

A Study of Bridging and Terminal Carbonyl Groups in Transition Metal Complexes by X-Ray Photoelectron Spectroscopy

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Abstract: The oxygen 1s x-ray photoelectron spectra of gaseous $\text{CH}_3\text{COMn}(\text{CO})_5$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, and $\text{Co}_4(\text{CO})_{12}$ can be readily resolved into separate peaks due to bridging and terminal carbonyl groups. From the spectra of $\text{CH}_3\text{COMn}(\text{CO})_5$ and $\text{Co}_4(\text{CO})_{12}$, we conclude that the O 1s binding energy of a bridging carbonyl group is lower than that of a terminal carbonyl group. This result is consistent with recent structural assignments of O 1s spectra of carbon monoxide adsorbed on metal surfaces. The C 1s spectrum of $\text{CH}_3\text{COMn}(\text{CO})_5$ can be resolved into three peaks; the two peaks due to the acetyl group are at lower binding energies than the peak due to the five terminal CO groups.

It is well known that there are two principal modes of coordination of the carbon monoxide ligand in transition metal carbonyls: terminal coordination, to a single metal atom, and bridging coordination, to two or more metal atoms. Aside from direct structure determination, as by x-ray and electron diffraction, the main, and perhaps only, physical methods which have been used to distinguish these modes of coordination are infrared and Raman spectroscopy¹ and carbon-13 NMR.² In this research we have shown that it is possible to distinguish and identify terminal and bridging carbonyl groups by means of x-ray photoelectron spectroscopy in the oxygen 1s region. Our results help clarify the interpretation of oxygen 1s XPS spectra of carbon monoxide adsorbed on metal surfaces.³⁻⁶

Previous attempts to study the x-ray photoelectron spectra of solid carbonyl complexes containing both bridging and terminal CO ligands have been unsuccessful because of extensive surface decomposition of the samples under intense x radiation. Therefore we restricted this work to the study of volatile molecular compounds in the gas phase.

Results and Discussion

Acetylpentacarbonylmanganese, $\text{CH}_3\text{COMn}(\text{CO})_5$, contains five terminal CO ligands and one keto group. Although the keto group in this molecule is not strictly a bridging CO ligand of the type in which we are principally interested, it may be considered structurally intermediate between a completely organic keto group (as in acetone) and a true metal-bridging CO ligand. The O 1s spectrum of acetylpentacarbonylmanganese is shown in Figure 1. The fact that we were able to resolve this spectrum clearly into a band due to the five terminal CO ligands ($E_B = 539.75$ eV) and a band due to the keto group ($E_B = 537.01$ eV) encouraged us to study molecules containing both terminal and true metal-bridging CO ligands. This result also suggested that we would find the O 1s binding energies of bridging carbonyls to be lower than those of terminal carbonyls.

The O 1s spectrum of the binuclear complex $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (containing two terminal CO ligands and two bridging CO ligands) is shown in Figure 2. The overall fwhm of the band is much greater than generally found for O 1s peaks and we feel justified in our deconvolution of the band into two peaks of reasonable fwhm (1.32 and 1.28 eV) and equal area, separated by 1.2 eV. We believe, on the basis of our data for $\text{CH}_3\text{COMn}(\text{CO})_5$ and $\text{Co}_4(\text{CO})_{12}$ (see below), that the peak of lower binding energy corresponds to the bridging CO ligands. Of course, there is no way of drawing this conclusion from the spectrum alone. Spectra of compounds of the type

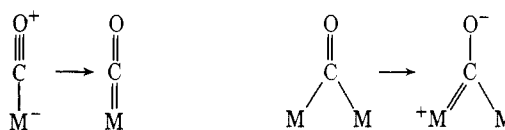
$\text{XMn}(\text{CO})_5$ indicate that the chemical shifts of the O 1s binding energies between cis and trans carbonyl groups are less than about 0.2 eV. We therefore believe that the extraordinary width of the O 1s line of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ is not due in any significant extent to the possible presence of cis and trans forms of the complex.

