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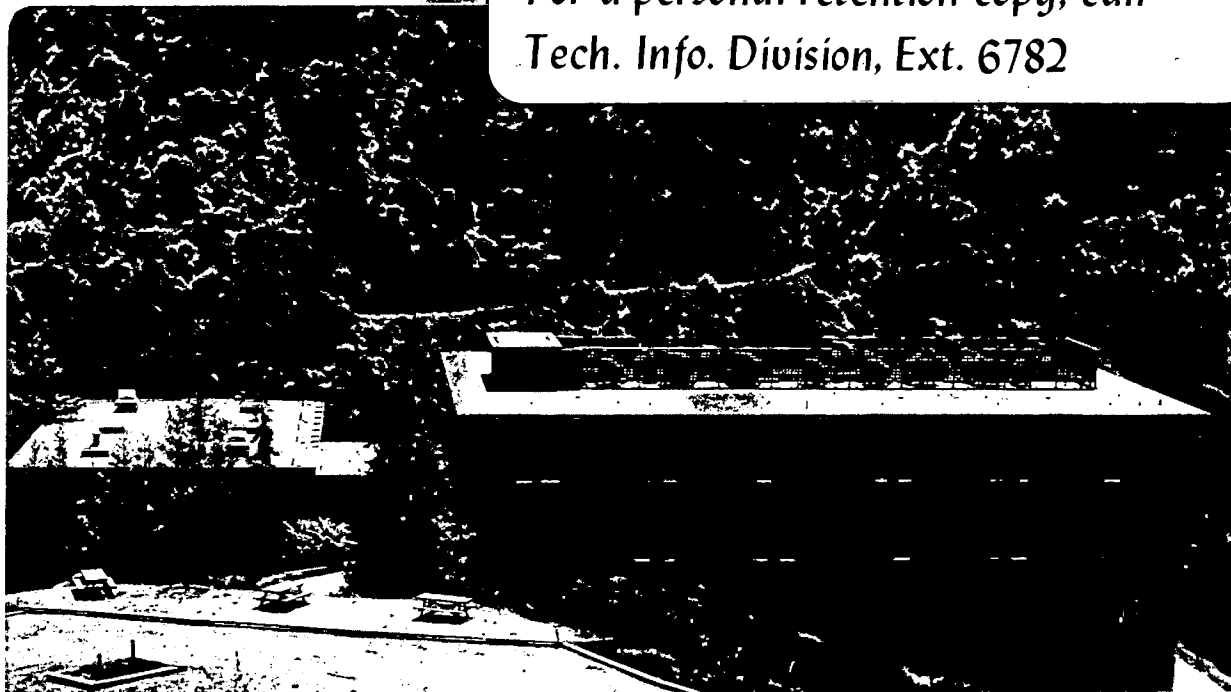
Si Fen Xiang, Albert A. Bakke, Hsiang-Wen Chen,
James L. Hoskins, Ting Ho Lee, Dietmar Seyferth,
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An XPS Study of the Bonding in
Alkylidynetricobalt Nonacarbonyl Complexes and
Related Compounds

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ABSTRACT

The core electron binding energy of the methyldyne carbon atom in $RC[Co(CO)_3]_3$ compounds is a function of the electronegativity of the R group; the trend of binding energy with R group is similar to that for the methyl carbon atom in the corresponding RCH_3 compounds. The core binding energies of the $[Co(CO)_3]_3$ cluster generally change similarly, but to a smaller extent, with changing R group. However, for $R = OCH_3$ and $R = N(CH_3)_2$, the core binding energies of the $[Co(CO)_3]_3$ cluster are significantly lower than expected. These data, and a combination of UPS and XPS data for the chloro and bromo compounds, indicate that groups such as OCH_3 , $N(CH_3)_2$, Cl, and Br act as π -donors toward the $C[Co(CO)_3]_3$ system. Binding energy data indicate that the bonding in $HC[Co(CO)_3]_3$ is very similar to that in $(HC)_2[Co(CO)_3]_2$. However the significantly lower binding energies of $[Co(CO)_3]_4$ reflect the fact that three of the carbonyl groups are bridging in this compound.

