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Infrared and Raman spectra of (η^6-mesitylene)M(CO)$_3$ complexes (M = Cr, Mo or W): an insight into metal–arene bonding

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Infrared and Raman spectra of mesitylene complexes of chromium, molybdenum and tungsten tricarbonyls have been studied. Bands have been assigned and intensities calculated for a number of important modes. The intensities are related to the polarities and polarizabilities of individual bonds within the molecules. Variations of bond properties with change of metal M in the (η^6-mesitylene)M(CO)$_3$ complexes have been examined. The results are interpreted in terms of the relative importance of π-donation from the arene to the metal and of δ-backbonding. A molecular orbital scheme is proposed which accounts for the changes observed in the degree of π- and δ-bonding within the group of complexes studied.

Keywords: Chromium, molybdenum, tungsten, mesitylene metal tricarbonyls, infrared, Raman, spectra, intensities, polarity, polarizability, arene–metal bonding

INTRODUCTION

The nature of the bonding between the arene and metal in (η^6-arene)M(CO)$_3$ complexes (M = chromium, molybdenum or tungsten) is a topic that has attracted much attention. Overlap of arene π-orbitals with metal valence orbitals can result in electron donation from the arene to the metal with both σ- and π-symmetry, and backbonding of δ-symmetry.[1] The relative contributions of these types of interaction are not known.

X-ray studies indicate a 'piano-stool' type geometry for the complexes (Fig. 1), having C_{3v} symmetry for appropriate arenes.[2-6] The C—C bonds in the complexed arene are somewhat longer than in the free arene, suggesting reduced aromaticity in the former.[7] Support for this comes also from some alternation in the C—C bond lengths of the coordinated arene ring observed in low-temperature crystallographic investigations[4,5] and in the room-temperature solid-state structure of hexamethylbenzene molybdenum tricarbonyl.[6]

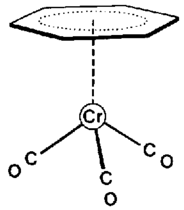

Figure 1 Structure of (η^6-arene)M(CO)$_3$ complexes.

The benzene and hexamethylbenzene compounds crystallize in a staggered conformation[6,8] whilst the mesitylene compounds crystallize in a *syn*-eclipsed geometric form (see Ref. 8, p. 1024). It has been argued that the latter geometry maximizes the overlap between the filled arene π-orbitals and those of the metal, resulting in a stronger metal–arene bond.

Much evidence is available to support the idea that the arene ring in these complexes is electron-depleted relative to that of the free arene. For instance, the chromium compounds have been shown to be more reactive to nucleophilic substitution and less susceptible to electrophilic substitution than the free arenes.[9,10] The arene appears to be positively charged relative to the M(CO)$_3$ group, as electron-releasing substituents on the arene ring increase the molecular dipole moment while electron-withdrawing groups decrease the moment (see Ref. 8, Table 15, p. 1029). The direction of the molecular dipole moment has been verified in NMR studies.[11] Semi-empirical molecular orbital calculations have predicted a net positive charge on the ring, with the size of this charge increasing down the chromium triad.[12,13]

A number of vibrational studies of the (η^6-arene)M(CO)$_3$ complexes have been made, concentrating generally on the carbonyl bands.[14–18] It has been found that the frequency of the carbonyl stretching bands decreases as the electron-donating power of the arene increases. A number of attempts have been made to assign the remainder of the vibrational spectra, but as yet no complete and unambiguous set of assignments has been achieved. A significant factor in solution-state work is the selection of an innocent solvent environment (such as cyclohexane); strongly interacting solvents have been shown to shift band frequencies by up to *ca* 20 cm^{-1}.

Previous evidence regarding the bonding interaction between the arene and the M(CO)$_3$ group has centred around two basic yet conflicting concepts. These are most succinctly stated as:

(1) the M(CO)$_3$ moiety withdraws electrons from the σ-framework of the arene ring, leaving the π-cloud effectively unchanged, and

(2) π-electrons are withdrawn by the M(CO)$_3$ fragment, thus decreasing the aromaticity of the ring.

Neuse[19] interpreted correlations between carbonyl-stretching force constants and Hammett and Taft substituent constants to suggest that the transfer of electronic charge from arene to metal affects the electrons of the σ-framework rather than those of the ring π-system. Support for this was provided from NMR studies detailed in Refs 20–22. Subsequent work in 1980 by Adcock and Aldous[23] dealt with the reinterpretation of the previous NMR data to indicate metal–arene bonding in terms of arene π-electrons alone. At about the same time, other NMR papers appeared both in support of ring current disruption of the arene on complexation[24] and in opposition to this notion.[25] Polarizability anisotropy studies of (η^6-arene)Cr(CO)$_3$ complexes have shown a diminution of 'in-plane' polarizability for the arene ring on coordination with the chromium tricarbonyl moiety, implying a lower aromatic character through π-density depletion.[26] Molecular orbital calculations by Clack and Warren[27] indicated that the π-orbitals of the ring make the dominant contribution to the metal–arene bond. Proposed molecular orbital schemes for these compounds are described in the Discussion section.

