Preparation of Mo₂(OPr-*i*)₆·Me₂NCN. To Mo₂(OPr-*i*)₆ (0.17 g, 0.31 mmol) in hexane (10 cm³) was added Me₂NCN (20 µL, 0.4 mmol (=25% excess)). On addition, the red solution instantly turned deep purple. The reaction mixture was allowed to stand for 12 h and then cooled to −20 °C. Deep purple crystals were subsequently filtered off from the mother liquor; yield 0.12 g, 63% based on Mo₂(OPr-*i*)₆.

Anal. Calcd for H₄₈C₂₁N₂Mo₂: C, 40.91; H, 7.85; N, 4.54. Found: C, 40.64; H, 7.72; N, 4.50. IR (Nujol mull between KBr plates): 1582 (vs), 1415 (m), 1320 (m), 1265 (w), 1168 (m), 1110 (vs), 970 (vs), 851 (s), 836 (s), 730 (s), 634 (br, s), 455 (m), 430 (m) cm⁻¹. ¹H NMR (220 MHz; toluene-*d₈*; −40 °C; low temperature limiting spectrum, i.e., Figure 3): δ(CH) A = 6.84, B = 5.16, C = 4.50, D = 4.20; δ(CH₃) E = 1.95, F = 1.74, G = 1.44, H = 1.02; δ(*N*-methyls) 3.27, 3.02. The δ values were measured relative to Me₄Si.

Preparation of Mo₂(OBu-*t*)₆·NCNMe₂. Mo₂(OBu-*t*)₆·NCNMe₂ was prepared in the manner described above by using Mo₂(OBu-*t*)₆ in place of Mo₂(OPr-*i*)₆. Anal. Calcd for H₅₄C₂₇N₂Mo₂: C, 46.28; H, 8.63; N, 4.00. Found: C, 46.04; H, 8.48; N, 3.79.

Registry No. Mo₂(OPr-*i*)₆Me₂NCN, 70576-08-8; Mo₂(OBu-*t*)₆Me₂NCN, 70576-09-9; Mo₂(OPr-*i*)₆, 62509-78-8; Mo₂(OBu-*t*)₆, 62509-80-2.

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Correspondence

Reassignment of the Satellites in the X-ray Photoelectron Spectra of Chromium Hexacarbonyl

Sir:

Bancroft, Boyd, and Creber have recently reported high-resolution, gas-phase, X-ray photoelectron spectra (XPS) of group 6B hexacarbonyls.[1] The authors interpreted the extensive satellite structure in terms of the allowed (monopole) excitations of the ground-state molecules.[2] While this may be adequate for the satellites of the metal core ionizations, we believe it is preferable to interpret the satellites of the carbon and oxygen core ionizations in terms of localized hole states. In fact, we believe that the reduction to C_{4v} symmetry in forming these localized hole states is responsible for the stronger satellite structure observed by Bancroft et al. for the carbon and oxygen core ionizations. In addition, transitions which are forbidden in O_h symmetry may have appreciable intensities in the lower, C_{4v}, symmetry of the localized hole states. In order to test our assumptions, we have carried out parameter-free molecular orbital (MO) calculations[3] on various hole states and calculated the intensity of the satellites via the sudden approximation.[4]

Since the satellite structure for all three metals is similar, we have calculated only that for Cr(CO)₆. The atomic basis set of Clementi was used for C and O[5] and the s functions were reduced to a single exponent.[6] Richardson's atomic functions were used for the Cr[7] and the 4s and 4p exponents were 1.70.[8] Final core hole states were calculated by removing the electron of interest and converging the localized or delocalized hole states. In accord with the equivalent core model,[9] the atomic basis functions of the photoionized atom with nuclear charge Z were replaced by functions for an atom with nuclear charge $Z + 1$, i.e., F for photoionized O(O*) and Mn for photoionized Cr(Cr*). Results obtained for unrelaxed basis sets were in qualitative agreement. The method for calculating satellite intensities has been described previously.[10] We have used the

orbital numbering scheme of Beach and Gray,[2] as did Bancroft et al.

When the symmetry of the core hole state was forced to remain octahedral by delocalizing the C or O 1s hole, no satellites were found. The probability of the main peak, calculated from the overlap of the initial and final states, was greater than 99%. When the symmetry was reduced to C_{4v} by localizing the hole, four relatively intense satellites were found, which correspond well to the four observed satellites. The carbon and oxygen satellites are similar in structure and arise from the same transitions, so we will limit our discussion to the oxygen satellites.

