Molybdenum-95 and Carbon-13 Nuclear Magnetic Shielding and Bonding Relationships in Sandwich Complexes

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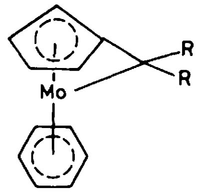
N.m.r. shifts of ^{95}Mo and ^{13}C in sandwich complexes with a range of C_5, C_6, and C_7 ring types are interpreted on a ligand-field model, by comparison with orbital ionisation energies. The shielding increases with forward- and back-bonding, also with η^5, σ-$C_5H_4CR_2$ bonding of the fulvene ligand. The shielding therefore decreases with increase in ring size and from closed to open π systems, and thus with increase in reactivity (or decrease in stability), as observed in sandwich compounds of other transition metals.

Sandwich compounds have been studied by photoelectron (p.e.),[1] e.s.r.[2] and electronic[2] spectroscopy, and by molecular orbital (m.o.) theory.[2–4] Direct n.m.r. observation of the metal nucleus has now been reported for related compounds of ^{25}Mg,[5] ^{91}Zr,[6] ^{57}Fe,[7–9] ^{59}Co,[10–12] ^{99}Ru,[13] and ^{103}Rh,[14] with some correlation of ^{59}Co deshielding and catalytic activity.[12] Our measurements of ^{95}Mo and ^{13}C shifts in sandwich compounds with rings of different types now allow some overall synthesis of the electronic, structural, and spectroscopic relationships.

Results and Discussion

Shielding of the Metal Nucleus.—As shown in the Table, the ^{95}Mo shifts cover a range of 2280 p.p.m. in the sandwich complexes, with inclusion of the benzene–fulvene complexes (**1**) in which the C_5 and C_6 rings are nearly parallel but the exocyclic carbon forms a σ bond to the metal.[15] The ^{95}Mo shielding in complexes (**1**) is at the high end of the known range, comparable with that in complexes of strong ligands such as carbonyl, η^5-C_5H_5, or hydride,[16] and some 560 p.p.m. higher than in bis(benzene)molybdenum. The shielding is very sensitive to ring size, decreasing by 875 p.p.m. from the bis(benzene) to the benzene–tropylium sandwich, or by 1 720 p.p.m. from the bis(benzene) to the bis(cycloheptatriene) complex. In the 'piano-stool' tricarbonyls,[16] also, the ^{95}Mo shielding decreases with increase in ring size, η^5-C_5H_5 > η^6-



(**1**) R = Me or Ph

Table. N.m.r. and other spectroscopic measurements of sandwich complexes of molybdenum[a]

	Compound	Solvent	$\delta(^{95}Mo)$/ p.p.m.	$W_{\frac{1}{2}}$[b]/Hz	$\delta(^{13}C)$[c]/ p.p.m.	$\Delta(^{13}C)$[c]/ p.p.m.	Ionisation energy[d]/eV			Ref. (p.e.s.)[e]
							a_1	e_2	e_1	
(1)	$[Mo(\eta^5, \sigma\text{-}C_5H_4CR_2)(\eta^6\text{-}C_6H_6)]$									
	R = Me	C_6H_6–C_6H_5Me	−1 923	40			6.04	6.55	8.78	28
								7.45	9.79	
	R = Ph	C_6H_5Me	−1 922	300						
	$[Mo(\eta^6\text{-}C_6H_6)_2]$	C_6H_5Me	−1 362	50	75.4	−53.3	5.52	6.59	9.47	30
									10.15	
	$[Mo(\eta^6\text{-}C_6H_5Me)_2]$	C_6H_5Me	−1 270	55	75.0 (C^3)		5.32	6.33	9.05	30
					75.9 (C^4)	−53.5			9.75	
					78.6 (C^2)					
					89.6 (C^1)					
	$[Mo(\eta^6\text{-}C_6H_6)(\eta^7\text{-}C_7H_7)]PF_6$	CH_2Cl_2	−487	150						
	$[Mo(\eta^5\text{-}C_7H_9)(\eta^7\text{-}C_7H_7)]$	C_6H_6–C_6H_5Me	−469	170	82.5(C^2,C^4)		5.62	7.04		
					83.9 (C_7H_7)	−72.4 (C_7H_7)				
					93.1(C^1,C^5)					
	$[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)]PF_6$	CH_2Cl_2	−457	150	102.6 (C^3)					
					86.8 (C_7H_7)	−69.5 (C_7H_7)				
					97.1 (C^4)	*ca.* −30 (C_6H_5Me)				
					98.1 (C^3)					
	$[Mo(\eta^6\text{-}C_7H_8)_2]$	C_6H_5Me	358	100	100.7 (C^2)					[f]

