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Dielectric, electro-optic and spectroscopic properties of (η^6-arene)M(CO)$_3$ complexes (M = Cr, Mo or W): a study of metal-arene interactions

M.J. Aroney, R.M. Clarkson, R.J. Klepetko, A.F. Masters and R.K. Pierens
Department of Inorganic Chemistry, University of Sydney, Sydney, N.S.W. 2006 (Australia)

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Abstract

Electric dipole moments, optical polarisabilities, infrared, ^{1}H and ^{95}Mo NMR spectra of a number of (η^6-arene)M(CO)$_3$ complexes, where M is Cr, Mo or W, were examined to provide information on metal-arene interactions and on intramolecular electronic transmissions. It was shown that greater electron displacements from the arene to the metal occur with the heavier metals, but this is largely localised in the metal-arene electron system with the carbonyl ligands little affected by change of metal M.

Coordinative interaction between the arene and M(CO)$_3$ fragments results in a metal-arene moiety with very high polarisability along the bond axis and relatively free electron transmission in that direction. The observations also suggest strong π-, and possibly δ-, character for the metal-arene bond and magnetic anisotropy of the electron system with the maximum susceptibility perpendicular to the M-arene bond axis. Further evidence for π-bonding is provided from ^{95}Mo NMR studies of (η^6-arene)Mo(CO)$_3$ complexes. Polarisability data and *ortho*-benzylic ^{1}H NMR couplings are interpreted to show decreased aromaticity in the arenes on complex formation with M(CO)$_3$; from the latter, it appears that ring current depletion is greatest for complexes of the heavier metals.

Introduction

The nature of the metal-arene bond in (η^6-arene)M(CO)$_3$ complexes is not well understood. Further, little is known of the effects on such bonding of change of the metal component M. The work now reported is a sequel to an earlier study by Aroney et al. [1] in which chromium-arene interactions were investigated by studies of electric dipole moments, infrared carbonyl stretches, and anisotropic optical polarisabilities of a range of (η^6-arene)tricarbonylchromium(0) complexes. A similar approach has now been applied to the study of (η^6-arene)M(CO)$_3$ complexes to

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explore changes in such properties and on metal–arene interactions resulting from replacement of Cr by Mo or W.

Experimental

The complexes were prepared by published methods [2–4], and were purified by repeated vacuum sublimation to recognised criteria of purity (m.p/dec.p., IR, ^{1}H NMR and mass spectra). Solvents (analytical grade) were purified and dried immediately before use.

Solute dipole moments μ and electric birefringences, the latter expressed as molar Kerr constants $_{\mathrm{m}}K$, were determined in cyclohexane at 298 K. The experimental procedures, symbols, methods of calculation and solvent constants are given in refs. 5–7. Oxygen was removed from the solvents by saturating them with dry nitrogen; the preparations and handling of solutions were carried out under a dry, inert (N_2) atmosphere. Infrared spectra were obtained on a DIGILAB FTS 80/20 Fourier transform infrared spectrometer. ^{1}H NMR spectra were recorded in deuterated cyclohexane at 298 K on a Bruker WM400 NMR spectrometer; the spectra were referenced to the residual proton resonances in the solvent ($C_6D_{11}H$ in C_6D_{12} taken as δ 1.38 ppm). ^{95}Mo NMR spectra were recorded at 26.06 MHz using dichloromethane as the solvent; these were referenced to an external aqueous solution of 2 *M* Na_2MoO_4 at pH 11 taken to be 0.00 ppm.

Results and discussion

Infrared spectra

The carbonyl stretching frequencies for the (η^6-mesitylene)M(CO)$_3$ complexes in cyclohexane are shown in Table 1. They are in reasonably good agreement with values previously reported [8,9]; computer handling of the data allows small differences between the positions of the peak maxima to be determined.

