_{10}$ are shifted[2] by $\sim$+0.5 eV relative to the corresponding features in the XPS of $M(CO)_6$ (M = Cr, Mo, or W).

Of the two rhodium(I) complexes that we studied, only the XPS of $[Rh(CNCMe_3)_4]PF_6$ exhibited any evidence of satellite structure. A poorly resolved, broad N 1s satellite was located at $\Delta E_{sat} \approx 5$ eV with $I_s/I_p \approx 0.09$. This feature was only detected when the spectra were recorded to very high statistics so it is not surprising that no such satellite was observed in the XPS of $[Rh(CNCMe_3)_3(PPh_3)_2]PF_6$, where the $CNCMe_3$ ligand constitutes a much smaller proportion of the molecular composition. This is a particularly significant result since in previous XPS studies on the isocyanide complexes $Ni(CNCMe_3)_4$, $[M(CNCH_3)_4](PF_6)_2$, and $[M_2(CNCH_3)_6](PF_6)_2$, where M = Pd or Pt,[35,36,44] the failure to observe N 1s and C 1s satellites may reflect the fact that the spectra were not recorded to sufficiently high statistics.

Once again a similarity to the carbonyl systems is seen in the case of $[Rh(CNCMe_3)_4]PF_6$. The value of ΔE_{sat} for the O 1s shake-up energy of $Rh_6(CO)_{16}$ is the largest for any of the mononuclear and polynuclear carbonyls measured,[2] and its relative intensity is the smallest of all of them. This is analogous to the situation we find for $[Rh(CNCMe_3)_4]PF_6$ relative to the other isocyanide complexes listed in Table II. Once again we see a close similarity between trends in the shake-up satellites associated with the M–CO and M–CNR moieties.

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Registry No. $Cr(CNPh)_6$, 17375-15-4; $[Cr(CNPh)_6]PF_6$, 57016-33-8; $[Cr(CNCMe_3)_6](PF_6)_2$, 75215-52-0; $[Cr(CNC_6H_{11})_6](PF_6)_2$, 75215-58-6; $[Cr(CNCMe_3)_7](PF_6)_2$, 75215-56-4; $[Cr(CNC_6H_{11})_7](PF_6)_2$, 75215-58-6; $Mo(CNPh)_6$, 14154-60-0; $[Mo(CNCH_3)_7](PF_6)_2$, 66632-84-6; $[Mo(CNCMe_3)_7](PF_6)_2$, 41982-05-2; $[Mo(CNC_6H_{11})_7](PF_6)_2$, 72155-82-9; $[Mo(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$, 74096-63-2; $[Mo(CNCH_3)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$, 74081-67-7; $[Mo(CNC_6H_{11})_5(PEtPh_2)_2](PF_6)_2$, 74096-57-4; $[Mo(CNCMe_3)_5(dppe)](PF_6)_2$, 74096-49-4; $[Mo(CNC_6H_{11})_5(dppm)](PF_6)_2$, 74096-45-0; $[Mo(CNC_6H_{11})_5(dppe)](PF_6)_2$, 74096-51-8; $W(CNPh)_6$, 14128-11-1; $[W(CNCH_3)_7](PF_6)_2$, 81643-42-7; $[W(CNCMe_3)_7](PF_6)_2$, 66687-57-8; $[W(CNC_6H_{11})_7](PF_6)_2$, 76705-37-8; $[W(CNCMe_3)_6I]I$, 66652-48-0; $[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$, 76721-74-9; $[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$, 76721-76-1; $[W(CNCMe_3)_5(dppe)](PF_6)_2$, 76721-72-7; $[Re(CNCMe_3)_6]PF_6$, 81625-51-6; $[Rh(CNCMe_3)_4]PF_6$, 42744-96-7; $[Rh(CNCMe_3)_3(PPh_3)_2]PF_6$, 51197-27-4.

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