[a] $\delta(^{95}Mo)$ relative to 1 mol dm^{-3} Na_2MoO_4(aq) at pH 11. [b] Linewidth at half-height. [c] δ values are shifts of ring carbons (numbered in parentheses); Δ values are co-ordination shifts relative to the free ligand (see text). [d] Vertical; eV ≈ 1.60×10^{-19} J. [e] Photoelectron spectroscopy. [f] Decomposes.

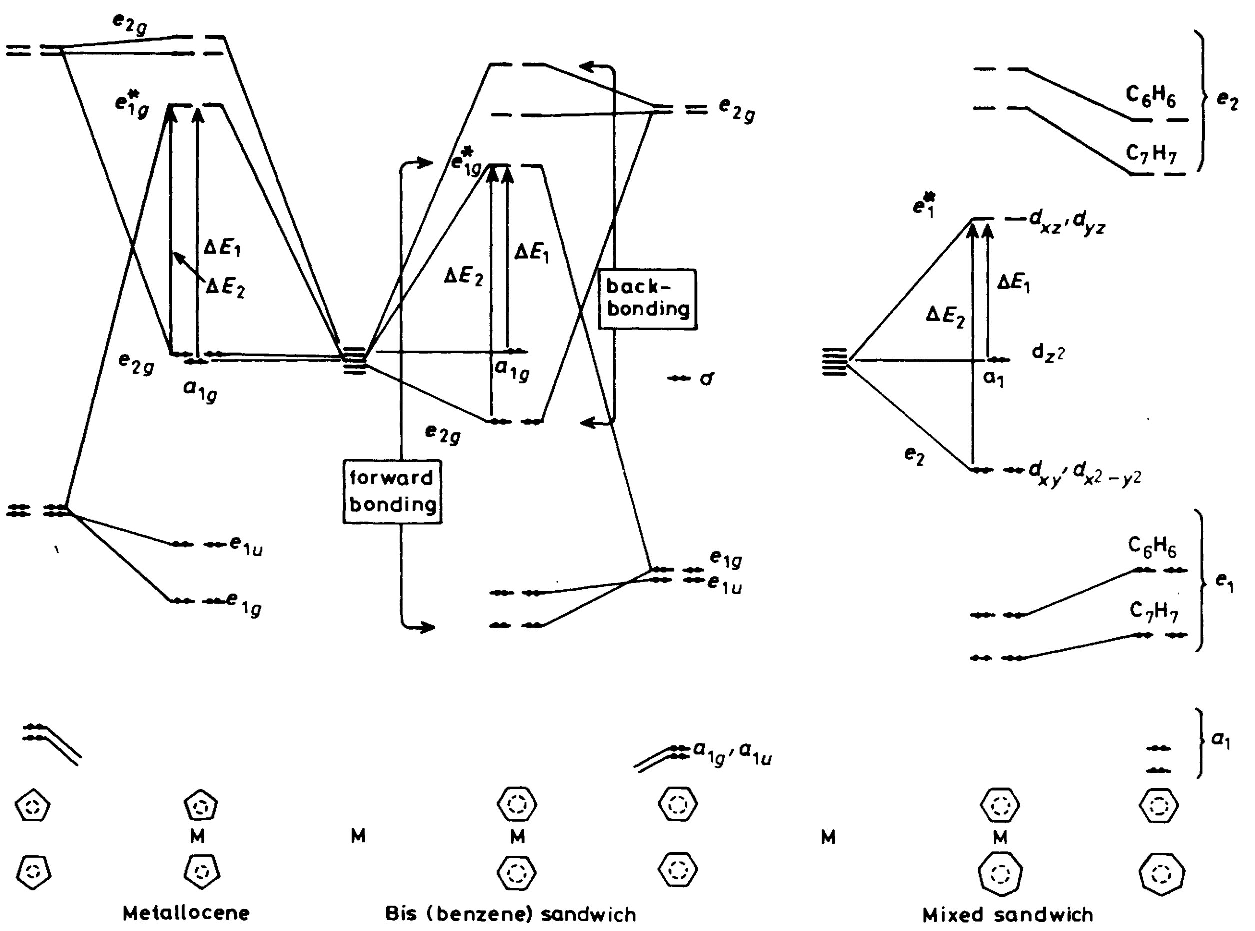


Figure. Orbital interaction diagram for different ring sizes in sandwich complexes