The frequencies of both the A_1 and E modes show group irregularities. Those for the A_1 stretches are in the order Cr < W < Mo confirming that found by Fisher [8] and in contradiction to that, Cr > Mo > W, reported by Kobayashi et al. [10]. Hambley and Lay [11,12] have suggested a number of factors which may contribute to the change in carbonyl stretching frequency resulting from replacement of one metal by another. These include (i) changes in σ-polarisation of the M←CO bond leading to a different degree of inductive withdrawal of electrons from CO; (ii) π-back bonding between filled *d*-orbitals on the metal and carbonyl π^*-orbitals;

Table 1

Infrared carbonyl stretching frequencies for (η^6-mesitylene)M(CO)$_3$ complexes in cyclohexane [a]

Metal in (η^6-mesitylene)M(CO)$_3$	Cr	Mo	W
A_1 (cm^{-1}) [b]	1969.8	1973.4	1972.0
E (cm^{-1}) [c]	1902.3	1902.5	1898.7

[a] Uncertainty is ±0.5 cm^{-1}. [b] A sharp band resulting from the symmetric vibration A_1. [c] A broad band of lower energy resulting from the doubly-degenerate vibration E.

Table 2

Electric dipole moments, molar Kerr constants and molecular polarisabilities of complexes (η^6-mesitylene)M(CO)$_3$ from measurements in cyclohexane at $T = 298$ K and $\lambda = 589$ nm [a]

Metal in (η^6-mesitylene) M(CO)$_3$	$10^{30}\mu$ [c] (C m)	$10^{27}_{\infty}({}_{m}K_2)$ [d] (m^5 V^{-2} mol^{-1})	$10^{40}\Gamma$ [e] (C m^2 V^{-1})	$10^{40}\Gamma$(calc.) (C m^2 V^{-1})	$10^{40}b_1$ (C m^2 V^{-1})	$10^{40}b_2$ ($= b_3$) (C m^2 V^{-1})
Cr [b]	17.7 ± 0.1	1323 ± 28	4.24 ± 0.09	−6.1	33.5 ± 0.1	29.3 ± 0.1
Mo	19.5 ± 0.6	2285 ± 60	6.01 ± 0.34	−6.1	37.2 ± 0.2	31.1 ± 0.1
W	20.9 ± 0.4	2640 ± 170	6.05 ± 0.36	−6.1	37.5 ± 0.2	31.5 ± 0.1

[a] Dipole moments, molar Kerr constants and polarisabilities are expressed in SI units. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are, respectively: 1 C m = 0.2998×10^{30} D, 1 m^5 V^{-2} mol^{-1} = 0.8988×10^{15} e.s.u. mol^{-1}, 1 C m^2 V^{-1} = 0.8988×10^{16} cm^3. [b] Parameters for (η^6-mesitylene)Cr(CO)$_3$ are quoted from [1]. [c] Determined by the refractivity method on the basis that the molar distortion polarisation is equal to 1.05 times the molecular sodium D-line refractivity. [d] $_{\infty}({}_{m}K_2)$ designates the solute molar Kerr constant at infinite dilution. [e] Solution of the quadratic equation (1) yields an alternative set of Γ values; these, however, are physically impossible and have been ignored.

and (iii) π-forward bonding between filled $p\pi$ carbon orbitals of the carbonyl group and available empty d orbitals of the metal. Factor (i) depends on the relative electronegativities of Cr, Mo and W, which is a contentious issue, while (ii) and (iii) depend on the matching of energies of metal d-orbitals with those of carbonyl. From the infrared results it is not possible to separate these effects and to gauge the relative importance of each. However, it appears from the very small differences observed between the carbonyl stretches of the three complexes that the balance between the factors and the net electron distribution associated with the bound carbonyl groups are not sensitively affected by change of metal within the group.

Polarity and polarisability

Electric dipole moments measured in the non-interacting solvent cyclohexane, are listed in Table 2. The moments are large and increase in the order Cr < Mo < W, suggesting greater electron displacements from the arene to M with the heavier metals [13]. SCCC molecular orbital calculations by Brown and Rawlinson [14] support this view. Such changes in electron distribution are largely localised in the metal–arene bonding system since the infrared data show that the electron charge densities in the carbonyl groupings are almost invariant.

