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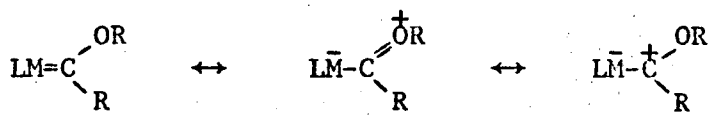
Determination of the Electron Distribution in a Transition Metal Carbene Complex by X-Ray Photoelectron Spectroscopy

Sir:

Much interest centers on the structure and bonding of transition metal carbene complexes.[1,2] For a carbene complex in which the carbene carbon atom is bonded to a hetero-atom with nonbonding electrons, as in LMC(OR)R, we may write the following resonance structures.



I II III

We have used X-ray photoelectron spectroscopy[3,4] in an attempt to determine the relative importance of these structures in methoxy(methyl)carbene-pentacarbonylchromium(0), $(CO)_5CrC(OCH_3)CH_3$.[5] This complex has sufficient volatility at room temperature so that we could study it as a gas and avoid the problems associated with solid-state spectra.[6] The carbon 1s spectrum is shown in Figure 1. The only features due to pure core ionization are the peak at 292.37 eV and its low binding energy shoulder. Undoubtedly the main peak is principally due to the five carbonyl carbon atoms. The shoulder and perhaps part of the intensity of the main peak are due to the other three carbon atoms. This band has been resolved by a least-squares curve-fitting routine into four peaks with intensity ratios of 5:1:1:1 and binding energies of 292.37(10), 291.7(3), 291.7(3), and 290.4(3) eV, respectively.

The band with a binding energy 5.4 eV higher than that of the main peak, with an intensity 0.18 of that of the main peak, is similar to a band observed in the oxygen 1s spectrum, about 5.0 eV from the main peak, with a relative intensity of 0.24. These bands we assigned to shakeup,[7] just as analogous bands in the spectra of hexacarbonylchromium(0) (Figure 2) and other chromium complexes[8] have been assigned. Two facts argue against a carbon 1s peak being fortuitously submerged in the shakeup band of the carbene complex. (1) The intensity of the shakeup band is approximately one-sixth that of the main band, corresponding to one carbon atom. Therefore if any significant fraction of the observed intensity is to be ascribed to shakeup, all of it must be, and none of the intensity can be ascribed to a carbon atom. (2) We calculated relative carbon 1s binding energies for $(CO)_5CrC(OCH_3)CH_3$ using the potential model equation[3] ($E_B = kQ + V + \ell$) and CHELEQ atomic charges[9-11] for I, II, III, and various hybrids thereof. The only cases for which a carbon binding energy was calculated to be near that of the shakeup band were those for which <u>two</u> such binding energies were calculated to be much greater than that of the carbonyl carbon binding energy; these structures were ruled out because they are obviously inconsistent with the spectrum. We conclude that there is no plausible electronic structure for which a carbon atom has a binding energy near that of the shakeup band.

Thus the spectrum shows that none of the carbon atoms in the $C(OCH_3)CH_3$ ligand has a binding energy greater than that of the carbonyl carbon atoms. If we assume a proportionality between binding energy and atomic charge, we may conclude that the compund contains no carbon atom with a high positive charge. This conclusion is in agreement with analyses of the

data based on the potential model, in which binding energies were calculated using CHELEQ atomic charges. As can be seen in Table I, the calculated relative binding energies for two hybrid structures agree fairly well with the experimental values. If we increase the percentage of structure II, the fit of the oxygen binding energies improves, but the fit of the carbon binding energies deteriorates. Very poor fits are obtained for hybrids weighted more than 80% in either I, II, or III or weighted less than 20% in I. It appears that (1) none of the ligand atoms in the carbene complex is highly charged, either negatively or positively, (2) no one resonance structure can satisfactorily account for the electron distribution, and (3) contrary to previous interpretations of other physical properties,[2] structure I contributes significantly to the bonding. The fact that the carbene carbon atom bonded to the chromium atom is less positive than the carbonyl carbon atoms may be rationalized by considering the carbene as a CO molecule to which two electropositive (relatively electron-donating) methyl groups have been added.