$C_6H_5Me > \eta^6$-C_7H_8, though with smaller decrements than in the sandwich compounds. Similarly, the ^{95}Mo shielding decreases from a closed to an open π system in the ring, as in the η^5-C_7H_9 and η^6-C_7H_8 complexes in the Table.

The shifts are usefully related to an m.o. diagram, as shown in the Figure, by a ligand-field 'atom-in-a-molecule' formulation of Ramsey shielding theory.[17] This was given in approximate form for octahedral Co^{III} by Griffith and Orgel,[18] and adapted to the quasi-$D_{\infty h}$ symmetry of the cobalticenium ion $[Co(\eta^5\text{-}C_5H_5)_2]^+$ by Lucken *et al.*[10] Near-constancy of the diamagnetic term being assumed, the isotropic paramagnetic term σ^P (which is opposite in sign to the chemical shift δ as now defined) was given by equation

$$\sigma^P = -\frac{8\beta^2}{3}\left(\frac{4}{\Delta E_1} + \frac{4}{\Delta E_2}\right)\langle r^{-3}\rangle_d \qquad (1)$$

(1)[10], where ΔE_1 and ΔE_2 are the ligand-field splittings as shown in the Figure, r is the valence d-electron radius, and β the Bohr magneton. The greatest contributions to the deshielding are expected to come from the metal-centred a_1 and e_1 h.o.m.o.s (high-lying occupied m.o.s) because of the low energy of the magnetically active (d–d) excitations. With the quasi-axial symmetry of metallocenes or other bis(arenes) σ^P_{zz} vanishes (in this approximation) leaving 'free' (diamagnetic) electronic circulation about the axis in the magnetic field, but σ^P_{xx} ($=\sigma^P_{yy}$) is more negative, depending on the energy and radial factors in equation (1). Thus sizeable values were observed for the ^{59}Co axial shielding tensor element [σ_{zz} = 67 p.p.t. (parts per thousand)] and for the anisotropy (33.5 p.p.t.).[11]

The chemical shifts are readily related to changes in the bonding *via* the ligand-field excitations. The valence d orbitals lie between the ligand $\pi(e_1)$ and $\pi^*(e_2)$ levels, and ligand-π to metal-σ (L ⟶ M) donation is responsible for the e_{1g}–e^*_{1g} (d_{xz}, d_{yz}) splitting. More efficient forward bonding thus tends to raise the e_{1g} l.u.m.o. (low-lying unoccupied m.o.), increasing ΔE_1 and ΔE_2 and the metal shielding. The (M ⟶ L) back-donation is responsible for the e_{2g}–e^*_{2g} (d_{xy}, $d_{x^2-y^2}$) splitting, so that increased back-bonding tends to lower the e_{2g} h.o.m.o., increasing ΔE_2 and the metal shielding. The a_{1g} (d_{z^2}) level is largely non-bonding (the ionisation energy resembles that of the free metal atom) as overlap with the ligand orbitals is poor, but the energy is expected to vary with the charge on the metal. Increase in negative charge on the metal tends to raise the a_{1g} h.o.m.o. (deshielding) but also to increase $r(d)$, decreasing the radial term $\langle r^{-3}\rangle_d$ (shielding) as a nephelauxetic effect, and conversely. Increased M–L covalency and delocalisation of d electronic charge onto the ligands may also be linked with decrease in the radial term.[17]

Ligand Shieldings.—Co-ordination shifts of the ligand nuclei, also, may be related to the m.o. diagram of the Figure and can be used to cross-check interpretations of the metal shielding. For carbon the dominant excitation energies ΔE are $2p$ (σ ⟷ π), and the angular momentum factors take account of the $2p$ involvement in the M–L bonding. In the Karplus–Pople formulation[19] (2), the ΣQ factor decreases from *ca.* 2.6 for

$$\sigma^{P} = -K\langle r^{-3}\rangle_{2p}\Sigma Q/\Delta E \qquad (2)$$

aromatic carbon ($C_5H_5^-$, C_6H_6, $C_7H_7^+$,..) to 2 for sp^3 carbon.[19] The radial term again depends on the atomic charge but changes in this are relatively small (despite the formal charges).