The satellite intensities for 35 C_{4v}, symmetry-allowed transitions were calculated. Only four of these transitions showed appreciable intensities. The satellite assignments and their octahedral parentage are given in Table I. The molecular orbital diagram, Figure 1, shows how the important orbitals in C_{4v} symmetry arise from the O_h orbitals. The first and strongest satellite is due to the 7e → 8e transition and involves charge transfer from the chromium–carbonyl π bonds, mainly M–C–O*, to the 2π orbitals of the photoionized carbonyl. The 7e orbital is derived primarily from the 2t₂ₘ (96%), while the 8e is 40% 2t₂ᵤ, 40% 4t₁ᵤ, and 10% 3t₂ₘ. The second satellite arises from the 7e → 10e and 2b₂ → 3b₂ and is again M → L*, in which the 10e involves the 2π of the trans carbonyl and some CO* 2π contribution and the 3b₂ involves the 2π of the four cis carbonyls. The 10e and 3b₂ orbitals both contain significant metal character (40%). These transitions have their parentage in the 2t₂ₘ → 3t₂ₘ O_h transition, which was assigned by Bancroft et al. to the primary satellite. The third satellite corresponds to the 6e → 8e transition, where the 6e is a component of the 3t₁ᵤ (98%). This satellite is primarily a 5σ → 2π transition from the cis OC–Cr–CO framework to the photoionized carbonyl and, again, both orbitals have a significant metal character. The fourth peak is assigned as the 1e → 8e, where the 1e is an equal mixture

Table I. Comparison of the O $1s_{1/2}$ XPS Satellite Structure with Our Theoretical Results

satellite peak	assignt			ΔE, eV		intensity, %	
	Bancroft[a]	this work	O_h parent	obsd[a]	calcd[b]	obsd[a]	calcd[c]
L_1	$2t_{2g} \rightarrow 3t_{2g}$	$7e \rightarrow 8e$	$2t_{2g} \rightarrow 2t_{2u} + 4t_{1u}$	5.1	7.28	20	6.4
L_2	$3t_{1u} \rightarrow 4t_{1u}$	$2b_2 \rightarrow 3b_2$	$2t_{2g} \rightarrow 3t_{2g}$	6.0	11.13	14	0.3
		$7e \rightarrow 10e$	$2t_{2g} \rightarrow 3t_{2g}$		11.63		0.1
L_3	$1t_{1g} \rightarrow 2t_{1g}$	$6e \rightarrow 8e$	$3t_{1u} \rightarrow 2t_{2u} + 4t_{1u}$	10.1	14.37	5	0.3
	$1t_{2u} \rightarrow 2t_{2u}$						
	$2t_{1u} \rightarrow 4t_{1u}$						
L_4	$1t_{2g} \rightarrow 3t_{2g}$	$1e \rightarrow 8e$	$mix.^d \rightarrow 2t_{2u} + 4t_{1u}$	15.5	24.54	3	3.6
	$1t_{1u} \rightarrow 4t_{1u}$						

[a] Reference 1. [b] Energies show only qualitative ordering due to approximations. [c] No other transitions gave intensities greater than 0.05%. [d] 1e is an equal mixture of $1t_{1g}$, $1t_{2u}$, $2t_{1u}$, and $1t_{2g}$.
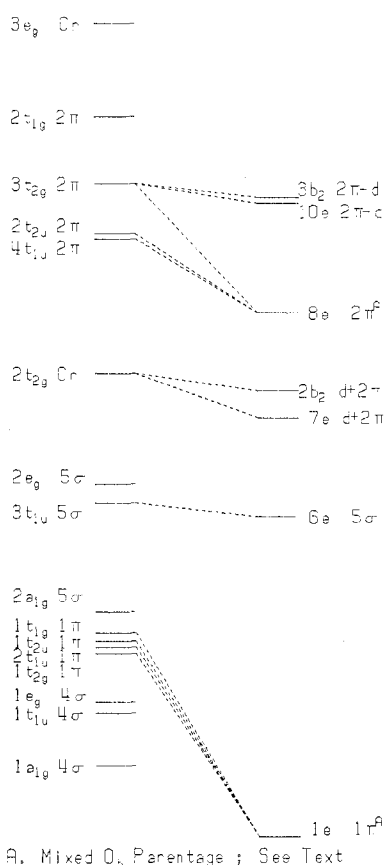