The (η^6-mesitylene)M(CO)$_3$ molecules have a "piano-stool" type geometry and can be represented by polarisability ellipsoids of revolution. The latter are defined by the principal molecular polarisabilities b_1 and $b_2 = b_3$, where 1 is along the M–arene bond axis (the molecular C_3 symmetry axis). The molecular optical anisotropy Γ, defined as $(b_1 - b_2)$, can be obtained from the experimental molar Kerr constant using equation (1) [15].

$$ {}_{m}K = (N/405kT\epsilon_0)\left[({}_{D}P/{}_{E}P)\Gamma^2 + (kT)^{-1}\mu^2\Gamma\right] \qquad (1)$$

where $_{D}P$, $_{E}P$, N, k, T, and ϵ_0 refer to the molar distortion polarisation, the molar electron polarisation, Avogadro's number, the Boltzmann constant, the absolute temperature and the permittivity of a vacuum, respectively. The ratios $_{D}P/_{E}P$ were taken as 1.1, a sufficiently good approximation in this work [1]. The Γ values so found are given in column 4 of Table 2. In column 5 are shown anisotropies Γ(calc.) which are obtained by additivity of Γ of the arene and of the $M(CO)_3$ fragments before they are mutually perturbed through bonding interactions *.

For each of the complexes studied, it is seen that coordination of the free arene with $M(CO)_3$ leads to a dramatic change in the optical anisotropy giving sign reversal of Γ. This means that the coordinative interaction results not only in permanent electron charge displacement from the benzenoid ring to M but also in a very large enhancement of electron polarisability in the same direction. The change in anisotropy $\Delta\Gamma = \Gamma - \Gamma(\text{calc.})$, is 10.3, 12.1 and 12.2 ($\times 10^{-40}$ C m^2 V^{-1}) for Cr, Mo and W, respectively. Since π-electron systems are known to be highly polarisable along the bond axis, in contrast to systems where electrons are constrained in σ-bonds [6,15], the present results are regarded as providing strong evidence for a substantial π- and possibly δ-bond character for the metal–arene bonds.

The directional molecular polarisabilities for a complex can be deduced from the experimental Γ value and the sum $(b_1 + 2b_2)$ obtained from the molar electron polarisation ** using equation 2 [15]. These are shown in columns 6 and 7 of Table 2.

$$_{E}P = N(b_1 + 2b_2)/9\epsilon_0 \tag{2}$$

Inspection of the principal components of the molecular polarisability tensors clearly indicates the predominance of b_1 relative to b_2 and b_3 in each of the complexed species.

Polarisability parameters for the (η^6-mesitylene)M segment cannot be accurately determined. An approach adopted in this work is to subtract from the molecular b_i values of the complex, the polarisability contribution of the metal tricarbonyl group obtained from the appropriate $M(CO)_6$ compound. The $M(CO)_3$ groups are ca. isotropic (as explained previously) with b(mean) values of 10.8, 12.1 and 12.3 ($\times 10^{-40}$ C m^2 V^{-1}), respectively; i.e. half of the b(mean) for Cr, Mo and W hexacarbonyl, respectively [20]. The polarisability estimates for the (η^6-mesitylene)M segments are listed in Table 3 together with differences Δb_i between the b_i values of the (η^6-mesitylene)M group and those of the uncomplexed mesitylene ligand. These data can only be regarded as approximate since the electron density and hence b(mean) for the $M(CO)_3$ group in (η^6-arene)$M(CO)_3$ would differ from that in the corresponding $M(CO)_6$ compound. The Δb_1 values are seen to be large and positive. The electron system constituting the metal–arene bond is in each case very highly polarisable along the bond axis. This is consistent with a high electron mobility along that axis and with substantial π-character for the M–arene bond. The differences between the Δb_1 estimates with change of metal cannot be regarded as meaningful in view of uncertainties up to $\pm 1 \times 10^{-40}$ C m^2 V^{-1}.

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[*] The anisotropy of the free mesitylene molecule is -6.1×10^{-40} C m^2 V^{-1} [16], the negative sign arising from our designation of axes in this work. The in-plane polarisabilities $b_2 = b_3$ are greater than b_1 which is perpendicular to the aromatic ring plane, and $\Gamma(= b_1 - b_2)$ is negative. In the case of the $M(CO)_3$ fragment, tensor additivity of three anisotropic M–CO groups which are near mutually perpendicular, i.e. C–M–C angles are close to 90°, [17,18], leads to a ca. optically isotropic $M(CO)_3$ moiety [15].