We attempted to obtain an O 1s spectrum of $\text{Co}_2(\text{CO})_8$, which contains, at least in the solid state, unequal numbers of terminal and bridging CO ligands. However, the sample underwent essentially complete decomposition to cobalt metal and carbon monoxide in the x-ray flux and no useful data could be obtained. However a successful spectrum was obtained for $\text{Co}_4(\text{CO})_{12}$, which contains nine terminal CO ligands and three bridging CO ligands.⁷ The spectrum, shown in Figure 3, has a peak at high binding energy corresponding to free carbon monoxide formed by some thermal and x-ray decomposition of the sample. The band at lower binding energy, attributed to $\text{Co}_4(\text{CO})_{12}$, has been resolved into two peaks with relative areas of 3:1 and separated by 1.25 eV. The lower binding energy corresponds to the bridging carbonyls.

The fact that a lower O 1s binding energy was found for bridging carbonyls than for terminal carbonyls is what one might expect assuming greater back-bonding in the bridging carbonyls. It is also the expectation from simple valence bond formulas in which the terminal carbonyl is represented with no back-bonding and the bridging carbonyl is represented by a simple keto structure. The oxygen atom with the lower formal



charge would be expected to have the lower 1s binding energy. Of course considerable relaxation is undoubtedly associated with both of these O 1s ionizations. The possibility of d π electron transfer from the metal during the ionization is present in both cases.



In recent years Yates et al.³ and Atkinson et al.⁴ have identified several forms of carbon monoxide adsorbed on tungsten and molybdenum surfaces by means of oxygen 1s photoelectron spectra. A peak at relatively low binding energy, formed principally at low temperatures and low surface cov-

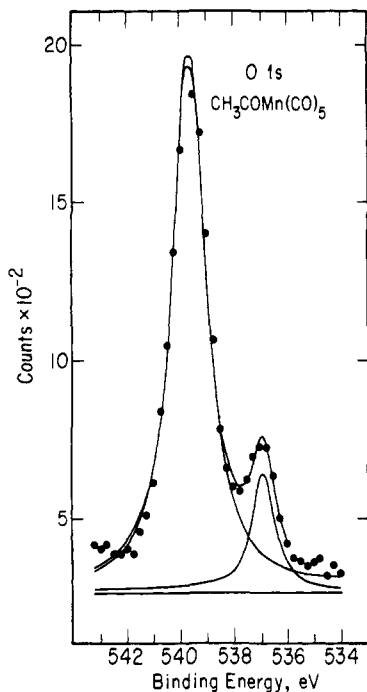


Figure 1. The oxygen 1s spectrum of $\text{CH}_3\text{COMn}(\text{CO})_5$.

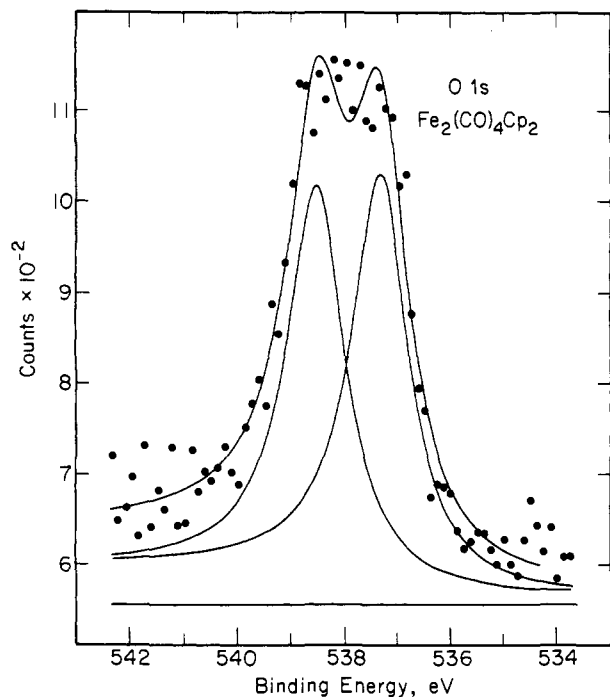


Figure 2. The oxygen 1s spectrum of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$.

