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Photoelectron Study of Additivity and Ligand Field Effects on the Tungsten 5d Orbitals in $[W(CO)_{6-n}(PR_3)_n]$ Compounds

Sir:

Recently, Bursten[1] has formulated an additive model for rationalizing the shifts and splittings of the t_{2g} orbitals in d^6 $[M(CO)_{6-n}L_n]$ (e.g. M = Cr, Mo, W; L = PR_3, CNR) complexes. On the basis of a qualitative molecular orbital picture, the ratios of the t_{2g} splittings should be 2:–1:1:0 for *trans*-$[M(CO)_4L_2]$, *cis*-$[M(CO)_4L_2]$, $[M(CO)_5L]$, and *fac*-$[M(CO)_3L_3]$ complexes, respectively, and a plot of the first IP vs. *n* should give a linear trend. These predictions have not yet been confirmed with use of photoelectron spectroscopy, but similar additive models have been used to rationalize the same ratios in a variety of spectra of d^6 metal complexes: the electronic spectra of Co^{III} complexes,[2] Mössbauer and NQR quadrupole splittings in Fe^{II},[3,4] Ir^{III},[5] and Co^{III}[6] complexes, and ^{59}Co NMR line widths of Co^{III} complexes.[4,7] However, in photoelectron spectra, relaxation effects can sometimes be as important as ground-state effects in determining shifts and splittings. Indeed, for $Cr(CO)_5L$ complexes, Hillier et al.[8] claimed that relaxation effects dominate the t_{2g} splittings. In contrast, other papers[1,9,10] have used ground-state arguments (the difference in π back-bonding between CO and L) to rationalize the t_{2g} splittings in $M(CO)_5L$ and $Re(CO)_5X$ complexes.

To confirm the additive model predictions, and to investigate the importance of relaxation shifts, we have measured the W 5d photoelectron spectra of $[W(CO)_6]$, $[W(CO)_5L]$ (L = PMe_3, PEt_3), *cis*- and *trans*-$[W(CO)_4L_2]$, and *fac*-$W(CO)_3L_3$.

The complexes (Table I) were prepared by known methods,[11-14] and the purity was confirmed by melting points, IR, MS, and thin-layer chromatography. A satisfactory photoelectron spectrum of *cis*-$[W(CO)_4(PEt_3)_2]$ could not be obtained due to isomerization to the trans isomer on sublimation in the photoelectron gas cell. All other complexes gave good He I photoelectron spectra with use of techniques previously described.[15,16] The spectra were fitted to Lorentzian–Gaussian line shapes with use of an iterative procedure.[17]

Table I. Ionization Potentials, Spin–Orbit Coupling Constants (ζ), and t_{2g} Splittings (eV) for the $[W(CO)_{6-n}(PR_3)_n]$ Compounds

compd	IP (±0.02)	ζ (±0.01)	b_2–e or b_{2g}–e_g (±0.01)
$[W(CO)_6]$	8.29, 8.58	0.19	0
$[W(CO)_5(PMe_3)]$	7.45, 7.66, 7.92	0.17	0.31
$[W(CO)_5(PEt_3)]$	7.40, 7.60, 7.83	0.17	0.29
cis-$[W(CO)_4(PMe_3)_2]$	6.72, 7.00, 7.25	0.19	–0.34[a]
trans-$[W(CO)_4(PMe_3)_2]$	6.68, 6.90, 7.34	0.19	0.51
trans-$[W(CO)_4(PEt_3)_2]$	6.60, 6.83, 7.28	0.20	0.52
fac-$[W(CO)_3(PMe_3)_3]$	6.31, 6.60	0.19	0

[a] This splitting was approximated by using $\zeta = 0.19$ eV and a double-group interaction of 0.04 eV.