[**] Molar electron polarisations were estimated from molecular refractivities to be 75.1 cm^3 and 75.9 cm^3 for the Mo and W complexes, respectively [19].

Table 3

Anisotropic polarisabilities $10^{40}b_i$ (C m^2 V^{-1}) of (η^6-mesitylene)M in comparison to those of the free mesitylene ligand

Metal M in (η^6-mesitylene) M(CO)$_3$	(η^6-mesitylene)M		mesitylene [b]		b_i(η^6-mesitylene)M − b_i(mesitylene) [c]	
	b_1	$b_2 = b_3$	b_1	$b_2 = b_3$	Δb_1	$\Delta b_2 = \Delta b_3$
Cr [a]	22.7	18.5	13.2	19.3	9.5	−0.8
Mo	25.0	19.0	13.2	19.3	11.8	−0.3
W	25.2	19.2	13.2	19.3	12.0	−0.1

[a] From data in [1]. [b] Anisotropic polarisabilities of mesitylene are from [16]. [c] Uncertainty may be as high as $\pm 1 \times 10^{-40}$ C m^2 V^{-1}.

The polarisabilities b_2 and b_3 of the (η^6-mesitylene)M segment contain contributions from the "in-plane" electrons of the complexed arene as well as from the electron system directly involved in metal–arene bonding. The Δb_2 and Δb_3 values are close to zero and it follows that the "in-plane" polarisabilities of the coordinated arene would in each case be substantially smaller than those of the free arene molecule. This is consistent with π-electron depletion and reduced aromatic character for the arene in the complex. Such conclusions, earlier drawn for (η^6-arene)Cr(CO)$_3$ complexes [1], are now shown to apply as well to those of molybdenum and tungsten. The relative closeness of the Δb_2(Δb_3) estimates, in view of possible errors, does not allow further interpretation in terms of periodic group trends.

^{1}H NMR chemical shifts

Upfield shifts of 2.053, 1.758 and 1.900 (ppm) * are found for the mesitylene ring proton resonances on complex formation with Cr, Mo and W tricarbonyl, respectively. The cause of such shifts and the trend, Cr > W > Mo, have been the subject of earlier studies [21] but no definitive explanation has emerged [22]. Following ref. 1, the large polarisability anisotropy found for each M–arene moiety is taken to indicate a large magnetic anisotropy for the metal–arene bonding electrons with the maximum magnetic susceptibility at right angles to the metal–ring bond axis. This is an important factor in accounting for the shifts upfield of the arene resonances following complex formation. A ^{13}C solid-state NMR study by Maricq et al. [23] supports such conclusions.

An alternative approach in probing the aromaticity of the coordinated arenes is afforded by studying benzylic couplings between an arene proton and those of an *ortho* methyl group. Sternhell and coworkers [24] have shown for methyl substituted aromatics that the benzylic coupling constants correlate well with the π-bond order of the connecting C$_{ar}$–C$_{ar}$ bond. The coupling constants for the (η^6-mesitylene)M(CO)$_3$ complexes of this study could not be resolved but the peak widths at half height for the proton resonances were recorded—see Table 4.

The smaller peak widths on complexation indicate reduced *ortho* benzylic couplings and hence decreased aromaticity in the coordinated arene. The couplings decrease in the order Cr > Mo ≈ W, which is evidence to suggest that bonding with

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* Measured in deuterated cyclohexane (±0.005 ppm)

Table 4

Peak width at half height (Hz) for proton resonances of mesitylene and of (η^6-mesitylene)M(CO)$_3$ complexes [a,b]

Compound	Methyl protons	Arene protons
mesitylene	2.14	2.23
(η^6-mesitylene)Cr(CO)$_3$	1.54	1.92
(η^6-mesitylene)Mo(CO)$_3$	1.12	1.48
(η^6-mesitylene)W(CO)$_3$	1.00	1.34

[a] Measurements in deuterated cyclohexane. [b] Uncertainty ±0.05 Hz.

the heavier metals decreases the aromaticity of the coordinated mesitylene to a greater extent than that with chromium.