Thus, despite the vigorous efforts of numerous researchers over many years, the nature of the metal–arene bond remains a contested subject. Our aim in this study is to try to contribute to an understanding of this problem using evidence from infrared and Raman spectroscopy.

EXPERIMENTAL

Pure samples of the (η^6-mesitylene)M(CO)$_3$ complexes supplied by Mrs R. Clarkson of these laboratories were repurified by vacuum sublimation immediately before use; melting and decomposition points agreed with literature values. The solvents (analytical grade) were degassed with dry nitrogen; solutions were prepared in a dry nitrogen atmosphere using Schlenk techniques. Use of cyclohexane as solvent was attempted but discarded because of low solubilities and absorptions overlapping those of the complexes. Instead, chloroform (infrared) and tetrahydrofuran (Raman) were used.

Infrared spectra were recorded using a Digilab FTS-80 Fourier transform infrared spectrometer with two optical benches, FTS 15/80 and FTS 20/80, configured respectively for far-IR and mid-IR. Raman spectra were excited using 514.5 nm radiation from a Spectra-Physics Model 2025–05 Ar$^+$ laser. The solution samples were held in a quartz cell spinning at 1600 rpm, and the 90° scattered radiation was focused onto the slits of a Jobin–Yvon U1000 double monochromator equipped with a cooled RCA C31034 photomultiplier and photon-counting electronics. Scanning and spectral acquisition were computer-controlled using a Hicom AT personal computer with ISA Enhanced Prism Software (versions 2.1 and 3.0). The spectra were plotted using a Hewlett–Packard 7475 graphics plotter.

Solution samples of known concentration were prepared in an inert atmsophere and transferred by syringe to the solution sample cells for immediate use. Pressed disks in KBr and polythene were prepared in the open, as the compounds are sufficiently air-stable in the solid state. Far-IR solution spectra were recorded using a 0.9 mm solution cell with polythene windows. Mid-IR spectra were recorded using a solution cell with KBr windows having separations 0.10 or 0.025 mm. The resultant spectra were solvent-subtracted using routines contained in the relevant software packages.

The intensities were calculated by measuring the peak areas using the spectroscopic software packages, and also measuring the area of a standard solvent peak for normalization purposes. The peak areas were divided by the molar concentration of the compound and then by the area of the solvent peak to give a normalized area which could be compared directly with results from other spectra. This normalization

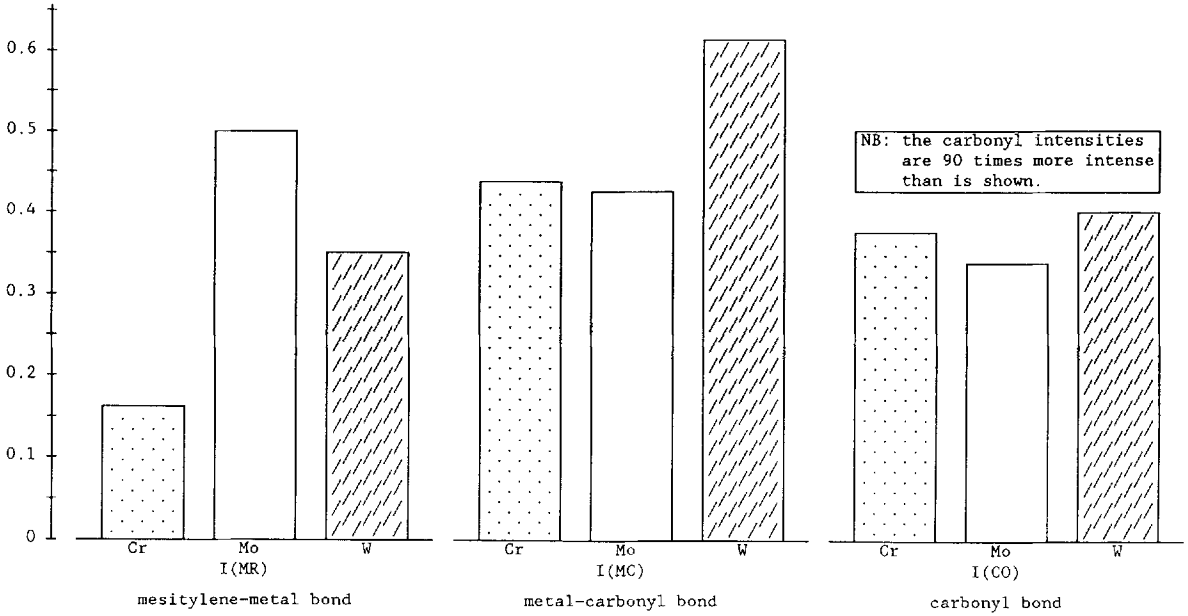

Figure 2 Infrared intensities of (η^6-mesitylene)M(CO)$_3$ complexes (A_1 species).