Figure 1 shows the W 5d spectra for some of the substituted $[W(CO)_6]$ species. $[W(CO)_6]$ and *fac*-$[W(CO)_3(PMe_3)_3]$ show a doublet of intensity ~2:1 due to the spin–orbit splitting of the t_{2g} molecular orbital level of mainly W 5d character.[18] The other spectra show three peaks due to the splitting of the t_{2g} level in C_{4v} or D_{4h} symmetry,[19,20] combined with the spin–orbit splitting of the e (or e_g) MO. When L is a poorer π acceptor than CO (as is the case for our compounds), the b_2 (or b_{2g}) MO has a larger IP than the e (or e_g) MO in $[W(CO)_5L]$ and *trans*-$[W(CO)_4L_2]$, with the opposite order in *cis*-$[W(CO)_4L_2]$.[1] The large splitting in the *trans*-$[W(CO)_4(PMe_3)_2]$ spectrum (Figure 1c) immediately confirms the above ordering of b_{2g} and e_g. Moreover, it is apparent from the spectra in Figure 1 that, qualitatively, the magnitude of the splittings agrees with the theoretical predictions:[1]

$$\textit{trans}\text{-}[W(CO)_4L_2] > \textit{cis}\text{-}[W(CO)_4L_2] \approx [W(CO)_5L] > \textit{fac}\text{-}[W(CO)_3L_3]$$

Table I summarizes the binding energies and also gives the calculated spin–orbit coupling parameters (ζ) and the t_{2g}

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(19) As pointed out by Ballhausen,[20] the symmetry groups of both cis and trans are in practice D_{4h}.

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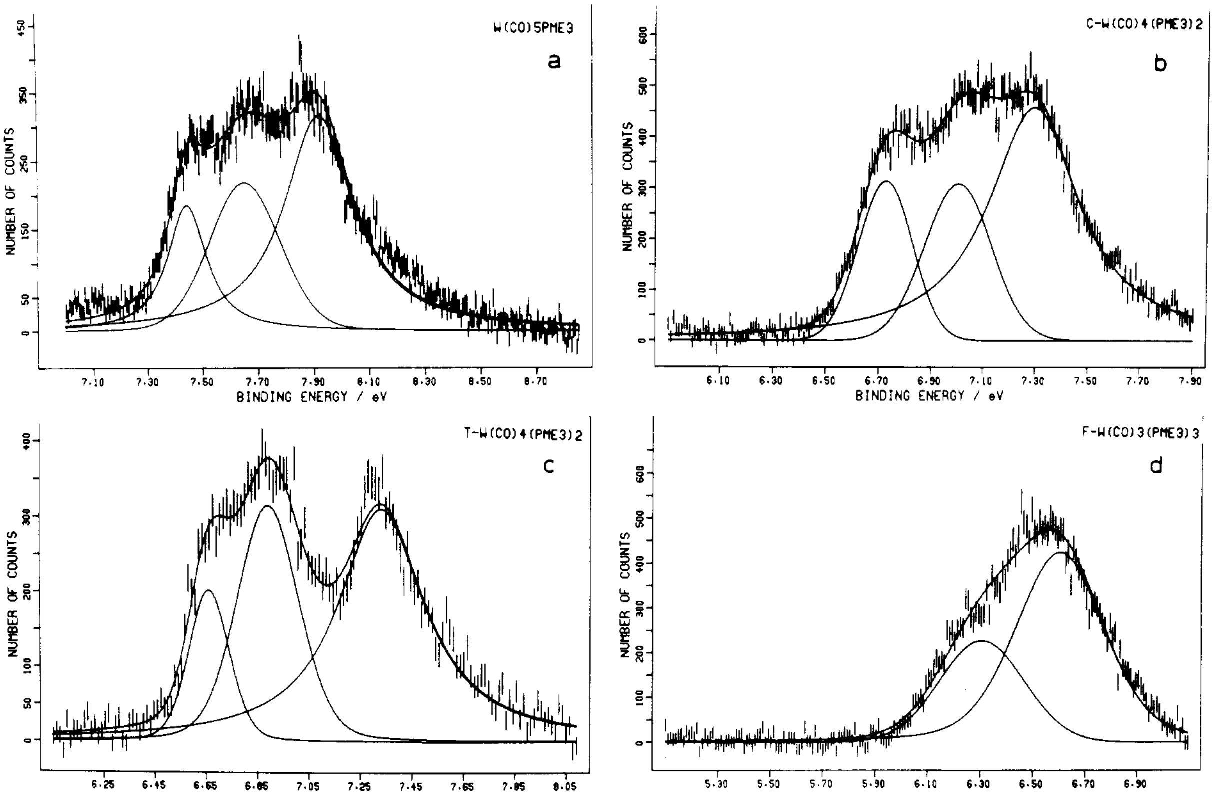