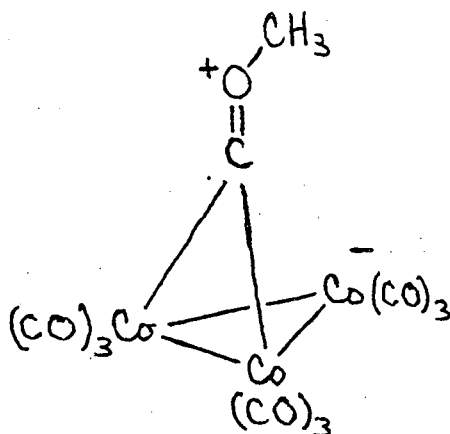
The nature of the bonding in the alkylidyne tricobalt nonacarbonyl complexes, $\text{RC}[\text{Co}(\text{CO})_3]_3$, is a topic which has intrigued chemists ever since the first characterization of these compounds.² According to polyhedral cluster theory,³ the $\text{Co}(\text{CO})_3$ group is analogous to the CH group; therefore the parent complex, $\text{HC}[\text{Co}(\text{CO})_3]_3$, can be looked upon as an analog of tetrahedrane. The complexes may also be considered as analogs of CR groups chemisorbed on a metal surface. Clearly the nature of the interaction of the CR groups with the $\text{Co}_3(\text{CO})_9$ cluster is of interest. In this study we have used gas phase x-ray photoelectron spectroscopy (XPS) to probe the valence electron density on the various atoms in this family of complexes and, for comparison, in compounds which are structurally and electronically related. For each compound we have obtained spectra in the Co $2p_{3/2}$, O 1s, and C 1s regions. Each C 1s spectrum shows a strong peak near 293 eV due to the CO groups and a band near 290 eV due to the CR groups. As an example, the C 1s spectrum of the parent compound, $\text{HC}[\text{Co}(\text{CO})_3]_3$, is shown in Figure 1.

The $\text{RC}[\text{Co}(\text{CO})_3]_3$ Compounds

The binding energy data for the $\text{RC}[\text{Co}(\text{CO})_3]_3$ compounds are presented in Table I. The binding energy of the methylidyne carbon atom appears to be a straightforward function of the electronegativity of the attached R group. Indeed the trend in binding energies of the methylidyne carbon atom is very similar to that of the methyl carbon atom in the corresponding RCH_3 compounds.⁴ To emphasize this correlation

and the normalcy of the methylidyne binding energies, we have plotted these binding energies against one another in Figure 2.

The binding energies of the cobalt atoms and the carbon and oxygen atoms of the carbonyl groups are relatively insensitive to changes in the R group. However, slight effects can be seen as the electronegativity of R is changed. Thus, in each set the binding energy is low when R is the relatively electropositive SiEt_3 group and is high when R is the relatively electronegative chloro group. The remarkable feature of the data is that the cobalt and carbonyl binding energies of the methoxy and dimethylamido compounds are much lower than one might expect on the basis of the high electronegativities of these groups. The effect is most obvious in the carbonyl oxygen binding energies. In Figure 3 we have plotted the carbonyl oxygen binding energy vs the methyl carbon binding energy in the corresponding RCH_3 compound. It appears that the methoxy and dimethylamido groups withdraw electrons from the $\text{Co}_3(\text{CO})_9$ cluster less effectively than would be expected on the basis of their electronegativities. These groups also happen to be those which have readily available nonbonding π electron density and which are known to be good π -donor groups. Therefore we believe that the data indicate π -donor interaction of the methoxy and dimethylamido groups with the $\text{CCo}_3(\text{CO})_9$ cluster, of the type implied by the following valence-bond resonance structure.



This type of delocalized π bonding between the R group and the $\text{CCo}_3(\text{CO})_9$ cluster has been suggested in previous studies. Thus Miller and Brill⁵ have observed that ^{59}Co nqr coupling constants correlate with the Taft σ_{R} parameters for the R group but show no correlation with the corresponding Taft σ_{I} parameters. Chesky and Hall⁶ have found that both UPS spectra and MO calculations are consistent with a π bonding system in the cluster that can act either as a donor or an acceptor. They propose that the methylidyne carbon forms a bond to the metal triangle with an sp hybrid orbital and that the two remaining p orbitals form multi-centered π bonds to the Co_3 system.

Analogous Compounds

Because of the formal electronic analogy of the CH group and the $\text{Co}(\text{CO})_3$ group, we have studied other tetrahedral cluster compounds containing these groups, i.e. $[\text{Co}(\text{CO})_3]_4$, $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$, and

derivatives of these compounds. The binding energy data are given in Table II. First let us compare the three acetylene complexes, or C_2Co_4 cluster compounds. Substitution with the relatively electron-donating Me_3Si and Me_3C groups, as expected, causes all the binding energies to decrease significantly. The differences between the compound with two Me_3Si groups and that with one Me_3Si and one Me_3C group are only about twice the uncertainties in the data, and we have no explanation for these small differences.

