(4.05 mmol) was mixed with $[(n\text{-}C_4H_9)_4N]Mo(CO)_5Br$ (1.33 mmol). Upon addition of a solution of CH_2Cl_2 (~40 ml) containing $[(n\text{-}C_4H_9)_4N]Br$ (6.73 mmol), a reaction began with vigorous evolution of CO. After 24 hr CO evolution ceased with a total of 5.86 mmol of CO evolved (88%). Attempts to isolate the $[(n\text{-}C_4H_9)_4N]^+$ salt resulted in oils; however, the $[(n\text{-}C_3H_7)_4N]^+$ salt was isolated by adding the solution to a solution of 1.8 g of $[(n\text{-}C_3H_7)_4N]Br$ in 20 ml of CH_2Cl_2. The product (1.44 mmol) precipitated immediately as a red powder. Recrystallization was accomplished by the slow addition of ether to a solution of the salt in CH_3CN. *Anal.* Calcd for $C_{36}H_{84}N_3Mo_2Br_9$: Mo, 13.0; Br, 49.0. Found: Mo, 13.0; Br, 48.5.

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Registry No. $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$, 51472-37-8; $[(n\text{-}C_4H_9)_4N]_3Mo_2Br_9$, 51472-38-9; $[n\text{-}C_4H_9)_4N]Mo(CO)_5Cl$, 32424-52-5; $MoCl_5$, 10241-05-1; $[n\text{-}C_4H_9)_4N]Mo(CO)_5Br$, 32592-48-6; $MoBr_4$, 13520-59-7.

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

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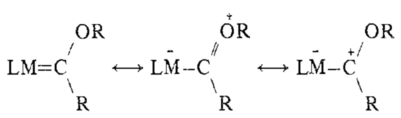
There is much current interest in the structure and bonding of transition metal carbene complexes.[1,2] A carbene complex in which the carbene carbon atom is bonded to a heteroatom with nonbonding electrons, such as LMC(OR)R, may be represented as a resonance hybrid of structures I–III.



I II III

Recent carbon-13 nmr data have been interpreted as evidence for electron deficiency in the carbene carbon and for characterization of such compounds as "transition metal stabilized carbonium ions."[3,4] Davison and Reger[5] have pointed out that the reactivity patterns of the compounds warrant their description as "carboxonium rather than carbenoid compounds." Cardin, *et al.*,[1] discussed other physical and chemical data which have been interpreted as evidence that II and III are the principal contributing structures. In view of the current interest in the charge distribution in such complexes, we have used X-ray photoelectron spectroscopy[6,7] to determine the relative importance of the resonance structures in methoxy(methyl)carbenepentacarbonylchromium(0), $(CO)_5CrC(OCH_3)CH_3$.[8] 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.

Table I. Relative Core Binding Energies and Calculated Atomic Charges

Compd and atom[a]	Rel E_B, eV		Calcd[b] charge
	Exptl	Calcd[b]	
$Cr(\overset{*}{C}O)_6$	0.0	0.0	0.20
$(\overset{*}{C}O)_5CrC(OCH_3)CH_3$	−0.7	−0.6	0.19
$(CO)_5Cr\overset{*}{C}(OCH_3)CH_3$	−2.7[c]	−2.3	0.11
$(CO)_5CrC(O\overset{*}{C}H_3)CH_3$	−1.4[c]	−0.1	0.10
$(CO)_5CrC(OCH_3)\overset{*}{C}H_3$	−1.4[c]	−1.9	0.01
$Cr(C\overset{*}{O})_6$	0.0	0.0	−0.03
$(C\overset{*}{O})_5CrC(OCH_3)CH_3$	−0.8[d]	−0.3	−0.03
$(CO)_5CrC(\overset{*}{O}CH_3)CH_3$	−0.8[d]	−2.1	−0.14
$\overset{*}{Cr}O_2Cl_2$	0.0	0.0	0.92
$\overset{*}{Cr}(CO)_6$	−5.4	−5.5	−1.02
$(CO)_5\overset{*}{Cr}C(OCH_3)CH_3$	−6.2	−6.1	−1.02

[a] Asterisked atoms correspond to the listed binding energies and charges. [b] Calculated for a hybrid structure (see text). [c] These values are relatively uncertain; they are based on a computer resolution of the C 1s band (see text). [d] A single O 1s peak was observed.