Figure 1. He I photoelectron spectra of the W 5d region in (a) [$W(CO)_5PMe_3$], (b) *cis*-[$W(CO)_4(PMe_3)_2$], (c) *trans*-[$W(CO)_4(PMe_3)_2$], and (d) *fac*-[$W(CO)_3(PMe_3)_3$].

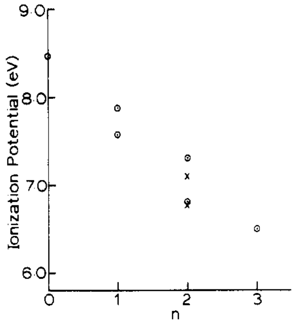

Figure 2. Plot of the W 5d IP vs. *n* for the series $W(CO)_{6-n}(PMe_3)_n$ for $n = 0$–3. The IP's (without spin–orbit splitting) are given for the unsplit t_{2g} level ($n = 0, 3$), the b_{2g} and e_g levels for $n = 1$ and $n = 2$ (trans), and the b_2 and e levels (X) for $n = 2$ (cis).

splittings with use of Hall's equations.[9] The spin–orbit parameters (0.17–0.20 eV) are the same as those obtained for a number of other [$W(CO)_5L$] compounds.[10] More importantly, the ratio of the t_{2g} splittings is 1.0:–1.1:1.7:0 for [$W(CO)_5L$], *cis*-[$W(CO)_4L_2$], *trans*-[$W(CO)_4L_2$], and *fac*-[$W(CO)_3L_3$], respectively—in rather good agreement with the theoretical predictions. The smaller than predicted trans splitting is due to two possible effects. First, the π-acceptor abilities of the CO ligands in the [$W(CO_5L$] and cis species will, on average, be greater than the CO π-acceptor ability in the trans compound. Trans–cis quadrupole splittings in Fe^{II}, Co^{III}, and Ir^{III} compounds are usually less than 2:–1,[35] although the quadrupole splitting is determined by both π-acceptor and σ-donor effects. Second, relaxation effects could readily cause this effect, which would result from very small differences in relaxation energies of <0.1 eV.

Finally, a plot of IP for the W 5d levels vs. *n* shows a good linear correlation (Figure 2), and the first IP's of cis and trans isomers are very similar as predicted by Bursten.[1] Because the phosphines are better σ donors than CO, the W t_{2g} peaks are chemically shifted to lower IP as *n* increases. This plot once again shows that differential relaxation effects are very small.

In conclusion, this work confirms the general validity of a ground-state treatment for explaining the shifts and splittings of the W t_{2g} levels in $W(CO)_{6-n}L_n$ compounds. These splittings and shifts should now be more useful for studying structure and bonding in d^6 low-spin systems.

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Registry No. [$W(CO)_6$], 14040-11-0; [$W(CO)_5(PMe_3)$], 26555-11-3; [$W(CO)_5(PEt_3)$], 21321-31-3; *cis*-[$W(CO)_4(PMe_3)_2$], 16104-05-5; *trans*-[$W(CO)_4(PMe_3)_2$], 30513-08-7; *trans*-[$W(CO)_4(PEt_3)_2$], 51154-69-9; *fac*-[$W(CO)_3(PMe_3)_3$], 30513-09-8.

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Bimetallic Porphyrins: Synthesis and Rapid Intramolecular Electron Transfer of *meso*-Tritolyl[*N*-(pentaammineruthenio)pyridyl]porphyrin

Sir:

Interest in electron transfer reactions has increasingly focused on reactions in which the reactants are held at a fixed distance or orientation.[1-10] Such studies are particularly

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(1) Classic examples are provided by the work on mixed-valence systems, cf.: Taube, H. In "Tunneling in Biological Systems"; Chance, B., Ed.; Academic Press: New York, 1980.

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