On going from $HC[Co(CO)_3]_3$ to $(HC)_2[Co(CO)_3]_2$, the cobalt, oxygen and carbonyl carbon binding energies do not change significantly. We conclude that, in these two compounds, the electron densities on these atoms are very similar and that the nature of the bonding between and within the $Co(CO)_3$ groups is essentially constant. The fact that the CH and $Co(CO)_3$ groups seem to be interchangeable with little effect on electron density distribution is undoubtedly fortuitous, but the result does give credence to the approach to transition metal cluster bonding which emphasizes the orbital properties of the cluster vertex atoms. In this approach, a vertex like CH is recognized as equivalent to (isolobal with) a $Co(CO)_3$ vertex.⁷⁻⁸ An alternative and more complicated approach is to consider, for example, the Co_3 cluster and to identify the orbitals which are accessible for holding together the cluster and for bonding to peripheral ligands.⁹⁻¹⁰

There is a marked decrease in the C 1s binding energy of the CH carbon atom on going from $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$ to $\text{HC}[\text{Co}(\text{CO})_3]_3$. In view of the essential constancy of the other binding energies, we believe this decrease is due mainly to an increase in relaxation energy. Presumably the $\text{Co}(\text{CO})_3$ group is considerably more polarizable than the CH group, and therefore one would expect greater relaxation energy for a CH group bonded to three $\text{Co}(\text{CO})_3$ groups than for one bonded to two $\text{Co}(\text{CO})_3$ groups and a CH group. One might expect the same sort of effect on the cobalt relaxation energies, but in the case of cobalt, most of the relaxation probably corresponds to a reduction in the degree of back-bonding to the CO groups, and therefore cobalt-cobalt interactions are less important.

On going from $\text{HC}[\text{Co}(\text{CO})_3]_3$ or $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$ to $[\text{Co}(\text{CO})_3]_4$, the cobalt binding energy decreases markedly and the carbonyl binding energies decrease slightly but significantly. At first, these changes seem inconsistent with the lack of change between $\text{HC}[\text{Co}(\text{CO})_3]_3$ and $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$. However, it must be remembered that the basic structure of $[\text{Co}(\text{CO})_3]_4$ differs from that of the CCo_3 and C_2Co_2 cluster compounds in Table II. In $[\text{Co}(\text{CO})_3]_4$ three of the carbonyl groups are bridging between pairs of cobalt atoms on the edges of one face of the Co_4 tetrahedron. Bridging CO groups are known to have lower binding energies than terminal CO groups,¹¹ and thus the weighted average binding energy of the CO groups in $[\text{Co}(\text{CO})_3]_4$ is

lower than one would expect if all the groups were terminal. We believe that the cobalt binding energy of $[\text{Co}(\text{CO})_3]_4$ is lower than in the unbridged CCo_3 and C_2Co_2 compounds because the average number of coordinated CO groups is 3.75 rather than 3, and consequently the relaxation energy is greater. It has been previously noted that the electron-flow contribution to relaxation energy increases with an increase in the number of bonds, or avenues for electron flow.^{12,13}

It is interesting that the cobalt, oxygen and carbon binding energies of $(\text{CO})_3\text{FeCo}_3(\text{CO})_9\text{H}$ (which is isoelectronic and isostructural with $[\text{Co}(\text{CO})_3]_4$) are similar to those of $[\text{Co}(\text{CO})_3]_4$.

Information from Valence-Shell Ionization Potentials

Evidence for increased back-bonding in $\text{Co}_4(\text{CO})_{12}$ due to the bridging carbonyl groups can be obtained from a combination of UPS and XPS spectral data. The low-energy bands due to the "nonbonding" cobalt 3d orbitals observed in the UPS spectra of $\text{HC}[\text{Co}(\text{CO})_3]_3$, $\text{CH}_3\text{C}[\text{Co}(\text{CO})_3]_3$, $\text{ClC}[\text{Co}(\text{CO})_3]_3$, $\text{BrC}[\text{Co}(\text{CO})_3]_3$, $\text{CH}_3\text{OC}[\text{Co}(\text{CO})_3]_3$ and $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$ appear at 8.8, 8.7, 8.8, 8.9, 8.6, and 8.7 eV, respectively.^{6,14-16} These values are very similar to the corresponding value for $\text{Co}_4(\text{CO})_{12}$, viz. 8.9 eV.¹⁶⁻¹⁷ However, in order to use these data to judge the relative bonding characters of the 3d orbitals, the ionization potentials for the $\text{RC}[\text{Co}(\text{CO})_3]_3$ compounds should be corrected for the changes in relaxation energy and atomic charge on going from

$\text{Co}_4(\text{CO})_{12}$ to $\text{RC}[\text{Co}(\text{CO})_3]_3$. This can be approximately accomplished¹⁸ by subtracting from each ionization potential eight-tenths of the difference in the cobalt $2p_{3/2}$ binding energy, $0.8[E_B(\text{RCCo}_3(\text{CO})_9) - E_B(\text{Co}_4(\text{CO})_{12})]$. Thus we calculate that, if the cobalt 3d orbital MOs of the $\text{RC}[\text{Co}(\text{CO})_3]_3$ compounds and $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$ had the same degree of bonding character as in $\text{Co}_4(\text{CO})_{12}$, the ionization potentials would be 8.3, 8.3, 8.3, 8.4, 8.3 and 8.3 eV, respectively. Clearly the cobalt 3d orbitals of the $\text{RC}[\text{Co}(\text{CO})_3]_3$ compounds and $(\text{HC})_2[\text{Co}(\text{CO})_3]_2$ are very similar in character and have about 0.6 eV less bonding character than the corresponding orbitals in $\text{Co}_4(\text{CO})_{12}$.