The well known increase in carbon shielding on polyhapto coordination may thus be linked with decrease in CC bond order (*cf.* the increase in CC stretching frequency) and in the e_1–e_2^* (π–π^*) splitting, the proton resonance following suit. The ligand σ levels are less strongly perturbed by bonding to the metal. The benzene σ-h.o.m.o. in $[Mo(C_6H_6)_2]$, as in benzene, is quite high-lying,[20] and $\sigma \longrightarrow \pi^*$ and $\pi \longrightarrow \sigma^*$ excitations are likely to be relevant. The ^{13}C shielding is increased by stronger forward bonding, increasing $\Delta E(\pi \longrightarrow \sigma^*)$, and by stronger back-bonding, increasing $\Delta E(\sigma \longrightarrow \pi^*)$, each decreasing ΣQ.

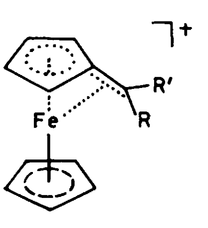
Again, the orbital interpretation can be checked against the shielding tensor elements, reported for $[Cr(arene)(CO)_3]$ complexes.[21] Highest shielding in benzene[22,23] (comparable to that for saturated carbon) is observed for $\sigma_\perp$, dependent on (high energy) $\sigma \longrightarrow \sigma^*$ excitations, lowest shielding for the radial element σ_r, dependent on $\sigma \longleftrightarrow \pi$ excitations, and intermediate shielding for the tangential element σ_t, dependent on ring and substituent $\sigma \longleftrightarrow \pi$ excitations,[24] with anisotropy 180 p.p.m. Complexation of benzene in $[Cr(C_6H_6)(CO)_3]$ changes $\sigma_\perp$ very little (with little change in the σ orbital manifold), increases σ_t slightly, but increases σ_r by 80 p.p.m., following the increase in $\Delta E(\sigma \longleftrightarrow \pi)$. The anisotropy thus decreases by 100 p.p.m., with increase also in local electronic symmetry.

Similarly, in the $C_5H_5^-$, C_6H_6, $C_7H_7^+$ series the well known[25,26] decrease in ^{13}C shielding with increase in ring size is now[23] seen to be mainly in σ_r (in steps of 52 and 46 p.p.m.) and to a lesser extent in σ_t (32 then 22 p.p.m.), whereas $\sigma_\perp$ increases and then decreases (by +12 then −13 p.p.m.). These changes point to the importance of $\sigma \longrightarrow \pi^*$ (rather than $\pi \longrightarrow \sigma^*$) excitations to the carbon shielding: the progressive stabilisation of the π^* l.u.m.o.s with increase in ring size is evident in the Figure.

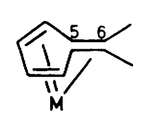
The relatively small influence of inductive or nephelauxetic effects (*via* the $\langle r^{-3}\rangle$ term) is indicated by the small and irregular changes in $\sigma_\perp$, as also by the very small change in σ_r for the *ipso* carbon in C_6H_5X compounds (X = H, F, Cl, Br, I),[27] changes in the other tensor components being sizeable. In all these examples, therefore, the $\sigma \longleftrightarrow \pi$ splittings are important to the shielding, and it is of interest to see if changes in $\delta(^{13}C)$ as well as $\delta(^{95}Mo)$ follow the changes in orbital energy as the ligands are varied in the sandwich complexes.