^{95}Mo NMR chemical shifts

A study was also undertaken of the ^{95}Mo NMR chemical shifts of the benzene, mesitylene, and hexamethylbenzene molybdenum tricarbonyl complexes. The data are listed in Table 5, together with those for other complexes in the series [(η^6-Me$_{6-x}$C$_6$H$_x$)Mo(CO)$_3$] ($x = 0$–6).

The spectra show very highly shielded signals which are consistent with the high electron density of the zero-valent molybdenum centre [25,26]. The progressive deshielding of the molybdenum nucleus as electron-donating methyl groups are successively added to the benzene ring has been correlated with increasing bond strength of the Mo–arene bond [26]. This interpretation has been supported by relaxation time measurements of the ^{95}Mo, ^{13}C and ^{17}O NMR signals [27]. Thermochemical [28–31] and kinetic [32–34] studies have shown that the Mo–arene bond is strong, but these data do not distinguish between σ- and π-bonding. The relaxation time measurements had established that the relative magnitude of $\delta(^{95}\mathrm{Mo})$ within the series was predominantly due to significant orbital angular momentum contributions to the Mo–arene bonding. Such an orbital angular momentum contribution would be consistent with the presence of Mo–arene π-bonding.

Table 5

^{95}Mo NMR chemical shifts (ppm) for (η^6-arene)Mo(CO)$_3$ complexes in dichloromethane [a]

Arene in (η^6-arene)Mo(CO)$_3$	$\delta(^{95}\mathrm{Mo})$ [b]	Ref.
benzene	−2095.4	[c]
toluene	−2034.0	[d]
o-xylene	−1987.8	[d]
p-xylene	−1979.2	[d]
m-xylene	−1970.6	[d]
mesitylene	−1906.8	[c,e]
	−1906.9	[d]
hexamethylbenzene	−1799.1	[c]

[a] Data obtained from saturated solutions in CH$_2$Cl$_2$ at ambient temperature, and are quoted vs. an external aqueous solution of 2 *M* Na$_2$MoO$_4$ at pH 11, taken to be 0.00 ppm. [b] Uncertainty of present values ±0.2 ppm. [c] This work. [d] Ref. 26. [e] A small solvent dependence of the data is evident. Thus, $\delta(^{95}\mathrm{Mo})$ for (η^6-mesitylene)Mo(CO)$_3$ in CDCl$_3$ is −1902.4 ppm. [19]

The present study extends the range of the ^{95}Mo data to include the terminal members of the (η^6-$Me_{6-x}C_6H_x$)$Mo(CO)_3$ ($x = 0$–6) series, and provides direct and independent evidence for a large π-component in the Mo–arene bonding. The relative magnitudes of $\delta(^{95}Mo)$ within this series of complexes reflect increasing π-bond character of the Mo–arene bond as the number of methyl groups on the arene increases.

Conclusions

Electric dipole moments, optical polarisabilities, infrared, ^{1}H and ^{95}Mo NMR spectra of a number of (η^6-arene)$M(CO)_3$ complexes, where M is Cr, Mo or W, were examined to obtain information on the nature of metal–arene bonding and on intramolecular electronic transmissions. For the complexes (η^6-mesitylene)$M(CO)_3$ it was shown that only small effects on the electron distribution of the carbonyl ligands as a consequence of changing the metal M could be detected by infrared spectroscopy (the carbonyl A_1 stretching frequencies increase in the order Cr < W < Mo); the electric dipole moments increase in the order Cr < Mo < W indicating greater electron displacement from the arene to M with the heavier metals; coordinative interaction between the arene and $M(CO)_3$ fragments results in a bonding electron system for each metal–arene group which is very highly polarisable along the bond axis and this is correlatable with a strong π-component; the metal–arene bonds are magnetically anisotropic with the maximum magnetic susceptibility perpendicular to the M–ring bond axis; the "in-plane" polarisabilities of the coordinated arene are significantly less than those of the free arene indicating decreased aromatic character on complexation; *ortho*-benzylic ^{1}H NMR couplings provide corroborative evidence of decreased aromaticity in the complexed arenes and the ring current depletion is greatest for complexes of the heavier metals. ^{95}Mo NMR spectra of (η^6-arene)$Mo(CO)_3$ complexes are interpreted in terms of metal-arene π-bonding of increasing strength with progressive methyl substitution.

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