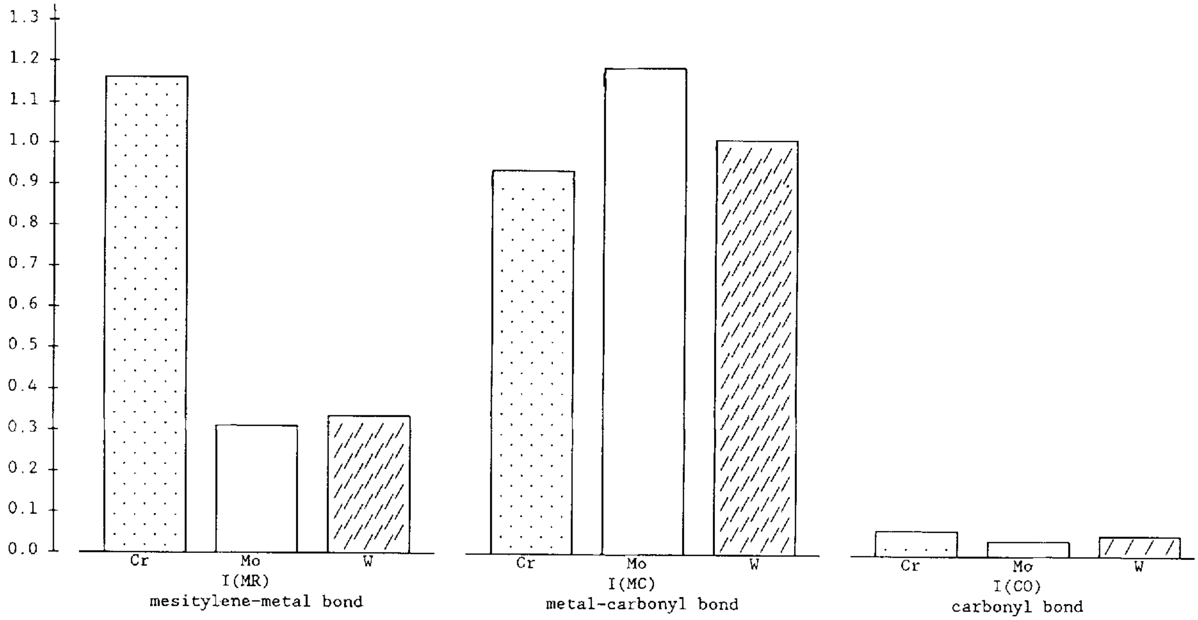

Figure 3 Raman intensities for the (η^6-mesitylene)M(CO)$_3$ complexes (A_1 species).

Table 1 Experimental values for the infrared frequencies of (η^6-mesitylene)M(CO)$_3$ complexes in the solid (KBr) state

Assignment		Experimental values of the infrared frequencies (cm^{-1})		
Sym.	Band[a]	MesCrT	MesMoT[b]	MesWT[b]
A_1	$\delta(\text{R–M–C})$	69	64	67
E	$\delta(\text{R–M–C})$	103	95	99
E	$\delta(\text{C–M–C})$	110	114	120
A_1	$\delta(\text{C–M–C})$		124	129
A_1	$\delta(\text{C–Me})_{\text{oop}}$	199	174 sh 182	168 sh 177
			242	
E	$\delta(\text{C–Me})_{\text{oop}}$	275	274	274
A_1	$\nu(\text{M–R})$	327	303	308
E	$\nu(\text{M–R})$	356	356	361
E	$\delta(\text{C–C–C})_{\text{oop}}$	419	413	
		453		465
A_1	$\nu(\text{M–C})$	487	450	476
E	$\nu(\text{M–C})$	499	461	482
E	$\delta(\text{R})_{\text{oop}}$		492	490
E	$\delta(\text{R})_{\text{ip}}$	513	528	527
A_1	$\delta(\text{R})_{\text{ip}}$	575		
E	$\delta(\text{M–CO})_{\text{ip}}$	549	505	505
E	$\delta(\text{M–CO})_{\text{oop}}$	634	588	579
A_1	$\delta(\text{M–CO})$	675	615	600
A_1	$\delta(\text{R})_{\text{oop}}$		665	657
E	$\delta(\text{C–H})_{\text{oop}}$	864	849	852
E	$\nu(\text{C–Me})$	887	872	869
E	$\delta(\text{C–H})$	967		
A_1	$\nu(\text{C–C})$	1003	986	989
				1004
E	CH_3 rock	1032	1033	1032
			1084	
E	$\delta(\text{C–H})_{\text{ip}}$	1156	1151	1150
			1175	
A_2	$\delta(\text{C–H})_{\text{ip}}$	1224	1227	
		1268	1272	
A_1	$\nu(\text{C–Me})$	1302		1299
A_1	$\delta(CH_3)$	1379	1376	1380
A_2	$\delta(\text{C–H})_{\text{ip}}$	1386	1384	
E	$\nu(\text{C–C})$	1451	1444	1444
E	$\nu(\text{C–C})$	1534	1521	1512
		1643	1636	1633
		1751		
E	$\nu(\text{C–O})$	1853	1859	1854
		1867		
		1872		1879
		1885	1883	
A_1	$\nu(\text{C–O})$		1948	1945
		1967	1960	1956
E	$\nu(CH_3)$	2881	2857	2862
A_1	$\nu(CH_3)$	2930	2924	2925
E	$\nu(\text{C–H})$	2971		2970
		2987	2988	2987
A_1	$\nu(\text{C–H})$	3052	3079	3077
		3086		