Similar calculations can be made for the valence $p\pi$ orbitals of the halogen atoms in $\text{ClC}[\text{Co}(\text{CO})_3]_3$ and $\text{BrC}[\text{Co}(\text{CO})_3]_3$, using the ionization potentials obtained from UPS spectra. We may reasonably assume that the lowest ionization potentials of HCl and HBr (12.8 and 11.8 eV, respectively^{16,19}) correspond to strictly nonbonding halogen $p\pi$ orbitals. From the differences in the halogen core binding energies⁴ between $\text{XC}[\text{Co}(\text{CO})_3]_3$ and HX , we calculate the following values for hypothetical nonbonding $p\pi$ orbitals in the $\text{XC}[\text{Co}(\text{CO})_3]_3$ compounds:

For $\text{ClC}[\text{Co}(\text{CO})_3]_3$:

$$12.8 + 0.8(205.69 - 207.39) = 11.4 \text{ eV}$$

For $\text{BrC}[\text{Co}(\text{CO})_3]_3$:

$$11.8 + 0.8(75.64 - 77.36) = 10.4 \text{ eV}$$

The observed ionization potentials for $\text{ClC}[\text{Co}(\text{CO})_3]_3$ and $\text{BrC}[\text{Co}(\text{CO})_3]_3$, 12.3 and 11.6 eV, respectively,^{6,14,16} are higher than the estimated nonbonding ionization potentials and thus are consistent with π -bonding between the halogen atoms and the $\text{CCo}_3(\text{CO})_9$ clusters. This result is not inconsistent with the points for $\text{ClC}[\text{Co}(\text{CO})_3]_3$ and $\text{BrC}[\text{Co}(\text{CO})_3]_3$ in Figure 3. Probably the straight line, corresponding to R groups with little or no π -donor character, should pass through the point for R = H with a greater slope than shown, thus indicating significant π -donor effects for R = Cl and R = Br. Unfortunately the appropriate valence and core ionization potentials for the CH_3O oxygen atom of $\text{CH}_3\text{OC}[\text{Co}(\text{CO})_3]_3$ and the nitrogen atom of $\text{Me}_2\text{NC}[\text{Co}(\text{CO})_3]_3$ have not been measured. Calculations using these data would allow us to test our conclusion, based on core binding energies alone, that these systems have even stronger π interactions between the R groups and the $\text{CCo}_3(\text{CO})_9$ clusters.

Experimental Section

The spectra were obtained in the gas phase using procedures described previously.²⁰ To obtain more accurate calibration, N_2 gas was run simultaneously with the compounds. A computer program corrected the peak centers for drift after every few scans. We also made some improvements in the fitting program²¹ to allow for vibrational broadening and the x-ray doublet. For instance, the $\text{MgK}\alpha_2$ line was assigned half the intensity of and an energy 0.33 eV higher than the $\text{K}\alpha_1$ line.²²

The new version of the fitting program expresses each peak in a spectrum as a sum of several lines. However all our reported binding energies are "vertical" ionization potentials, corresponding to the weighted averages of the constituent peak centers. The cluster compounds $\text{HC}[\text{Co}(\text{CO})_3]_3$ and $(\text{HC})_2[\text{Co}(\text{CO})_3]_3$, and most of the related substituted derivatives, are volatile enough that we were able to obtain their spectra at room temperature. However, it was necessary to maintain $\text{Et}_3\text{SiC}[\text{Co}(\text{CO})_3]_3$ and $[\text{Co}(\text{CO})_3]_4$ at 40°C , and $\text{H}[\text{Fe}(\text{CO})_3]-[\text{Co}(\text{CO})_3]_3$ at 50°C in order to obtain satisfactory spectra. All the binding energies are based on spectrometer calibrations with the free nitrogen N 1s, Ne 1s and Ne 2s lines, except the O 1s and C 1s spectra of $(\text{CH}_3)_2\text{NC}[\text{Co}(\text{CO})_3]_3$ where it was possible to measure the binding energies relative to the decomposition product, carbon monoxide. Some of the core binding energies have been published previously.²³

Several binding energies, not given in Tables I and II, were measured.