Figure 1. MO diagram for ground-state $Cr(CO)_6$ and for $Cr(CO)_6$ with a core electron removed from an oxygen 1s orbital demonstrating the splitting and energy changes of orbitals involved in the O 1s satellites.

of the $1t_{1u}$, $1t_{2u}$, $2t_{1u}$ and $1t_{2g}$, and is essentially a $1\pi \rightarrow 2\pi$ transition involving only the CO* moiety. The energy of this transition corresponds to that found for the O 1s photoionization spectrum of gaseous CO.[11] This transition in free CO has been described as $1\pi \rightarrow 2\pi$ by most authors,[11] but a different assignment for the C 1s has been made by Gelius.[12] The calculations suggest that transitions will arise only from orbitals involving or strongly coupled to the CO* moiety. In the photoionized state the valence orbitals of CO* are well separated from the other carbonyls and strongly coupled only to the metal. Thus, transitions from the 2e, 3e, 4e, and 5e or to the 9e and 11e are precluded as they contain no (<1%) CO* or M character.

The calculated energies and intensities of O 1s satellites are compared to the experimental results and previous assignments in Table I. The calculated energies are too large, which is not

Table II. Comparison of Cr Shake-up Structure with Our Theoretical Results

satellite peak	Bancroft[a] assignt	ΔE, eV		intensity, %	
		obsd[a]	calcd[b]	obsd[a]	calcd[c]
M_1	$2t_{2g} \rightarrow 3t_{2g}$	5.5	10.02	8	5.7
M_2	$2e_g \rightarrow 3e_g$	6.9	29.98	5	0.6
M_3	$1e_g \rightarrow 3e_g$	11.2	34.71	4	0.1

[a] Reference 1. [b] Energies show only qualitative ordering due to approximations. [c] No other transition gave intensities greater than 0.05%.

surprising considering the approximate nature of the calculation and the fact that these energies were simply calculated as differences in orbital energies. If one reduces all the calculated energies by about 35%, the agreement is quite good. Although we find only four satellites with appreciable intensity, their values are in error by an order of magnitude. This is due in part to errors in the sudden approximation, to the limited basis set, which does not allow sufficient relaxation of the valence molecular orbitals, and to the neglect of configuration interaction, which could redistribute the intensities between transitions of the same symmetry (nearly all the satellites are e $\rightarrow$ e transitions). In spite of the lack of quantitative agreement, these are the only satellites with an intensity greater than 0.05%, and we believe that they correspond to the four observed satellites.

The results for the Cr core ionizations are given in Table II. Our assignments are identical with those of Bancroft et al. In this case, the photoionized molecule retains O_h symmetry, and the ground-state molecular orbitals form a reasonable basis for the interpretation of the satellite structure. The somewhat better agreement in the calculated intensities may be due to the larger Cr basis, which contains the virtual 4s and 4p functions.

Previous work on small molecules strongly suggests that the XPS spectra are best interpreted in terms of localized hole states.[13] Likewise, for the metal hexacarbonyls we believe the correct interpretation must be made in terms of localized holes. Since localizing the hole reduces the symmetry, many more symmetry-allowed transitions must be considered in order to assign the satellite XPS spectra. Furthermore, the positions of the satellites are determined by the transition energies of the photoionized molecule and not by those of the ground-state molecule. Although our MO results are only qualitative, they do provide a reasonable means of determining the most important transitions and provide a reasonable assignment of the satellite structure of $Cr(CO)_6$.

Registry No. $Cr(CO)_6$, 13007-92-6.

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Relative Energies of Metal–Metal Bonding and Nonbonding Molecular Orbitals in Bridged Diiron Complexes

Sir:

Both oxidation and reduction of compounds containing metal–metal bonds are normally accompanied by concurrent metal–metal bond cleavage and fragmentation.[1] This is taken as evidence that the highest occupied and lowest unoccupied molecular orbitals are strongly associated with the metal–metal interaction, the former being bonding and the latter antibonding. The situation with mononuclear transition-metal compounds is distinctly different in that the donor and acceptor orbitals are usually metal d orbitals which are essentially nonbonding with respect to the primary structure of the complex. There are, however, three classes of multinuclear metal compounds that can retain structural integrity in more than one molecular oxidation state: namely, those containing ligand-bridged metal–metal bonds, those with metal–metal multiple bonds, and those with closed-cluster structures.[2] This correspondence concerns the nature of the metal–metal interaction in the first of these classes.

