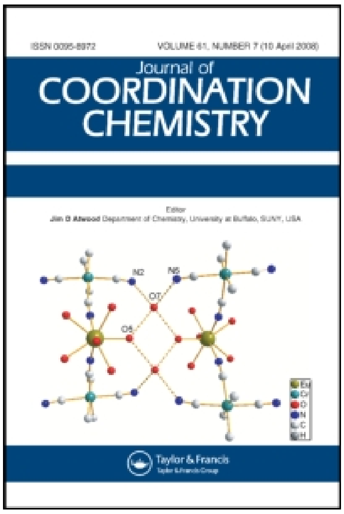

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AN APPROACH TO DIRECT EVALUATION OF PI BONDING IN METAL CARBONYLS[1a]

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The extent of π bonding between the metal atom and the ligand atoms in metal carbonyls and substituted metal carbonyls is a matter of great interest and importance and has accordingly been the subject of a great many studies by a variety of methods. In practically all such studies an indirect approach has been taken. The properties measured are not direct manifestations of electronic structure but rather they are properties whose own basis in electronic structure cannot be unambiguously defined.

One widely used general approach has been the measurement and interpretation of the frequencies of carbonyl modes.[2–5] The intensities of the carbonyl stretching modes,[6] the metal-carbon stretching frequencies,[7,8] equilibrium constants for ligand exchange,[9] X-ray crystallographic measurement of metal-ligand bond distances[10,11] and metal-ligand nmr coupling constants[12] are among the other properties used to assess the extent of M—CO π bonding.

There have also been some attempts to get more-or-less *directly* at electronic structure by means of molecular orbital calculations[13–16] and observation of electronic spectra,[16–18] separately or in combination. Photoelectron spectroscopy[19] is a very powerful technique for establishing the order of occupied energy levels. Results on the analogous $XMn(CO)_5$ species indicate that the highest filled orbital is of e symmetry (see below).

The rationale for the work reported here is as follows. We begin with an $M(CO)_6$ molecule of O_h symmetry. Specifically, $Cr(CO)_6$ is used. We consider what should happen to the "d" orbital pattern if one CO group is replaced by a ligand having different σ-donor and π-acceptor properties from those of CO, to give $Cr(CO)_5L$ with C_{4v} symmetry. In general the degeneracies of both the $e_g(\sigma^*)$ and $t_{2g}(\pi)$ orbitals must be lifted. If the ligand L is a better σ donor than CO (as most ligands will be) the e_g set will split with the energy pattern $d_{z^2} > d_{x^2-y^2}$. If L is a poorer σ donor the order will, of course, be reversed. For the $t_{2g}(d)$ orbitals, d_{xz} and d_{yz} will remain degenerate but will separate from d_{xy}. The energy of the $t_{2g}(d)$ orbitals in $M(CO)_6$ is depressed by their interaction with the $t_{2g}(CO\pi^*)$ orbitals, as shown in Figure 1. Thus, placing on the z axis a ligand L having π^* orbitals which interact less effectively than those of CO with the $t_{2g}(d)$ orbitals will cause the d_{xz} and d_{yz} orbitals to lie at higher energy than the d_{xy} orbital. It is, of course, likely that the CO group opposite the poor π-acceptor, L, will increase its degree of π interaction. However, this will only partially compensate for the replacement of a CO by L, thus leaving a net change in the energies of the xz and yz orbitals which is qualitatively in the sense just specified.

On the basis of the foregoing arguments we draw the diagram in Figure 2, in which two extreme cases are considered. In the one case we simply delete one CO group, so that both σ and π interactions at that position are abolished. In the other case, the substituent is one such as an amine, which is a better σ donor than CO but has essentially no interaction with the CO π^* orbitals.

In each case there are now four possible d-d transitions. One ($xy \rightarrow x^2 - y^2$) remains at the same energy as the $t_{2g} \rightarrow e_g$ transition in $M(CO)_6$ in each case. In the $M(CO)_5L$ case the $xy \rightarrow z^2$ transition must be at still higher energy, while the $(xz, yz) \rightarrow z^2$ transition may be higher or lower