These and the corresponding line widths are listed here. $\text{ClC}[\text{Co}(\text{CO})_3]_3$:

Cl $2p_{3/2}$ 205.69(6), 1.53(12); Cl $2p_{1/2}$ 207.29(10), 1.46(19). $\text{BrC}[\text{Co}(\text{CO})_3]_3$:

Br $3d_{5/2}$ 75.64(10), 1.80(30). $\text{Et}_3\text{SiC}[\text{Co}(\text{CO})_3]_3$: Si $2p_{3/2}$ 105.73(10),

1.22(28). $(\text{Me}_3\text{CC})(\text{Me}_3\text{SiC})[\text{Co}(\text{CO})_3]_2$: Si $2p_{3/2}$ 106.2(2), 2.1(9).

$(\text{Me}_3\text{SiC})_2[\text{Co}(\text{CO})_3]_2$: Si $2p_{3/2}$ 106.22(10), 1.49(26).

The compounds $\text{HC}[\text{Co}(\text{CO})_3]_3$,²⁴ $\text{ClC}[\text{Co}(\text{CO})_3]_3$ ²⁵ and $\text{BrC}[\text{Co}(\text{CO})_3]_3$ ²⁶ were prepared according to published procedures, described previously.²³

A sample of $\text{CH}_3\text{C}[\text{Co}(\text{CO})_3]_3$ was kindly provided by L. Stuhl. The

$(\text{HC})_2[\text{Co}(\text{CO})_3]_2$ was prepared by the method of Greenfield et al.²⁷ The product melted at 12.5–13°C (lit. mp 13°C) and was shown to be pure by its ^1H and ^{13}C NMR spectra, using C_6D_6 solvent. The $[\text{Co}(\text{CO})_3]_4$ was prepared by the method of Chini et al.²⁸ and sublimed twice. The infrared spectrum agreed with the literature.²⁸ The compounds $\text{Et}_3\text{SiC}[\text{Co}(\text{CO})_3]_3$,²⁹ $(\text{CH}_3)_2\text{NC}[\text{Co}(\text{CO})_3]_3$,³⁰ $\text{CH}_3\text{OC}[\text{Co}(\text{CO})_3]_3$,³⁰ $(\text{Me}_3\text{SiC}_2\text{SiMe}_3)[\text{Co}(\text{CO})_3]_2$,³¹ and $(\text{Me}_3\text{CC}_2\text{SiMe}_3)[\text{Co}(\text{CO})_3]_2$ ³² were prepared and characterized by the referenced procedures. The $\text{HFeCo}_3(\text{CO})_{12}$ was kindly supplied by Dr. M. Tachikawa. This compound was sublimed immediately before use; its infrared spectrum agreed with the literature.³³

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Table I. Core Binding Energies and Line Widths of Alkylidynetricobalt Nonacarbonyl Clusters, $\text{RC}[\text{Co}(\text{CO})_3]_3$ (eV)^a

R in $\text{RC}[\text{Co}(\text{CO})_3]_3$	Co 2p _{3/2}		O 1s		C 1s					
	E _B	FWHM	E _B	FWHM	E _B (RC*)	FWHM	E _B (R)	FWHM	E _B (CO)	FWHM
Et ₃ Si	786.18(5)	1.42(16)	539.48(4)	1.60(11)	--	--	289.95(7) ^b	1.74(24)	293.09(6) ^b	1.27(21)
H	786.38(5)	1.30(11)	539.63(5)	1.58(10)	289.50(8)	1.38(20)			293.32(3)	1.48(6)
CH ₃	786.26(4)	1.34(10)	539.56(4)	1.56(11)	289.79(12) ^c	0.96(24)	290.74(12) ^c	0.96(24)	293.32(4) ^c	1.46(9)
Br	786.33(4)	1.36(8)	539.66(5)	1.50(10)	290.5(2)	1.3(6)			293.28(4)	1.34(11)
Cl	786.38(4)	1.38(9)	539.67(6)	1.56(15)	290.87(10)	1.20(21)			293.34(5)	1.52(10)
(CH ₃) ₂ N	786.21(8)	1.32(26)	539.28(10)	1.99(49)	--	--	--	--	293.23(14) ^d	1.97(45)
CH ₃ O	786.11(4)	1.41(11)	539.47(4) ^e	1.67(10)	291.0(2) ^c	1.25	292.0(2) ^c	1.25	293.08(4) ^c	1.57(7)

^a The uncertainty in the last digit (usually estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. ^b Deconvoluted assuming E_B = 289.2 eV for the methylidyne carbon and an intensity ratio of 6:1. For the unresolved peak, E_B = 289.87 eV. ^c Deconvoluted assuming an intensity ratio of 9:1:1 for the three kinds of carbon atoms. ^d Deconvoluted assuming an average value of E_B = 291.3 eV for the (CH₃)₂NC group and an intensity ratio of 3:1. For the unresolved peak, E_B = 293.12 eV. ^e Deconvoluted assuming E_B = 538.7 eV for the CH₃O oxygen and an intensity ratio of 9:1. For the unresolved peak, E_B = 539.41 eV.