erage, has been identified with the "virgin" state of CO. This state is believed to consist of CO coordinated through the carbon atom to two or more metal atoms and, as such, is analogous to bridging carbonyl groups in molecular metal carbonyls. A band at relatively high binding energy, corresponding to weakly-bound CO, which can still be desorbed from the surface, is identified with "α" CO in the case of tungsten and "γ" CO in the case of molybdenum. These states presumably consist of CO coordinated through the carbon

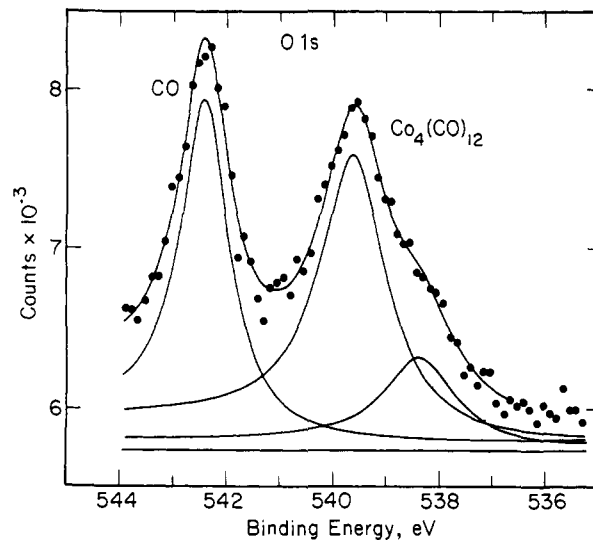


Figure 3. The oxygen 1s spectrum of $\text{Co}_4(\text{CO})_{12}$.

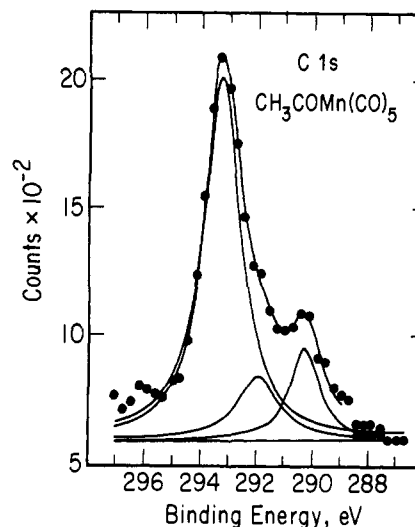


Figure 4. The carbon 1s spectrum of $\text{CH}_3\text{COMn}(\text{CO})_5$.

atom to only one metal atom and are thus analogous to the carbon monoxide in a terminal carbonyl group. The breadth of the α and γ bands suggests different degrees of back-bonding due to differences in the sites of the attached metal atoms. These structural interpretations of the virgin, α, and γ states of adsorbed CO are in qualitative agreement with our results; that is, we agree that the O 1s binding energy of a multiply coordinated CO molecule is lower than that of a singly coordinated CO molecule. In this respect our results confirm the assignments of the XPS spectra of adsorbed CO.

The C 1s spectrum of acetylpentacarbonylmanganese is shown in Figure 4. The spectrum is readily resolved into three peaks having appropriate relative intensities corresponding to the five CO ligands, the keto group, and the methyl group. According to the resolved spectrum, the binding energy of the keto carbon atom is less than that of the carbon atoms of the five carbonyl groups. This result strongly suggests that the positive charge of the keto carbon atom is less than that of any of the CO ligand carbon atoms. This result is contrary to recent calculations of Block et al.⁸