[a] R, arene; M, metal; C, carbon; H, hydrogen; Me, methyl; ip, in-plane; oop, out-of-plane. [b] sh, Shoulder.

was of particular importance in measuring the Raman intensities, as the measured peak area is affected by the optical alignment of the particular experiment.

RESULTS

The band frequencies for all vibrations observed in the infrared and Raman spectra of the (η^6-mesitylene)M(CO)$_3$ complexes are tabulated in Tables 1–3. In these tables, the complexes (η^6-mesitylene)M(CO)$_3$ are designated as MesCrT, MesMoT and MesWT for M = Cr, Mo or W, respectively. The assignments were made after detailed inspection and collation of material in Refs 14, 16–18, 28–41. The normalized band areas for the four A_1 vibrations ν(M–Ar), ν(M–CO), ν(C–C) (Raman only) and ν(C–O) for each compound are reported in Tables 4 and 5. For ease of comparison, the relative intensities of the vibrations for each of the three metals in the infrared and Raman spectra are presented graphically in Figs 2 and 3.

Chloroform was used as solvent for the solution-state infrared measurements but it was unsuitable for the Raman measurements because of strong solvent peaks in the low-wavenumber region. To overcome this difficulty and to obtain sufficient solubility, tetrahydrofuran was used (tetrahydrofuran was not suitable for the infrared measurements because of strong absorptions in some of the regions of interest). It was observed that the band frequencies exhibit a small state-dependence. They also differ slightly between the two solvent environments, presumably because of the different electron-donor properties for the solvent molecules in specific solute–solvent interactions.[11] To test the effect of such interactions on the intensities, infrared spectra of the tungsten compound in both solvents were recorded. The peaks which could be observed in both spectra showed small frequency shifts, and the ν(C–O) of E symmetry showed splitting in the chloroform spectrum but not in the tetrahydrofuran spectrum. The areas of the peaks of interest, however, were not affected by changing the solvent. As the compounds are so closely related, it would be expected that any small effects of solvent on the peak areas would not affect the relative intensities between the compounds.

The laser line used in these studies was chosen to be sufficiently distant from any absorbance band of the compounds for the intensities to be unaffected by pre-resonance effects.

DISCUSSION

Quantitative comparisons of the bond strengths are not possible for these compounds without detailed knowledge of the normal coordinates of vibration of each system. In the absence of such data another approach must be adopted.

The frequencies of the CO stretching vibrations can be compared meaningfully as these can be considered to be pure CO stretching modes, independent of the mass of the central metal atom. These modes show very little frequency shift between the compounds, indicating that the degree of back-acceptance by the carbonyl is very much the same for the three mesitylene compounds. The frequency variations of the other bands of interest show qualitatively that there are major differences in bond strengths between the compounds. All M–Ar and M–CO stretching frequencies for the molybdenum compound are lower than those for the tungsten compound which, as Mo is lighter than W, clearly indicates that the bonding is significantly weaker in the molybdenum compound.

Comparison of the intensities is performed only for modes of A_1 symmetry. This is because such modes are polarized along the dipole axis of the compounds and it is along this axis that significant changes in molecular electronic properties occur with substitution of the metal atom.[42]

The outstanding feature of the intensity data is that the intensities do not show a clear trend down the group. In every case, the intensity for the molybenum compound is well out of line with those of chromium and tungsten—see Figs 2 and 3. Whilst there is some variation in the intensity of the CO stretching band in the infrared and Raman, it is small compared with the variation in the M–Ar and M–CO band intensities. This is consistent with the earlier observation that the CO stretching frequencies are close to independent of the central metal atom, and indicates that the electronic structure of the carbonyl group is not greatly affected by the change of metal.