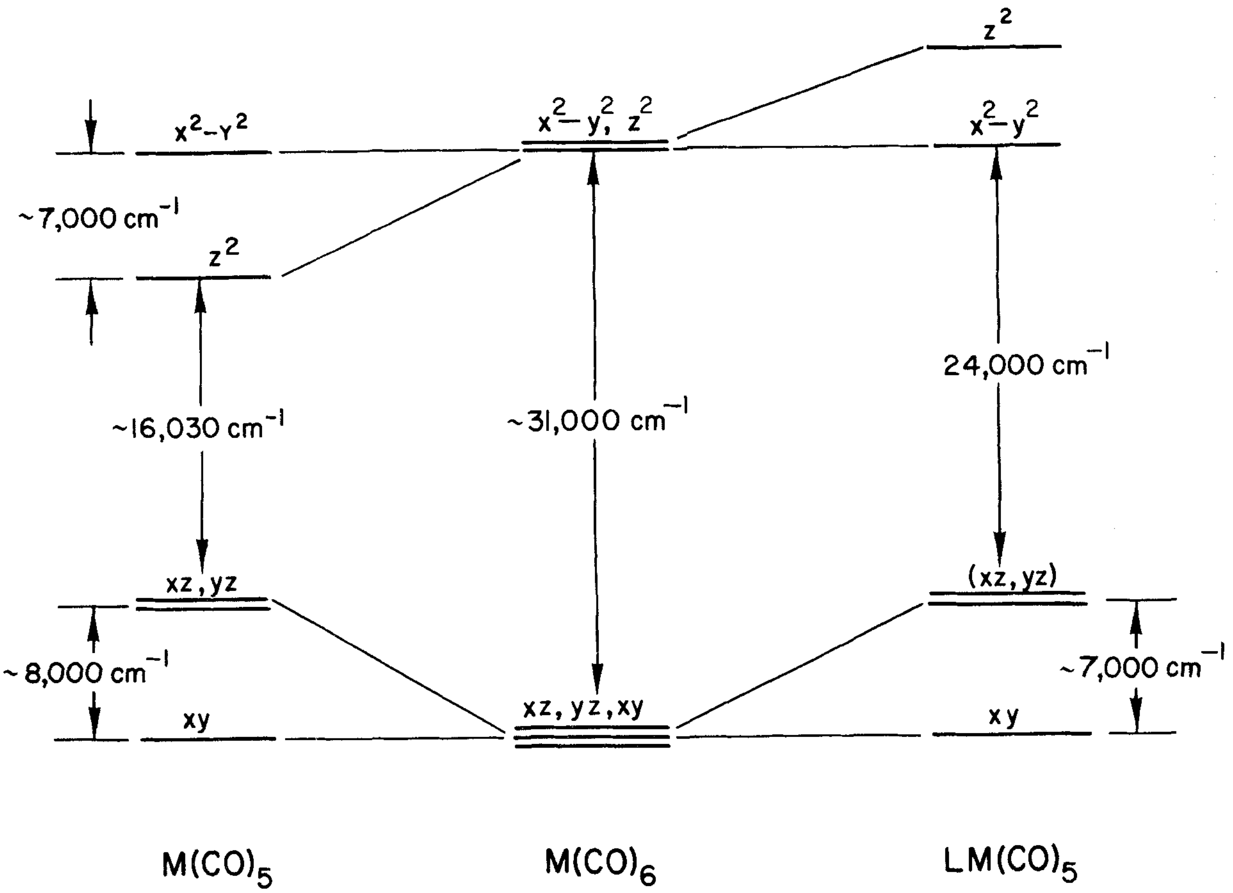

FIGURE 1 A diagram showing how the t_{2g} and e_g molecular orbitals of M(CO)$_6$ should be affected by (left) deletion or (right) replacement of one CO group.

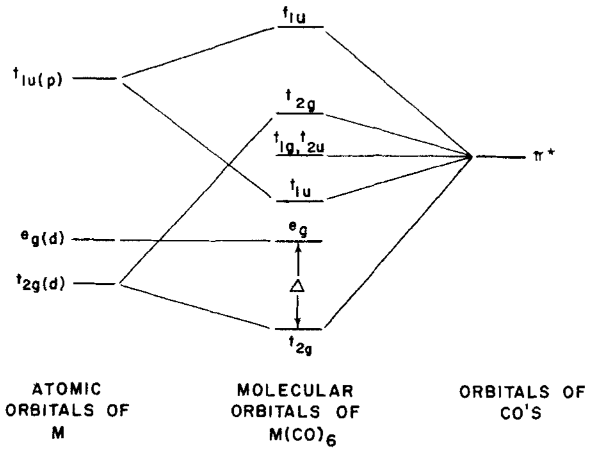

FIGURE 2 A simple molecular orbital diagram for a metal hexacarbonyl. This defines the starting point for deducing the effect of deleting or replacing one CO group.

depending upon the relative magnitudes of the two splittings. For the $(xz, yz) \rightarrow x^2 - y^2$ transition, the energy *must* be lower, by an amount related to the splitting of the $t_{2g}(d)$ set. In the M(CO)$_5$ case, the $(xz, yz) \rightarrow z^2$ transition should be at still lower energy than the $(xz, yz) \rightarrow x^2 - y^2$ transition of M(CO)$_5$L even when L has no π-acceptor capacity whatever.