Table I. Measured Core Binding Energies

Compd	O 1s		C 1s	
	E_B , eV ^a	Fwhm	E_B , eV ^a	Fwhm
CH ₃ COMn(CO) ₅				
CO ligands	539.75 (6)	1.48 ^b	293.36 (7)	1.50 ^c
Keto group	537.01 (9)	1.01 ^b	292.0 (3)	1.82 ^c
CH ₃ group			290.36 (12)	1.26 ^c
[π -C ₅ H ₅ Fe(CO) ₂] ₂				
Terminal CO's	538.55 (7)	1.32 ^d		
Bridging CO's	537.36 (7)	1.28 ^d		
C ₅ H ₅			290.29 (6)	
Co ₄ (CO) ₁₂				
Terminal CO's	539.62 (8)	1.48 ^e		
Bridging CO's	538.37 (14)	1.56 ^e		
Free CO	542.40 (5) ^f	1.10		

^a Probable uncertainty in the last digit indicated parenthetically.

^b The relative areas of the two resolved O 1s peaks were 6.6:1. ^c The areas of the two smaller C 1s peaks were constrained to be equal; the relative areas of the three resolved peaks were 4.78:1:1. ^d The peak areas were constrained to be equal. ^e The relative areas of the two resolved peaks were constrained to be 3:1. The binding energies changed by less than 0.14 eV when no constraint was imposed. ^f E_B value determined in separate experiment by W. B. Perry.

Experimental Section

Tetracobalt dodecacarbonyl was prepared from dicobalt octacarbonyl by the method of Chini et al.⁹ The synthesis and subsequent purification were carried out under a nitrogen atmosphere. The product was sublimed at 40–50 °C under high vacuum with continuous pumping. During the sublimation a small amount of decomposition (~10%) to metallic cobalt was observed. The infrared spectrum of the sublimed Co₄(CO)₁₂ agreed with the literature.

Cyclopentadienyliron dicarbonyl dimer was prepared from Fe(CO)₅ and dicyclopentadiene by the method of King.¹⁰ The product was sublimed at 70 °C under high vacuum without decomposition. The sublimed [π -C₅H₅Fe(CO)₂]₂ melted with decomposition at 194.5–196 °C (lit.¹⁰ 194 °C).

Acetylpentacarbonylmanganese was prepared by a modification of the method of Closson et al.¹¹ All steps in the reaction were carried out under a dry nitrogen atmosphere. The needle-like crystals of CH₃COMn(CO)₅ melted at 54–55 °C (lit.¹¹ 54–55 °C).

Gas-phase x-ray photoelectron spectra were obtained using the Berkeley iron-free double-focusing magnetic spectrometer.¹² Two

different gas cells were used to contain sample vapors. The CH₃COMn(CO)₅ was irradiated using a slit-plug device described by Banna.¹³ The sample was held at room temperature outside the spectrometer and sample vapors were introduced into the irradiation chamber through a glass and stainless-steel manifold. The Co₄(CO)₁₂ and [π -C₅H₅Fe(CO)₂]₂ were held in a heated gas chamber¹³ in the spectrometer. The gas cell was heated to a temperature which produced enough sample vapor pressure to yield a satisfactory spectrum.

Magnesium K α x rays (1253.6 eV) were used. Either argon or neon gas was introduced into the sample chamber along with the samples so that the peaks could be referenced to the Ar 2p_{3/2} line (E_B = 248.45 eV) or the Ne 1s line (E_B = 870.23 eV). The only exception was the O 1s spectrum of Co₄(CO)₁₂, which was referenced using the O 1s line of carbon monoxide (E_B = 542.40 eV). The binding energies were determined by a least-squares fitting of the data to Lorentzian line shapes and are summarized in Table I. The C 1s spectrum of [π -C₅H₅Fe(CO)₂]₂ consisted of a main peak at 290.29 eV (undoubtedly due to the C₅H₅ group) and a shoulder on the high binding energy side (due to the CO groups), but it was not possible to resolve the band satisfactorily into three peaks. No C 1s spectrum was obtained for Co₄(CO)₁₂.

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE73-05133 A02) and the Energy Research and Development Administration. We are grateful to Mr. Michael McKelvy for preparing the [π -C₅H₅Fe(CO)₂]₂.

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