More significant intensity variations occur among the M–Ar and M–CO stretching bands. The infrared intensities are correctly a measure of the change in molecular dipole μ with a change in vibrational state along a normal coordinate Q, i.e. $d\mu/dQ$. If it is assumed that the normal

Table 2 Experimental values for the infrared frequencies of (η^6-mesitylene)M(CO)$_3$ complexes in CHCl$_3$ solution

Assignment		Experimental values of the infrared frequencies (cm^{-1})		
Sym.	Band[a]	MesCrT[b]	MesMoT[b]	MesWT[b]
		53	52	52
E	δ(C–M–C)	75	74	73 76
E	δ(C–M–C)	107 112	108	100 109
A_1	δ(C–M–C)	123	122	
E	δ(R–M–C)	126	94	111
A_1	δ(C–Me)$_{\text{oop}}$	186 199	140 174 181 *sh*	170 173 *sh*
E	δ(C–C)$_{\text{oop}}$	261	260 261 264	261 276
A_1	ν(M–R)	328	300 303 sh	308
E	ν(M–R)	359 362	360 362	359 sh 363
A_1	ν(M–C)	479	452	474 479 sh
E	ν(M–C)	493	457	487
E	δ(R)$_{\text{oop}}$	497 498	493	491
A_1	δ(M–CO)		497	498
E	δ(M–CO)$_{\text{ip}}$	548	505	504
E	δ(R)$_{\text{ip}}$	516	533	531
A_1	δ(R)$_{\text{ip}}$			579
E	δ(M–CO)$_{\text{oop}}$	632	585	585
A_1	δ(M–CO)	669	617	599
E	δ(C–C–C)			645
A_1	δ(R)$_{\text{oop}}$	658	667	663
A_1	δ(C–H)$_{\text{oop}}$	674		
A_1	δ(C–H)$_{\text{oop}}$	836	766	784
E	δ(C–H)$_{\text{oop}}$		846	845
E	ν(C–Me)		872	
E	ν(C–Me)		916	
A_1	ν(C–C)	1002 1007	988 1005	990
E	CH$_3$ rock	1038	1037	1035
E	δ(C–C–H)	1156	1152 1167	1150
A_2	δ(C—H)$_{\text{ip}}$	1222		
A_1	ν(C—Me)	1303	1298	1300
A_1	δ(CH$_3$)	1382 sh 1387	1381	1382
E	ν(C–C)	1445 sh 1455 1492 sh	1453	1443 sh 1452
E	ν(C–C)	1536	1526	1517
		1858 sh	1857 sh	1861 sh 1868 sh

Table 2 (continued)

Assignment		Experimental values of the infrared frequencies (cm^{-1})		
Sym.	Band[a]	MesCrT[b]	MesMoT[b]	MesWT[b]
E	ν(C–O)	1866	1859	1873
		1898	1896	1885
		1900 sh	1899 sh	
A_1	ν(C–O)	1955	1958	1958
		1962	1963	1963
		1969	1970	
E	ν(CH$_3$)			2869
A_1	ν(CH$_3$)			2925
E	ν(C–H)	2988		2970
				2989
A_1	ν(C–H)	3033	3032	

[a] R, arene; M, metal; C, carbon; H, hydrogen; Me, methyl; ip, in-plane; oop, out-of-plane. [b] sh, Shoulder

coordinate is purely associated with the stretching of a given bond, and that the charge separation across this bond is unaffected by the vibrational state, the infrared intensity can be approximated to be a measure of the ground-state bond dipole moment. The Raman intensity can be related similarly to the ground-state bond polarizability.

The largest intensity variation in this series of compounds is for the metal–arene bond stretch in both the IR and Raman spectra. This band is three times more intense in the infrared for molybdenum than for chromium, tungsten being intermediate. The Raman intensity is very much greater for chromium than for the other two metals. This bond is shown therefore to be more polarizable for chromium than for molybdenum or tungsten, but significantly more dipolar for the latter two metals. The metal-arene bond polarizabilities discussed here are not strictly comparable with the estimates of (η^6-mesitylene)M polarizabilities in Ref. 42. The latter include a contribution not only from the polarizability of electrons constituting the metal–arene bond, but also from the intrinsic arene group polarizability in the complex. In addition, they contain an uncertainty arising from use in their derivation of M(CO)$_3$ group polarizabilities from the metal hexacarbonyls; the electron density of the M(CO)$_3$ group in the (η^6-arene)M(CO)$_3$ complexes would be different from that in the corresponding M(CO)$_6$ compound.