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Table I

Relative Core Binding Energies and Calculated Atomic Charges

Compound and atom[a]	Relative E_B, eV			Calcd charge	
	Expt	Calcd 33% I 67% III	Calcd 40% I 20% II 40% III	33% I 67% III	40% I 20% II 40% III
$Cr(\overset{*}{C}O)_6$	0.0	0.0	0.0	0.21	0.21
$(\overset{*}{C}O)_5CrC(OCH_3)CH_3$	-0.7	-0.4	-0.5	0.20	0.20
$(CO)_5Cr\overset{*}{C}(OCH_3)CH_3$	-2.7	-2.3	-3.7	0.10	0.06
$(CO)_5CrC(\overset{*}{O}CH_3)CH_3$	-1.4	-2.1	-0.6	0.05	0.11
$(CO)_5CrC(OCH_3)\overset{*}{C}H_3$	-1.4	-1.3	-2.5	0.04	0.02
$Cr(C\overset{*}{O})_6$	0.0	0.0	0.0	-0.06	-0.06
$(C\overset{*}{O})_5CrC(OCH_3)CH_3$	-0.8[c]	-0.5	-0.5	-0.08	-0.07
$(CO)_5CrC(\overset{*}{O}CH_3)CH_3$	-0.8[c]	-3.2	-3.0	-0.17	-0.16
$\overset{*}{C}rO_2Cl_2$[b]	-0.0	0.0	0.0	0.92	0.92
$\overset{*}{C}r(CO)_6$	-5.4	-5.9	-5.7	-0.88	-0.88
$(CO)_5\overset{*}{C}rC(OCH_3)CH_3$	-6.2	-5.7	-6.0	-0.76	-0.81

[a]Asterisked atoms correspond to the listed binding energies (C 1s, O 1s, Cr $2p_{3/2}$) and charges. [b]E_B(Cr $2p_{3/2}$) = 587.64 eV. [c]A single O 1s peak was observed, with E_B = 539.19 eV.

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(10) Although the CHELEQ electronegativity equalization method[9] was devised for elements of the first-row, we have found that it can be extended throughout the periodic table by using c = 1.8 for elements of atomic number greater than 18. In our calculations we have used a zero-charge electronegativity of 1.56 for the bonding orbitals of chromium.[11] For the calculation of the relative binding energies we used k values of 31.06 and 30.43 for carbon and oxygen, respectively.[9] The calculated relative chromium core energies correspond to least-

squares fits to the potential equation.

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Figure Captions

Figure 1. Carbon 1s spectrum of methoxy(methyl)carbenepentacarbonylchromium(0). The curve through the points is the sum of the computer-resolved curves for individual peaks. Two of the resolved peaks in the shoulder of the main peak are almost superimposed. The weak peak with $E_B \approx 284$ eV is due to the $MgK\alpha_{3,4}$ satellite of the exciting radiation.

Figure 2. Carbon 1s spectrum of hexacarbonylchromium(0). The shakeup satellite has a binding energy 5.5 eV greater than that of the main peak.