Table II. Core Binding Energies of $[\text{Co}(\text{CO})_3]_4$ and Some of its Structural Analogs (eV)^a

Compound	Co 2p _{3/2}	O 1s	C 1s		
			CO	CH or $\overset{*}{\text{C}}\text{R}$	$\overset{*}{\text{C}}\text{H}_3$
$[\text{Co}(\text{CO})_3]_4$	785.75(3)	539.43 ^b	293.22(7)		
$\text{HC}[\text{Co}(\text{CO})_3]_3$	786.38(5)	539.63(5)	293.32(3)	289.50(8)	
$(\text{HC})_2[\text{Co}(\text{CO})_3]_2$	786.23(4)	539.69(4)	293.24(3)	290.08(6)	
$(\text{Me}_3\text{SiC})_2[\text{Co}(\text{CO})_3]_2$	785.97(4)	539.37(5)	292.99(8)		289.80(5) ^c
$(\text{Me}_3\text{CC})(\text{Me}_3\text{SiC})[\text{Co}(\text{CO})_3]_2$	785.92(4)	539.23(6)	292.74(9)	289.3(2) ^d	290.3(2) ^d
$(\text{CO})_3\text{FeCo}_3(\text{CO})_9\text{H}$	785.86(7)	539.19 ^b	293.36(7)		

^a The uncertainty in the last digit (generally estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. ^b Weighted average for the bridging and terminal carbonyl groups. The individual peaks were deconvoluted as follows. For $\text{Co}_4(\text{CO})_{12}$, $E_B(\text{br}) = 538.48(17)$, $E_B(\text{t}) = 539.75(7)$. For $\text{FeCo}_3(\text{CO})_{12}\text{H}$, $E_B(\text{br}) = 538.08(14)$, $E_B(\text{t}) = 539.56(7)$. ^c Single peak observed for six CH_3 and two cluster carbons. ^d "Organic" C band deconvoluted into two peaks with 2:1 intensity ratio. Stronger peak corresponds to average CH_3 group, weaker to average of central t-butyl and two cluster carbons.

Figure Captions

- Figure 1. Carbon 1s spectrum of $\text{HC}[\text{Co}(\text{CO})_3]_3$ vapor.
- Figure 2. Plot of carbon 1s binding energy for the methylidyne carbon atom of $\text{RC}[\text{Co}(\text{CO})_3]_3$ vs the carbon 1s binding energy of the methyl group of RCH_3 .
- Figure 3. Plot of oxygen 1s binding energy for the carbonyl groups of $\text{RC}[\text{Co}(\text{CO})_3]_3$ vs the carbon 1s binding energy of the methyl group of RCH_3 .