The intensity variations of the M–CO stretching band are not as large and are very difficult to explain from the present data alone. In addition to changing the metal M in these complexes, modification of the electronic distribution may be obtained by changing the arene to benzene or hexamethylbenzene (maintaining the three-fold symmetry); such comparisons may provide greater insight into the electronic aspects of the metal–carbonyl bond. A full study of the nine (η^6-arene)M(CO)$_3$ compounds is in progress.

The intensity variations for the metal–arene stretch can be explained in a reasonably consistent manner. The Raman data indicate that there is much more electron density in the region between the metal and the arene for the chromium compound than for the Mo and W compounds. This is indicative of a greater degree of covalence in the chromium–arene bond. As well, the charge separation between arene and M(CO)$_3$ is substantially less in this compound than in the others. As the arene and the M(CO)$_3$ groups are formally neutral, this charge separation within the (η^6-arene)M(CO)$_3$ complex must arise from the interaction between these groups. These interactions, as discussed above, consist of forward-donation from the arene to the metal (σ and π) and back-donation from the metal to the arene (δ). The changes in molecular dipole moment as the arene is varied from benzene to mesitylene to hexamethylbenzene indicate that the arene is positively charged with respect to the M(CO)$_3$ moiety.[26] Methyl substitution on the arene increases its donor strength while decreasing its ability to back-accept electrons; thus the positive

Table 3. Experimental values for the Raman frequencies of (η^6-mesitylene)M(CO)$_3$ complexes in tetrahydrofuran solution

Assignment		Experimental values of the Raman frequencies (cm^{-1})		
Sym.	Band[a]	MesCrT	MesMoT	MesWT
E	δ(R–M–C)	127		
A_1	δ(C–Me)$_{oop}$	187 200	176 190	170
E	δ(C–Me)$_{oop}$	274	276	275
A_1	ν(M–R)	328	302	309
E	ν(M–R)	358	358	364
E	δ(C–C–C)$_{oop}$	413 446		
A_1	ν(M–CO)	482	452	467
E	ν(M–CO)	484	460	476
E	δ(R)$_{oop}$	495	496	
E	δ(R)$_{ip}$	515	514	530
A_1	δ(M–CO)$_{ip}$	545	505	501
A_1	δ(R)$_{ip}$	575	572	572
E	δ(C–C–C)	606		
E	δ(M–CO)$_{oop}$	634	576	
A_1	δ(M–CO)	674	619	603
A_1	δ(R)$_{oop}$	660	666	658
A_1	δ(C–H)$_{oop}$	830		
E	δ(C–H)$_{oop}$			851
E	δ(C–H)$_{ip}$			947
E	ν(C–Me)		898	
A_1	ν(C–C)	1002	987	989
		994	997	
E	CH$_3$ rock	1040	1040	1027
				1122
E	δ(C–H)$_{ip}$		1155	1155
A_2		1269		1254
A_1	ν(C–Me)	1303	1298	1299
A_1	δ(CH$_3$)	1388	1387	1387
		1415		
E	ν(C–C)	1449	1449	1454
		1475		
		1487	1490	1493
E	ν(C–C)	1538	1530	1521
			1677	
			1780	
E	ν(C–O)	1882	1880	1877
A_1	ν(C–O)	1959	1961	1958

[a] R, arene; M, metal; C, carbon; H, hydrogen; Me, methyl; ip, in-plane; oop, out-of-plane.

charge on the arene ring is expected to be least for benzene.

Infrared intensities indicate that the charge separation between arene and M(CO)$_3$ is least for chromium in the (η^6-mesitylene)M(CO)$_3$ series, whilst the Raman data show that the chromium complex has the greatest electron density in the internuclear space. These observations suggest that there are strong and nearly balanced forward and back chromium–arene bonding interactions.

Table 4 Relative intensities of the infrared bands of (η^6-arene)M(CO)$_3$

Complex	Vibration		Frequency ν(cm^{-1})	Intensity, $I_n = I_c/I_s$^{a}
	Sym.	Band		
MesCrT	A_1	ν(MR)	328	0.16
	A_1	ν(MC)	484	0.44
	A_1	ν(CO)	1962	33.2
MesMoT	A_1	ν(MR)	302	0.50
	A_1	ν(MC)	450	0.42
	A_1	ν(CO)	1950	
			1964	31.0
MesWT	A_1	ν(MR)	309	0.35
	A_1	ν(MC)	474	0.61
	A_1	ν(CO)	1946	
			1962	36.4

^{a} I_n = normalized intensity; I_c = intensity normalized for concentration; I_s = intensity of standard solvent peak.