Bridged dinuclear metal complexes have been the subject of numerous experimental and theoretical investigations. Previous discussions have focused on the metal–metal interaction vis à vis the metal-bridge interactions.[3–5] In this type of compound it has been clearly established that oxidation and reduction strongly affect the metal–metal distance.[6] It is logical that such a result be discussed in terms of electron gain or loss from high-lying orbitals associated with the metal–metal interaction. This interpretation is supported by the results of quantitative calculations on $Fe_2(CO)_6X_2$ complexes in which it was found that the lowest unoccupied molecular orbital is metal–metal antibonding while the highest occupied molecular orbital is metal–metal bonding.[4,7] In addition, it was found that the other metal d orbitals and ligand orbitals are at least 1–2 eV more stable than the metal–metal bonding orbital. On the other hand, recent structural work[8] and qualitative calculations[5] have drawn attention to the balance between the metal–ligand and metal–metal interactions in determining observed geometry and, in so doing, have implied that ar-
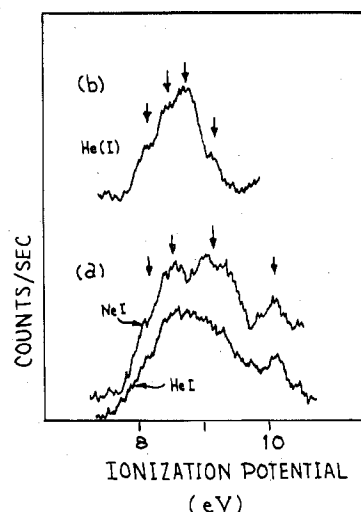

Figure 1. (a) The first band in the He I and Ne I photoelectron spectra of $Fe_2(CO)_6B_2H_6$. (b) The first band in the He I photoelectron spectrum of $Fe_2(CO)_6S_2$.

guments restricted to consideration of the metal–metal interaction are incomplete.[9]

Recently, we have prepared[10] a diborane(6)-bridged diiron hexacarbonyl, $Fe_2(CO)_6B_2H_6$, which is formally and structurally[11] analogous to the class of bridged dinuclear metal compounds exemplified by $Fe_2(CO)_6S_2$. As $Fe_2(CO)_6B_2H_6$ is a volatile compound, we have obtained its UV photoelectron spectrum. Empirical assignment allows the relative energies of the metal orbitals to be investigated.[12] The band at lowest ionization potential in the He I and Ne I spectra of $Fe_2(CO)_6B_2H_6$ is shown in Figure 1. On the basis of an analysis of the complete spectrum in terms of the known behavior of model compounds containing the $Fe(CO)_3$ fragment,[13] relative intensity changes with photon energy,[14] and semiempirical molecular orbital arguments,[15] it is certain that this is the only band that contains the iron d ionizations.[16] Of the seven expected iron d ionizations, six are from orbitals which are essentially nonbonding with respect to the molecular framework while one is associated with the metal–metal bonding orbital. If the shoulder on this band is assigned to the latter ionization, then the implication[17] is that the metal–metal bonding orbital is only about 0.4 eV less stable than one of the iron nonbonding orbitals. However, there is no empirical justification for such an assignment, and the ionization associated with the metal–metal bonding orbital could well lie anywhere within the band.

As the structure of $Fe_2(CO)_6B_2H_6$ has not been conclusively established by diffraction techniques and as the calculations were carried out on ligands other than B_2H_6, we have also measured the photoelectron spectrum of $Fe_2(CO)_6S_2$. The band at lowest ionization potential in this spectrum is shown in Figure 1. Again, analysis of the whole spectrum in the manner described above demonstrates that the seven iron d ionizations are contained within this band. As indicated by the arrows in the figure, the onsets of four of the ionizations are evident; any one of these could correspond to the ionization of the metal–metal bonding orbital. The conclusion is the same. Removal of an electron from the metal–metal bonding orbital takes about the same amount of energy as removal from the metal–metal nonbonding orbitals.[18] The calculations for $Fe_2(CO)_6S_2$ referred to above,[4] however, indicate that the metal–metal bonding orbital is about 1.5 eV above the least stable of the six iron orbitals that are essentially nonbonding with respect to the molecular framework.

Because of the possibility of a quantitative failure of Koopmans' theorem,[17,19] it may well be that the calculations