The Fulvene Ligand.—In the benzene–fulvene complexes (**1**)[15] p.e.s. studies have shown[28] that the bonding of the exocyclic carbon C(6) to molybdenum can be described by coordination of a (d_{z^2}, $d_{x^2-y^2}$) electron pair into a low-lying π^* l.u.m.o. which has a large coefficient on this carbon. The other five orbitals resemble those of an η^5-C_5H_5 ligand, so that this is effectively a mixed sandwich compound in which the d_{z^2} h.o.m.o. is stabilised by the σ-bonding to C(6) and the $d_{x^2-y^2}$ orbital is stabilised relative to the d_{xy} (as evident in the ionisation energies in the Table). The molybdenum is highly shielded (Table) and the shielding is likely to be greater than would be expected for a cyclopentadienyl–benzene sandwich.

Interestingly, the ^{95}Mo shielding is unaffected by replacement of methyl by phenyl substituents on C(6) [in the solid the benzene rings have a propeller-like conformation, minimising conjugation with C(6)].[15] In contrast, the ^{57}Fe shielding in the corresponding cyclopentadienyl–fulvene sandwich $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CRR')]^+$ (**2**) is very sensitive to substitution at C(6), decreasing by 300 p.p.m. from the CH_2 to the CHMe derivative, and by a further 440 p.p.m. to CHPh.[7] This demonstrates the difference in binding of the fulvene ligand in the molybdenum and iron complexes. In the ferrocenylcarbenium ions (**2**) the ligand is intermediate between the η^5, σ-$C_5H_4CR_2$ bonding observed in the molybdenum complexes (**1**) and η^6-fulvene bonding in (**3**), as shown by *X*-ray crystallographic measurements.[15,29] When C(6) only semi-bridges the ring and the metal [as in (**2**)] it is understandable that changes in the R groups can significantly affect the interaction with the d_{z^2} electron pair to which the metal nucleus shift is very sensitive. The ^{57}Fe deshielding by 800 p.p.m. from the CH_2 to the CMe_2 compound[7] suggests that the substitution at C(6) impairs the interaction with the metal.



(**2**) R,R' = H, Me, or Ph



(**3**) η^6-fulvene

Dependence of the Metal Shielding on Ring Size.—The large decrease in ^{95}Mo shielding with ring enlargement can be explained in terms of the orbital relationships in the Figure. Increase in ring size stabilises the ligand $e(\pi)$ h.o.m.o.s relative to the metal d orbitals so that the e_1 matching is impaired, as is the orbital overlap[30] (and correspondingly for the lower symmetries in the fulvene, C_7H_8, and C_7H_9 ligands). The forward ($L \longrightarrow M$) bonding is thus reduced, so that the $e_1^*(d_{xz}, d_{yz})$ l.u.m.o. is stabilised, reducing ΔE_1 and ΔE_2 and the metal shielding. The reduction in ΔE_2 may be offset by lowering of the e_{2g} h.o.m.o. with improved $M \longrightarrow L$ back-bonding, as the stabilisation of the $e(\pi)$ orbitals allows better matching of the ligand $\pi^*(e_{2g})$ and the filled equatorial orbitals (d_{xy}, $d_{x^2-y^2}$). This explains the possible inversion of the a_{1g} and e_{2g} d orbitals in metallocenes compared to bis(benzene) and larger-ring compounds (Figure). The e_2 energy is also influenced somewhat by electron transfer between metal and ligand in odd-membered rings.[30]

The dominant influence in the deshielding of the metal nucleus appears to be the stabilisation of the ligand-field l.u.m.o. with ring enlargement. The deshielding thus follows the spectrochemical sequence, as observed for sandwich and piano-stool complexes of chromium.[31] A similar rationale is possible for the large ^{95}Mo deshielding that is observed for $[Mo(\eta^5\text{-}C_7H_9)(\eta^7\text{-}C_7H_7)]$ and $[Mo(\eta^6\text{-}C_7H_8)_2]$, *i.e.* for open relative to closed (aromatic) π systems, as the smaller frontier orbital gap in the ligand reduces the ligand-field splitting in the complex. In ^{57}Fe and ^{59}Co resonance, also, deshielding is observed with increase in ring size, and from closed to open π systems, *e.g.* η^5-C_5H_5 > η^6-C_6H_6 > η^5-C_6H_7 for ^{57}Fe,[7] and η^4-C_4H_4 > η^5-C_5H_5 > η^4-C_8H_{12} for ^{59}Co,[12] in sandwich and in piano-stool compounds. The Table shows also that molybdenum is quite strongly deshielded in mixed sandwiches, as might be expected since the bonding and the shielding are the more strongly influenced by the larger ring, or by a ring with an open π system (with poorer mixing of the ring orbitals than in the symmetric sandwiches). Molybdenum is more highly shielded in bent sandwich compounds as the binding of further ligands stabilises (nearly) non-bonding d electrons;[32] in their absence, as in the $[Mg(\eta^5\text{-}C_5H_5)_2]$ sandwich,[5] the metal nucleus is deshielded on formation of bent sandwiches by the addition of basic ligands. Still higher ^{95}Mo shielding is observed in (corresponding) arene–molybdenum tricarbonyl complexes, as the stronger CO ligand increases the ligand-field splitting. The difference increases with ring size, reaching 2 000 p.p.m. for [Mo(η^6-C_7H_8)(CO)$_3$][16] relative to [Mo(η^6-C_7H_8)$_2$].