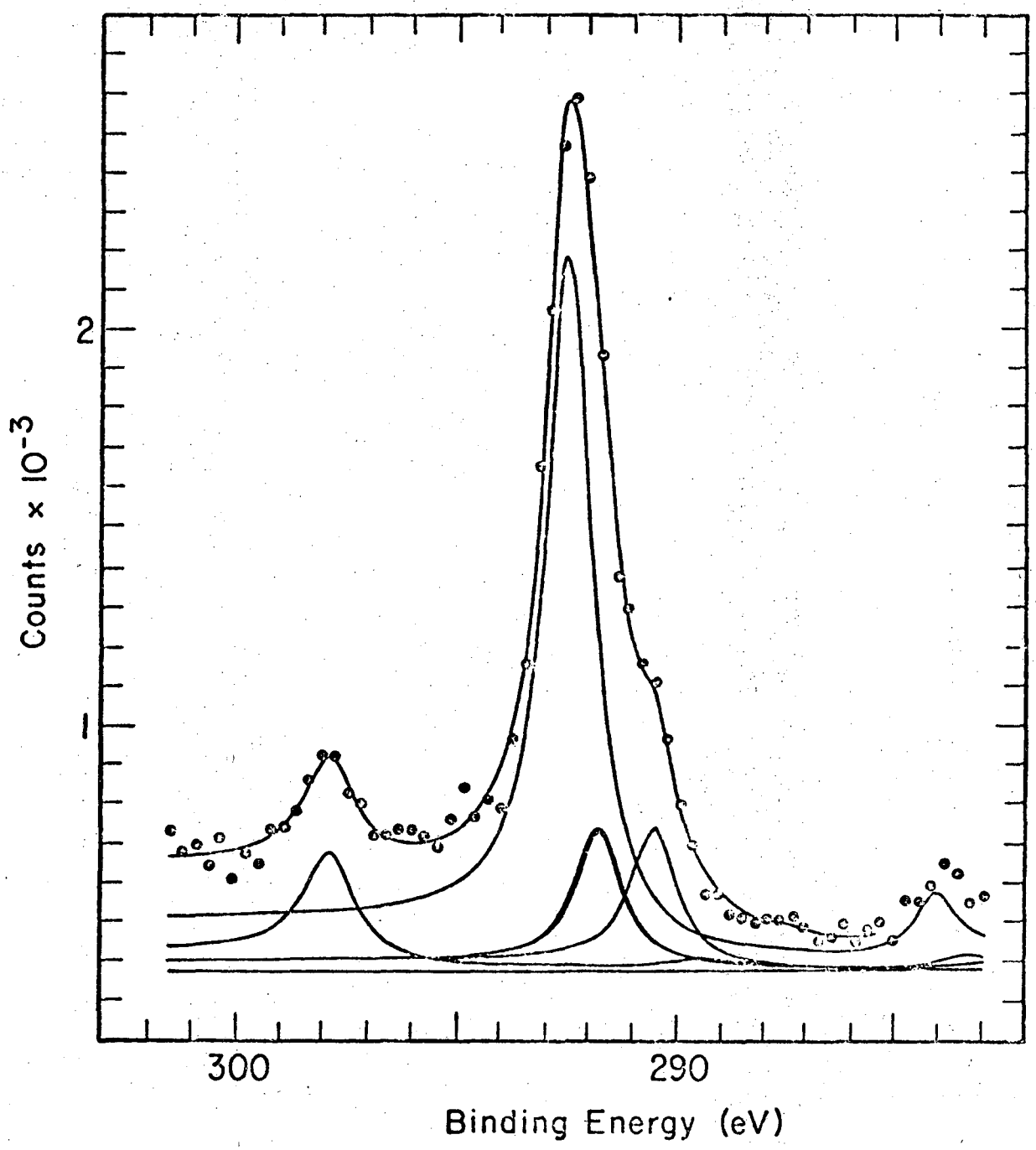

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Fig. 1

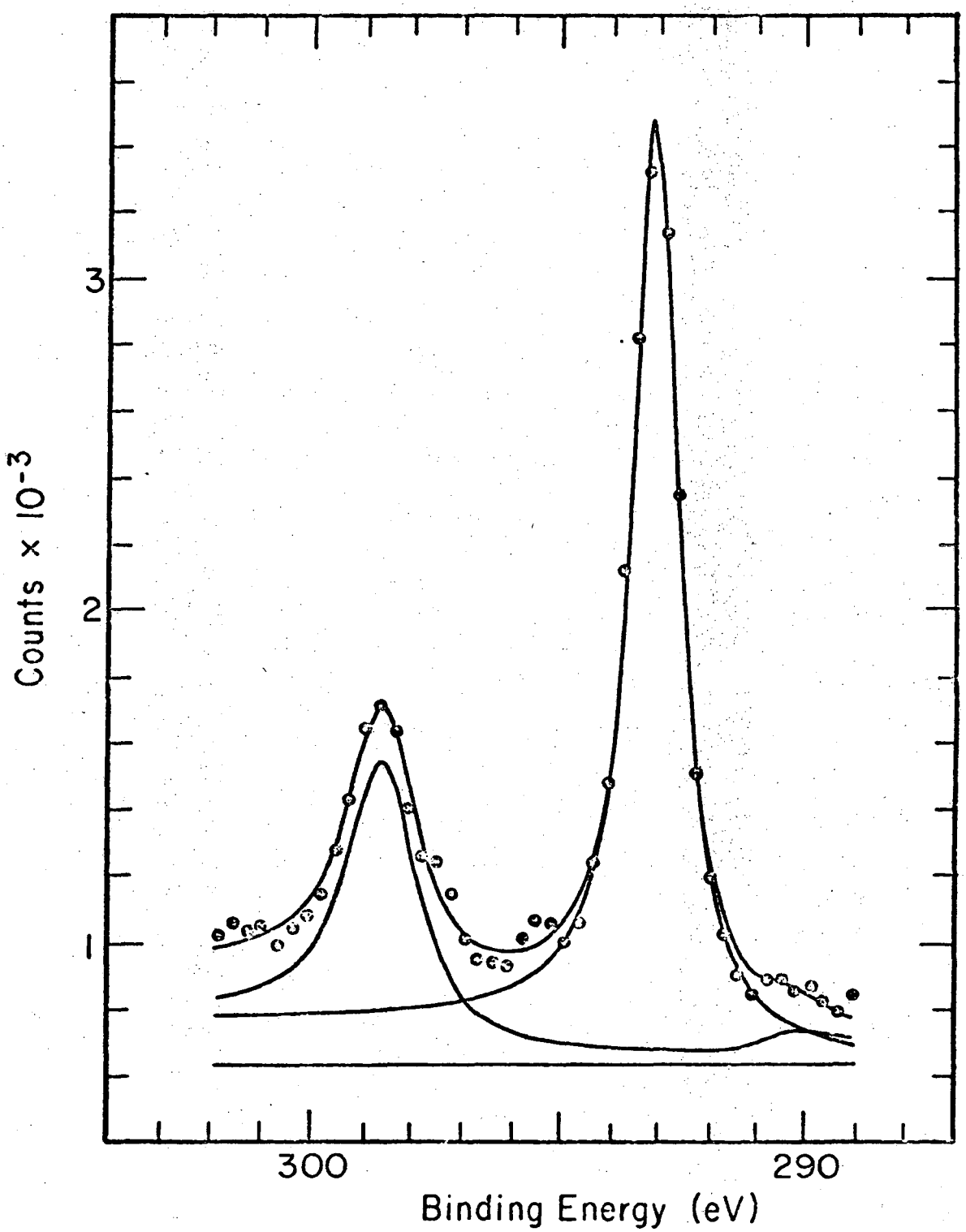

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Fig. 2

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