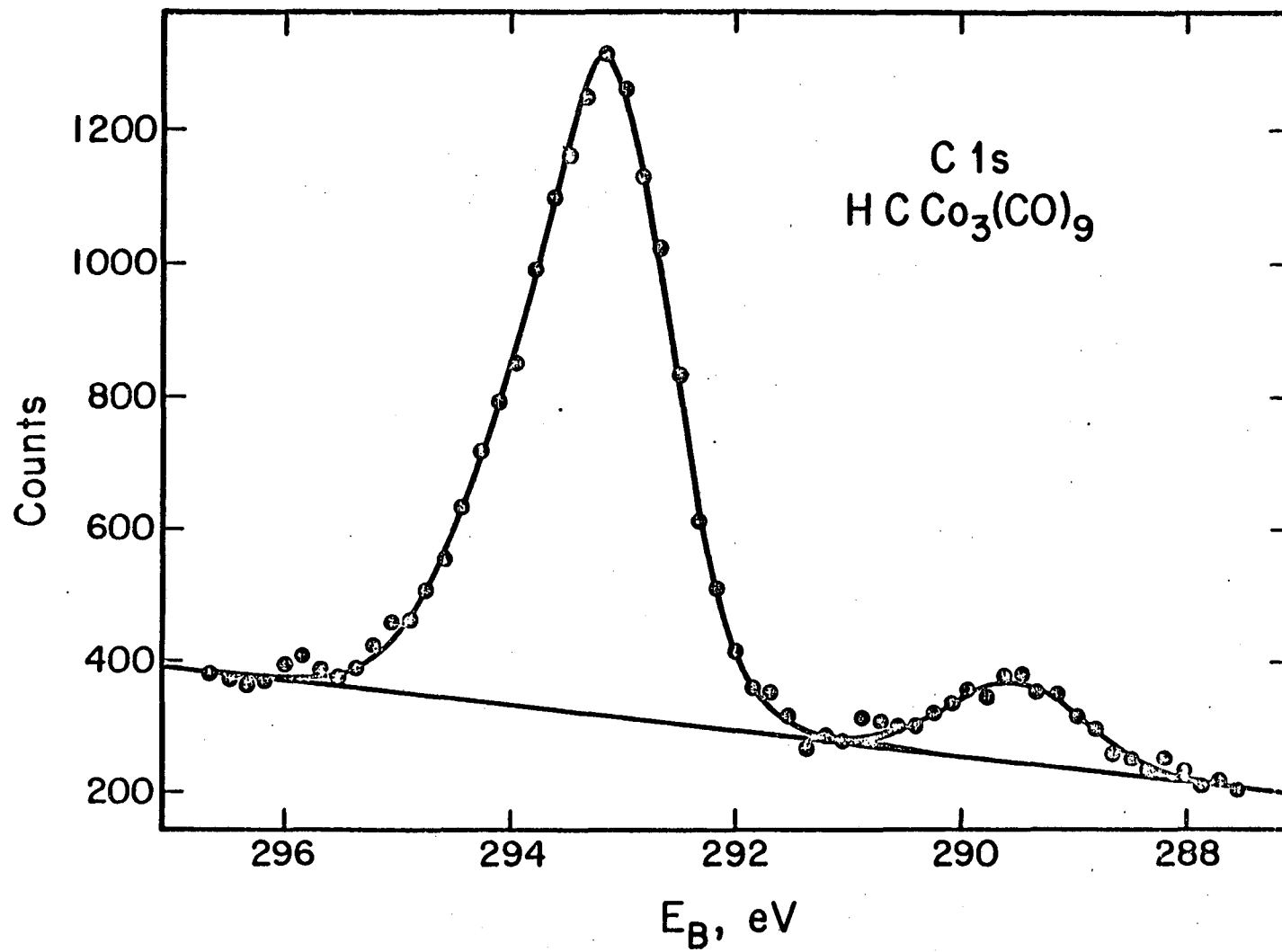


Figure 1

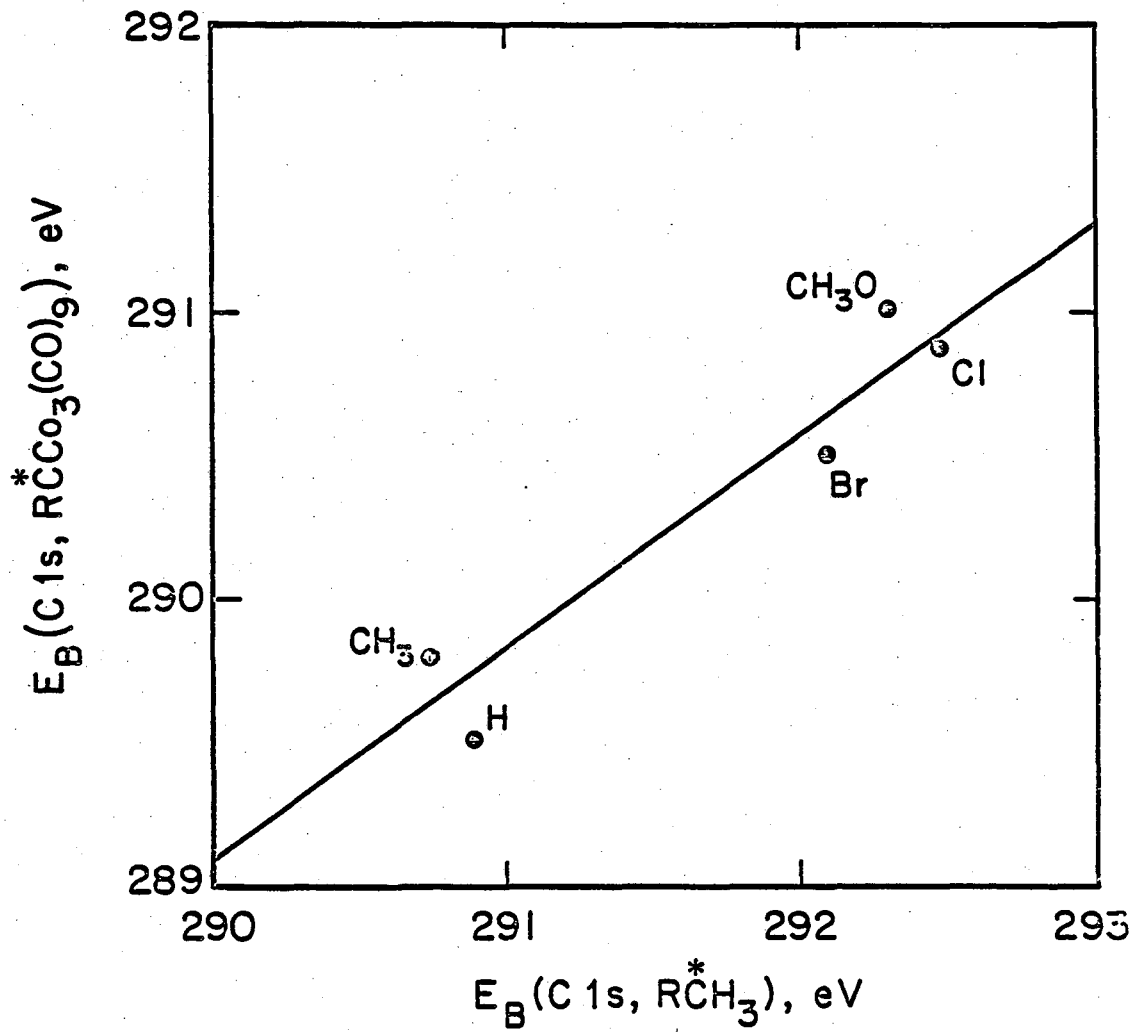


Figure 2

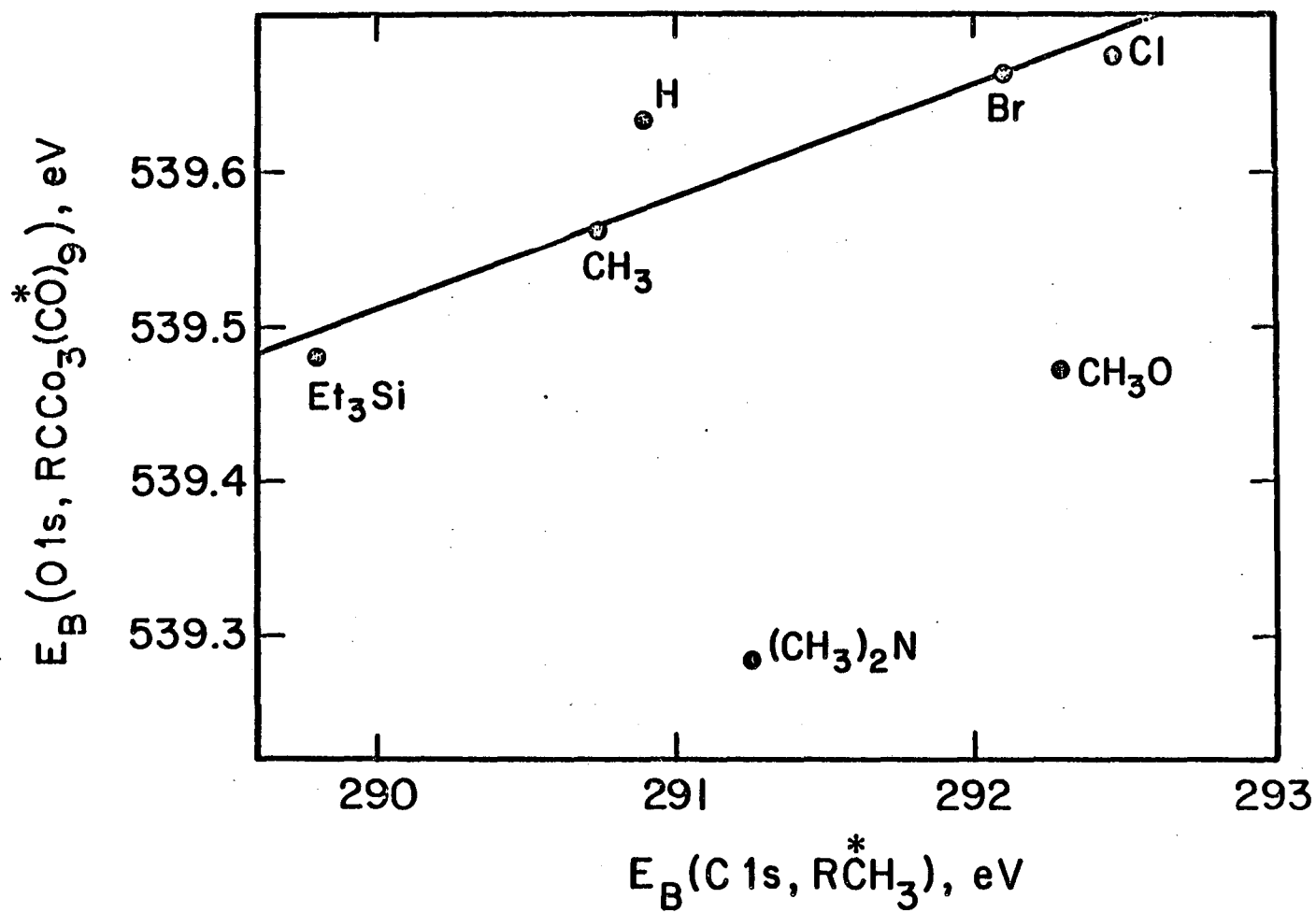


Figure 3

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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