The connection of the metal nucleus shielding with reactivity of the complex is of interest, given the importance of catalysis by molybdenum centres. Deshielding of ^{59}Co correlates with catalytic efficiency in complexes with cyclopentadienyl and cyclo-octadiene ligands in which the diene dissociates to allow co-ordination of alkynes and nitrile which add to form pyridines.[12] In the molybdenum sandwiches also the ^{95}Mo deshielding parallels increasing reactivity of the complex, or ease of loss of the more weakly bonded ring, the frontier orbitals being related to those for paramagnetic electronic circulations in the magnetic field.[17] In fact the compound in the Table showing the lowest ^{95}Mo shielding, [Mo(η^6-C_7H_8)$_2$], was observed in ^{95}Mo resonance to transform in the n.m.r. tube into [Mo(η^5-C_7H_9)(η^7-C_7H_7)], by intramolecular disproportionation of the ligand,[33] and was too thermally unstable for p.e.s. study.

^{13}C *Shieldings*.—Overall, carbon deshielding tends to follow the ^{95}Mo deshielding in the Table. The $\Delta(^{13}C)$ values are co-ordination shifts relative to the free ligand, with $\delta(C_5H_5^-)$ = 103, $\delta(C_6H_6)$ = 128.7, and $\delta(C_7H_7^+)$ = 156.3 p.p.m.[25,26] The increase in carbon shielding on complexation increases by 20 p.p.m. from the bis(benzene) or bis(toluene) compounds to the tropylium ligand, consistent with better back-bonding to the larger ring. Similarly the deshielding (by 20—30 p.p.m.) from the bis(toluene) complex to toluene in the mixed sandwich with tropylium is consistent with better back-bonding to the larger ring reducing the back-bonding to toluene. (These changes are much larger than would be expected from the changes in atomic charge.) Corresponding deshieldings relative to ferrocene are reported for the cyclopentadienyl ligand in mixed sandwiches with benzene or η^5-C_6H_7.[7] Thus the shielding of carbon, as well as the metal nucleus, appears to follow the strength of binding of the complex: similarly, the largest co-ordination shifts in cyclopentadienyl compounds are those observed for ferrocene, ruthenocene, and osmocene.[34]

Linewidths.—Quadrupolar broadening could have been reduced by higher working temperatures and (or) reduction in viscosity, as working conditions were chosen to maximise solute concentration and minimise spectrometer time. The lines are evidently broadened by increase in molecular size, particularly with bulky substituents such as Ph; interestingly, there is no obvious effect of non-planarity of the ring in the C_7H_8 and C_7H_9 compounds. Linewidths are greater for the mixed sandwiches, presumably by increase in electric-field gradient at the metal nucleus. Given the large shift dispersion the linewidths are acceptable, and ^{95}Mo spectroscopy is clearly of use for studying reactions of these systems.

Experimental

^{95}Mo measurements were normally made on a JEOL FX90Q spectrometer, with a pre-acquisition delay of 0.5 ms to reduce effects of probe ringing, and repetition times of *ca.* 0.2 s. Recourse to a Bruker WH400 spectrometer was needed for compounds with lower solubility. In view of the sensitivity of these compounds all manipulations were carried out in a dry inert atmosphere.

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