Table 5 Relative intensities of the Raman bands of (η^6-arene)M(CO)$_3$

Complex	Vibration		Frequency ν(cm^{-1})	Intensity, $I_n = I_c/I_s$^{a}
	Sym.	Band		
MesCrT	A_1	ν(MR)	328	1.18
	A_1	ν(MC)	481	0.93
	A_1	ν(CC)	994	0.22
	A_1	ν(CO)	1959	0.05
MesMoT	A_1	ν(MR)	303	0.32
	A_1	ν(MC)	451	1.17
	A_1	ν(CC)	987	0.16
	A_1	ν(CO)	1961	0.04
MesWT	A_1	ν(MR)	309	0.33
	A_1	ν(MC)	466	1.01
	A_1	ν(CC)	989	0.28
	A_1	ν(CO)	1958	0.05

^{a} I_n = normalized intensity; I_c = intensity normalized for concentration; I_s = intensity of standard solvent peak.

The lower Raman intensities for the molybdenum and tungsten compounds indicate that the corresponding covalent interactions are smaller. The relative strengths of the forward- and back-bonding interactions can be deduced from the metal–arene bond polarity, which is greater for molybdenum than for tungsten (from infrared intensities). Thus the forward donation from arene to metal appears to decrease down the group, Cr > Mo > W, while the extent of back-bonding appears to change in the order Cr ≫ Mo < W.

The strength of the interaction is a function of both the spatial overlap of the metal and the arene orbitals and the energy separation of the orbitals. A model of the orbital energies which gives results similar to the above and which is consistent with the known trends in energies may be constructed. It is shown in Ref. 43 that the energy of the metal bonding orbitals is lowest for molybdenum. This result is obtained by both Fenske–Hall MO calculations and photoelectron spectroscopy. The splitting of the metal *d* orbitals due to interaction with the carbonyls is somewhat less for chromium than for the other two metals.[13,44,45] This leads to the construction of the qualitative MO diagrams of Fig. 4. It can be seen that the energy matches for both forward- and back-donation are closest for chromium, while the energy match for forward-donation decreases in the order Cr > Mo > W, as does the degree of interaction observed experimentally. The energy match for the δ interaction is worst for molybdenum.

The MO scheme is similar to those in Refs 46 and 47. In the proposed scheme the energy separations of the arene π-system and the metal *d*-orbitals are such that the main metal–arene bonding interaction involves the arene π-electrons—these interactions are sufficient to account for the observations discussed so far. The results suggest that δ-back-bonding is important in these compounds and particularly in the case of the chromium complex. The energy denominators for the bonding interaction between the arene σ-system and the metal orbitals will be large and it is unlikely that the spatial overlap for such interactions will be as good as for the arene π-system. Our conclusions are consistent with other evidence[42] that the mobility of the arene π-system is substantially increased in a direction perpendicular to the arene ring in the complex relative to the free arene.

It is worthy of note that the A_1 CO stretching frequency is almost invariant within this group of compounds although, for a given metal, substitution on the arene can lead to significant shifts in the position of this band. It is probable that this result is coincidental, as there is no reason to expect that the degree of back-bonding between the metal and the carbonyl should be the same in all three cases. The effects of the arene are mediated through metal orbitals of varying energies. From the above discussion the electron

