Molecular Core Binding Energies for Some Transition Metal Carbonyls[1] and π-Cyclopentadienyls as Determined by X-Ray Photoelectron Spectroscopy

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Summary Molecular core binding energies have been measured for some transition metal carbonyls and π-cyclopentadienyls and are discussed qualitatively in terms of the charge distributions in these molecules.

STRUCTURE and bonding in transition metal carbonyls and biscyclopentadienyls is a subject for active discussion by both theoretical and experimental chemists, and there are still many unresolved problems. For example most semi-empirical calculations[2] on mononuclear carbonyls agree that the net consequence of σ-donation from CO to metal and reverse back donation into antibonding CO π^* orbitals leads to a net increase in electron density on the ligand. However, for $Ni(CO)_4$[2a] the somewhat surprising result has been obtained that electron migration on complex formation is in the reverse direction and that the nickel is overall negatively charged. A recent non-empirical calculation,[3] however, indicates a more realistic charge distribution, with the nickel being overall positively charged.

Numerous semi-empirical calculations[4] on the metallocenes have not resolved the problem of the charge distribution in these molecules. For ferrocene for example Shustorovish and Dyatkina[4a] obtained a positive charge of +0·69 on iron whilst Dahl and Ballhausen[4b] obtained a negative charge of the same magnitude.

We report here a study of the molecular core binding energies for some transition metal carbonyls and biscyclopentadienyls which goes some way to resolving some of these problems. The results are given in the Table. Spectra have been measured (A.E.I. ES100 electron spectrometer) with Mg-$K\alpha_{1,2}$ radiation and samples were studied as thin films on gold to minimize charging effects. Traces of water caused considerable broadening and spurious shifts in the O_{1s} peaks of the carbonyls and great care was taken to eliminate them. Only spectra for which the integrated intensities of the C_{1s} and O_{1s} levels were in the correct ratio for the molecular formulae have been included in the Table.

Molecular core binding energies in eV[a]

	$M(2p_{1/2})$	$M(2p_{3/2})$		C_{1s}	O_{1s}
$Cr(CO)_6$	587·5	578·5		289·1	536·2
$Cr(\pi\text{-}C_5H_5)_2$	585·9	576·9		285·4	
$Mn(CO)_3(\pi\text{-}C_5H_5)$	654·4	643·4	*CO*	288·4	535·6
			C_5H_5	286·4	
$Fe(CO)_5$	726·0	713·0		289·0	536·7
$Fe(\pi\text{-}C_5H_5)_2$	723·8	710·8		285·7	
$Co(\pi\text{-}C_5H_5)_2$	797·5	782·2		285·7	
$Ni(CO)_4$	876·4	859·2		288·8	536·4
$Ni(\pi\text{-}C_5H_5)_2$	874·9	857·7		285·6	
CO				290·5	536·7
C_5H_5[b]				284·9	

[a] Relative binding energies between different compounds depend on sample charging effects. By studying the samples as thin films on gold these are minimized and relative binding energies between molecules are estimated to be ±0·3 eV.

[b] The C_{1s} binding energies of simple carbon-hydrogen containing species are closely similar $\approx$ 285·0 eV (*cf.* CH_4, C_2H_2, C_2H_4, C_6H_6, ref. 5). There is no reason to suppose that the C_{1s} binding energy for the neutral C_5H_5 fragment would be different in this respect and the binding energy has therefore been equated to that for benzene previously reported (D. T. Clark, *Chem. Comm.*, 1971, 230).

C_{1s} and O_{1s} core binding energies have been reported[5] for gaseous CO where the reference is the vacuum level. Our results for thin films of the compounds on a conducting backing are with respect to the Fermi level and a direct comparison therefore requires that binding energies be expressed with respect to the same reference. We have corrected gas-phase measurements[5] to our reference level by comparison with CO_2 which has been studied in both gaseous and condensed phases. Comparison between these measurements shows a difference of 5·4 eV due to the difference in reference level (roughly the work function for the sample), and this is in good agreement with that found for a series of acetyl compounds AcX[6] where the difference between gas phase and thin film measurements was 5·6 eV. We have also compared our measured first ionisation potentials for the carbonyls with those previously published for the gaseous molecules measured by He(I) photoelectron spectroscopy and find an energy difference of 5·4 eV.[7,8]

Considering first the carbonyls, comparison of the C_{1s} and O_{1s} binding energies with those for the free ligand indicates a shift to lower binding energy on complex formation, the "shift" being much larger for the C_{1s} levels than for the O_{1s} levels. This suggests an overall electron transfer from metal to ligand [in this respect $Ni(CO)_4$ parallels the behaviour of the other carbonyls]. This supports the idea based on the lowering of the force constants for the CO stretching vibrations for example that the π^*- is stronger than the σ-interaction. This is also evidenced by the much larger shift to lower binding energy for C_{1s} relative to O_{1s} levels since the anti-bonding π^* orbital has a larger contribution from the carbon $2p$ orbitals. The overall electron drift from metal to ligand in the carbonyls is accommodated by a positive charge on the metal and this is seen by comparison with the biscyclopentadienyls where the ligand is now a better donor but weaker acceptor than CO. The binding energies for the metal core levels decrease on going from the carbonyl to the corresponding biscyclopentadienyl indicating an increased electron population on the metal. By contrast comparison of the C_{1s} binding energies of the cyclopentadienyl residues with that predicted for the neutral free ligand indicates a small positive charge in the rings which is the exact opposite of the currently accepted view. However the chemistry of the biscyclopentadienyls is more readily understandable in terms of a charge distribution in which the ring carbons are slightly positive and the metal negatively charged.[4b]

For comparison we also include results for $(\pi\text{-}C_5H_5)Mn(CO)_3$. Electron transfer from the ring to the carbonyl groups *via* the metal orbitals is clearly discernible and the C_{1s} and O_{1s} levels for the CO groups are shifted considerably to lower binding energy compared with the carbonyls. On the other hand the C_{1s} binding energies for the ring carbons are actually increased compared with the biscyclopentadienyls.

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[1] A preliminary report of some of this work has been presented at the Chemical Society Symposium on Valence in Inorganic Molecules, London, March 1971.

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[8] For $Ni(CO)_4$ the results are those of Prof. W. C. Price quoted in J. C. Green, D. I. King, and J. H. D. Eland, *Chem. Comm.*, 1970, 1121.