Experimental Section

Spectra were obtained with the Berkeley iron-free magnetic-focusing spectrometer using Mg $K\alpha_{1,2}$ X-rays.[9] Argon [$E_B(2p_{3/2})$ = 248.45 eV] was introduced as a standard reference with each sample. The $(CO)_5CrC(OCH_3)CH_3$ was prepared by the method of Fischer and Maasbol;[8] the $Cr(CO)_6$ was purchased; the CrO_2Cl_2 was prepared by the reaction of sodium dichromate with hydrochloric acid.[10] In Table I are listed the carbon 1s, oxygen 1s, and chromium $2p_{3/2}$ binding energies relative to the values E_B(C 1s) = 293.11 eV and E_B(O 1s) = 539.96 eV for $Cr(CO)_6$ and E_B(Cr $2p_{3/2}$) = 587.64 eV for CrO_2Cl_2.

Results and Discussion

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. To provide an objective analysis of this portion of the spectrum, we have resolved the band by a least-squares curve-fitting routine into four peaks with an enforced intensity ratio of 5:1:1:1. This analysis placed the intense peak at 292.37 ± 0.10 eV and the weak peaks at 291.7 ± 0.3, 291.7 ± 0.3, and 290.4 ± 0.3 eV. Although the latter three binding energies are not to be taken very seriously, the analysis does show that the binding energies of the weaker components of this band are lower than that of the intense carbonyl component.

The band with a binding energy 5.4 eV higher than that of the main peak, with an intensity 0.18 times that of the main peak, is similar to a band observed in the oxygen 1s spec-

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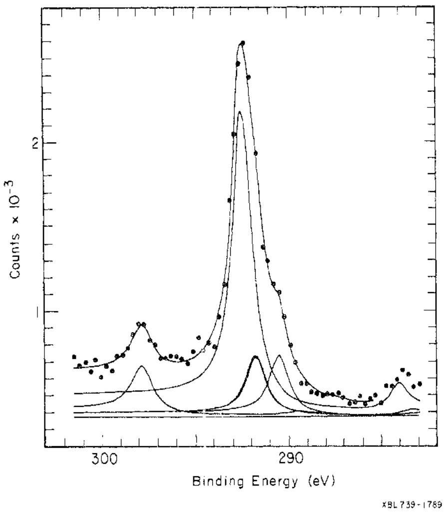

Figure 1. Carbon 1s spectrum of methoxy(methyl)carbenepentacarbonylchromium(0). The curve through the points is the sum of the computer-resolved curves for individual peaks. Two of the resolved peaks in the shoulder of the main peak are almost superimposed. The weak peak with $E_B \approx 284$ eV is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

trum, about 5.0 eV higher than the main peak, with a relative intensity of 0.24. These higher energy bands we assign to shake-up,[11] just as analogous bands in the spectra of hexacarbonylchromium(0)[12] and other chromium complexes[13] have been assigned. Two facts argue against a carbon 1s peak being fortuitously submerged in the shake-up band of the carbene complex. (1) The intensity of the high-energy band is such that it must either be ascribed entirely to shake-up or be ascribed almost entirely to a carbon 1s peak and an incredibly weak shake-up band. (2) We have calculated relative carbon 1s binding energies for $(CO)_5CrC(OCH_3)CH_3$ using the potential model equation[6] ($E_B = kQ + V + l$) and CHELEQ atomic charges[14-16] for structures I-III and various hybrids thereof. The only cases for which a carbon binding energy was calculated to be near that of the shake-up band were those for which *two* such binding energies were calculated to be much greater than that of the carbonyl carbon binding energy; these structures are inconsistent with the spectrum.

The fact 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 suggests, but does not prove, that none of the $C(OCH_3)CH_3$ carbon atoms has a charge more positive than that of the carbonyl carbon atoms. However the latter conclusion is supported by an analysis of the data with the potential model and CHELEQ atomic charges.[14-16] We have made calculations for a wide variety of hybrids of structures I-III. The best overall correlation of the carbon, oxygen, and chromium binding energies was obtained for a hybrid weighted 45% in I, 20% in II, and 35% in III. In Table I, the binding energies calculated for this hybrid are listed so that they may be compared with the experimental values. The corresponding calculated atomic charges are also listed. Poor correlations were obtained for hybrids weighted more than 80% in either I, II, or III or weighted less than 20% in either I or III. Thus we conclude, contrary to some previous interpretations, that to account satisfactorily for the electron distribution it is necessary to consider significant contributions from all three resonance structures.[17]

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Registry No. $(CO)_5CrC(OCH_3)CH_3$, 20540-69-6.

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(17) It should be recognized that, even if $d\pi \rightarrow p\pi$ back-bonding were complete and equally distributed among all the ligands in $(CO)_5CrC(OCH_3)CH_3$, the contribution of structure I would be only 50%. Thus a contribution of 45% is quite significant.