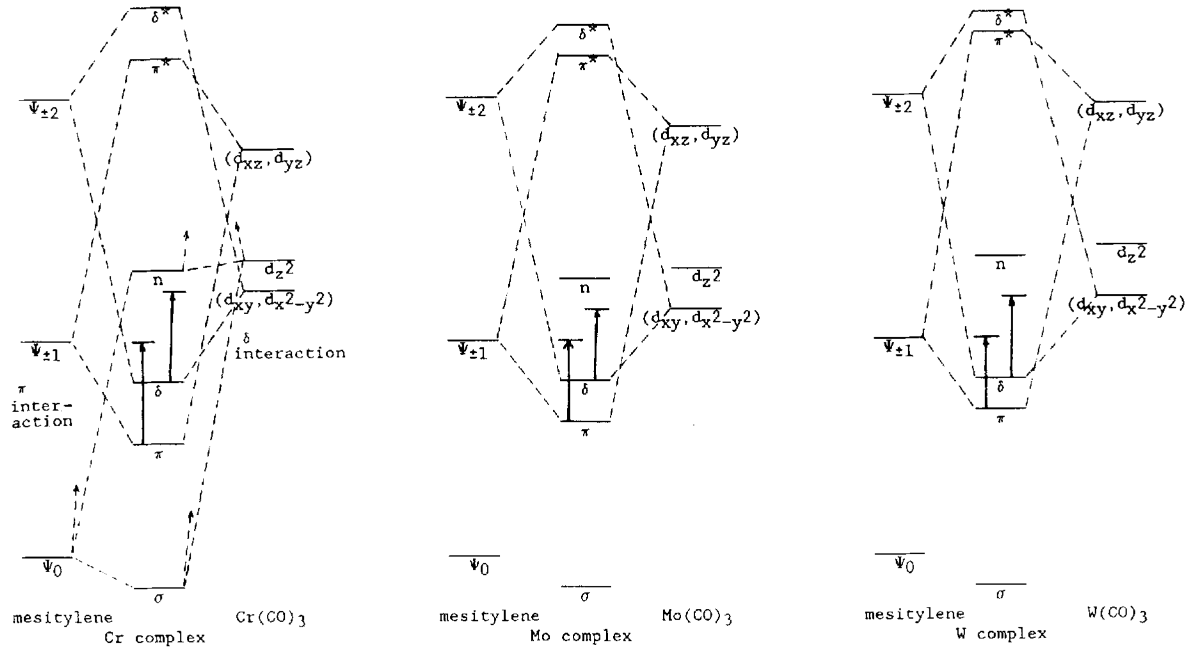

Figure 4 MO diagrams for the (η^6-mesitylene)M(CO)$_3$ complexes, where M = Cr, Mo and W.

density on the M(CO)$_3$ moiety varies significantly over this group of compounds, and this variation is centred about the metal, leaving the CO groups relatively unaffected. The strong similarities in the intensities of the CO stretch also indicate that the electronic structure of the carbonyl is similar in all cases considered.

There is some intensity variation in the M–CO stretch. In the case of chromium and molybdenum, the infrared intensities are very similar whilst the intensity for tungsten is greater. This may reflect variations in the σ-interaction between the metal and the carbonyl; such interaction would not be expected to affect the carbonyl stretch. Also, as shown in Tables 2 and 3, this mode is much closer in energy to other vibrations of the same symmetry than are the metal–arene stretch and the CO stretch. The intensity of this band may therefore reflect charge distributions other than the polarity of the M–C bond, due to coupling with nearby modes. The degree of coupling depends on the difference in frequency between the modes, and this varies between the metals.

Raman intensity measurements have also been made for the ring breathing mode of the coordinated mesitylene. Comparable intensity measurements in the infrared could not be made because the bands are weak, and the subsequent error in intensity would make meaningful comparison of the three compounds impossible. Structural studies have shown some localization of the arene π-system in these compounds.[4–6] It was hoped that the present study might give some further information concerning the bonding in the ring.

The π-bonding in the arene ring appears to be weaker in the molybdenum and tungsten compounds than in the chromium compound, as all bands assigned as ring C–C stretching modes occur at lower frequencies in the first two cases. This observation is contrary to the assertion that the forward- and back-bonding are both strongest in the chromium case, as this would lead to a decrease in π-bonding density and an increase in π-antibonding density on the ring. However, it is consistent with the more pronounced bond length alternation for tungsten and molybdenum relative to chromium. The Raman intensity of the ring breathing mode is variable among these compounds, being greatest for tungsten and least for molybdenum. Further information is required to allow the frequency and intensity observations to be related to the electronic structures of the compounds.

It is worth noting that the orbital symmetries are such as to virtually prevent synergistic electronic interactions between the carbonyls and the arene ring. The compounds may be regarded as pseudo-octahedral, with axes along the M–CO bonds. The orbitals involved in acceptance of electron density from the carbonyls in a σ-fashion are also involved in π-acceptance from the arene. The orbitals involved in δ-back-bonding with the arene are involved in π back-bonding to the carbonyls. There is one possible channel for synergistic interaction, as the orbital involved in σ-acceptance from the arene is of π-symmetry relative to the carbonyls, but the overlap of this metal orbital with the ring π-electrons may be small. This suggests that the CO stretching frequency in these compounds is influenced not by the electron donating power of the arene, but by competition with the arene for back-donated electron density. The back-accepting ability of the arene would be increased by the presence of electron-withdrawing substituents, along with the decrease in donating ability.

CONCLUSIONS

Vibrational frequencies and intensities of mesitylene complexes of chromium, molybdenum and tungsten tricarbonyls have been studied. Bands have been assigned and intensities calculated for a number of important modes. Relationships between infrared and Raman intensity data and individual bond properties have been determined but in some cases such relationships are difficult to establish. Variations in metal–arene stretching intensities, with change of metal M in (η^6-mesitylene)M(CO)$_3$ complexes, have been explained in terms of a molecular orbital scheme. An important result of this study is that δ-bonding, particularly between arene and chromium, is shown to be a significant contributor to the stability of these complexes.

The infrared intensity is a measure of the charge separation between M(CO)$_3$ and the arene, giving an indication of the relative electron depletion of the arene on coordination. The results correlate with earlier evidence showing decreased aromaticity of the coordinated arene and increased susceptibility to nucleophilic substitution compared with the free arene.[8,11,42] The present analysis has given only limited information concerning the electronic structures of the arene and M–CO groupings in the complexes; further data from benzene and hexamethylbenzene analogues are needed to allow a more detailed analysis of bonding in these complexes.

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