EXPERIMENTAL DETAILS

The LCr(CO)$_5$ species were all prepared by standard literature methods, and their identities confirmed by elemental analysis and infrared spectra. Their electronic spectra were recorded on a Cary model 14 spectrometer. The spectrum of Cr(CO)$_5$ was recorded by a matrix isolation technique described in full elsewhere.[20]

RESULTS

TABLE I

Proposed assignments of the $(xz,\ yz) \rightarrow x^2 - y^2$ or z^2 transitions in $LCr(CO)_5$ Molecules

Ligand(L)	Bands observed (cm^{-1})	Solvent[a]	ϵ	Reference[b]
——	16,030	neon matrix		
NH_3	23,260	$CHCl_3$	315[c]	
$C_7H_{13}N$	23,585		1500	
CH_3NH_2	23,420		1600	
$C_2H_5NH_2$	23,420		1600	
$C_5H_{11}N$	23,500		3500	18
C_5H_5N	24,570		1500	
	27,400		1500	
	30,770		1500	
$(n\text{-}C_4H_9)_3P$	27,250		900	
	30,770		900	
Ph_3P	27,800		1300	
	27,850		1380	18
	30,900		—[d]	18
	32,000		—[d]	18
Ph_2PH	29,250		1680	18
$(C_6H_{11})_3P$	29,400		1850	18
$(Me_2N)_3P$	29,400		1770	18
$(PhO)_3P$	30,400		1850	18
CO	31,500	acetonitrile	2670	16

[a] The solvent is hexane unless otherwise noted.

[b] Absence of a reference number means data are from present work.

[c] This is a lower limit since $Cr(CO)_5NH_3$ tends to decompose to $Cr(CO)_6$ and the sample used was probably a mixture of these two compounds.

[d] Not reported

Tables I lists the lower energy absorption bands which have been observed and which we propose to assign to the $e \rightarrow b_1$ and $e \rightarrow a_1$ transitions of the $LCr(CO)_5$ and $Cr(CO)_5$ species. Some data from the literature for $LCr(CO)_5$ species are also included. The spectrum of argon matrix isolated $Cr(CO)_5$ has been published.[20b] More recent measurements[20c] using an improved technique for obtaining ultraviolet spectra give a value of 624 nm (16,030 cm^{-1}) for the visible transition in a neon matrix. When the matrix material is a hydrocarbon glass rather than argon, there is a substantial shift of the visible band to higher frequency.[21,22] This may reflect an appreciable intereraction of the metal atom with the hydrocarbon.[23] Furthermore, there is no unequivocal evidence that the species observed in flash photolyses studies[21] is an unpertubed $Cr(CO)_5$ fragment of C_{4v} symmetry.

DISCUSSION

All of the amine-substituted compounds have a band at 23,000–24,000 cm^{-1}. This is some 8000 cm^{-1} below the approximate energy of the $t_{2g} \rightarrow e_g$ transition in $Cr(CO)_6$. When the amine substituent, which has essentially no capacity to engage in π interaction with the chromium atom, is replaced by phosphine ligands, the bands move to higher energies as expected.

As indicated in Figure 2, when one of the positions in the octahedron is *devoid* of both σ and π interactions, the $e \rightarrow a_1$ transition should occur at even lower energy than the $e \rightarrow b_1$ transition. In accordance with this the $Cr(CO)_5$ group has a weak transition at 16,030 cm^{-1}. Evidence that $Cr(CO)_5$ does have a C_{4v} structure under the conditions used to record the electronic spectrum is provided by its ir spectrum.[20b,24]

While the suggested assignment of the low energy bands lacks conclusive proof we think it is an entirely plausible one which gains credence from the way in which the energy of the band varies from (amine)$Cr(CO)_5$ to $R_3PCr(CO)_5$ to $Cr(CO)_5$. While the bands under discussion have intensities which are somewhat greater than the values found for "*d–d*" transitions in the majority of more conventional complexes, we do not believe that any serious doubt about the assignment need be engendered on this basis. It must be recognized that in cases such as the present ones there are strong ligand fields, highly covalent σ and π metal-ligand bonds, and there is no center of symmetry. Therefore, both metal-ligand orbital mixing and *d–p* metal orbital mixing can become great enough to increase intensities from the range of 10–10^2 usually considered typical for *d–d* transitions to about 10^3 as observed here. It may be noted that in several tetrahedral Co^{II} complexes (e.g. those with Br^-, SCN^- and $SeCN^-$ as ligands) molar extinction coefficients well in excess of 10^3 are observed[25] for the visible absorption band which is unquestionably a "*d–d*" band. The visible band has previously[18] been described simply as a charge transfer band; this extreme view does not appear to be necessary.

In the carbonyl compounds considered here another way to interpret the intensities is to say that orbital mixing gives the transitions in question appreciable charge transfer character. Thus under the low symmetry prevailing, these transitions may be "borrowing intensity" from some of the intrinsically strong charge transfer bands in the near ultraviolet. Since intensity borrowing is necessarily accomplished by an interaction which also influences the transition energies, the more so as the energies of the weaker bands approach those of the strong ones, the exact positions of the weaker bands can probably not be reliably predicted by the simple orbital picture used here. In short, while we believe the picture presented has basic qualitative validity, we seriously doubt that *close* and *detailed* comparisons of the π-acidity and/or σ-basicity of a series of ligands can be made without a more refined theoretical basis.[26] Another point which would suggest caution in making quantitative interpretations is the probable variability of the angle between the axial and basal C–M bonds as the matrix and/or ligand is varied.[27] Gross trends, as we have indicated, seem understandable, and the main virtue of the work reported here seems to us to be that it gives a useful order-of-magnitude estimate of the basic bonding components involved.

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