

^{95}Mo and ^{199}Hg NMR studies on complexes containing molybdenum–mercury bonds and substituted-cyclopentadienyl ligands: $[(\text{C}_5\text{H}_{5-n}\text{R}_n)(\text{CO})_3\text{Mo}]_x\text{HgX}_{2-x}$ ($\text{R} = \text{Me}$, $n = 0, 1, 4, 5$; $\text{R} = \text{Ph}$, $n = 4$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $x = 1, 2$)

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Abstract

NMR data for ^{95}Mo and ^{199}Hg nuclei have been obtained for di- and tri-metallic complexes containing molybdenum–mercury bonds and substituted-cyclopentadienyl ligands $[(\text{C}_5\text{H}_{5-n}\text{R}_n)(\text{CO})_3\text{Mo}]_x\text{HgX}_{2-x}$; $\text{R} = \text{Me}$, $n = 0, 1, 4, 5$; $\text{R} = \text{Ph}$, $n = 4$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $x = 1, 2$. The ^{95}Mo chemical shifts vary markedly with the substituent on the C_5 ring, with the shielding decreasing in the order $\text{C}_5\text{H}_5 > \text{C}_5\text{H}_4\text{Me} > \text{C}_5\text{HMe}_4 > \text{C}_5\text{Me}_5 > \text{C}_5\text{HPh}_4$, but for a given cyclopentadienyl ligand they are little affected by changes in the X ligands. In contrast, the ^{199}Hg shifts are only slightly affected by ring substitution, except in the case of C_5HPh_4 (which it is suggested may give rise to intramolecular mercury–phenyl interactions), but are strongly influenced by the ligands X. Some aspects of the chemistry of the complexes studied are considered.

Introduction

For some years we have been interested in systematic NMR characteristics of the metallic nuclei in cyclopentadienyl complexes involving transition metal–heavy metal bonds [1–3]. The ^{95}Mo resonances in monocyclopentadienyl complexes range over about 2000 ppm [4,5], but only over some 300 ppm (in the high field part of the overall range) for compounds containing molybdenum–heavy metal bonds (Sn [5], Pb [3], Hg [1]).

In the cyclopentadienylmetal chemistry substituted $C_5H_{5-n}R_n$ rings are usually used to modify solubility, steric hindrance, or electron-donation which can result in significant changes in reaction patterns stability, sensitivity to oxidation, and many other properties [6–10]. A detailed ESCA study recently showed that the C_5Me_5 ligand increases the electron density on the metal by about one electron more than that caused by the unsubstituted C_5H_5 ring [7]. Such a large effect seemed to us to be of potential value for NMR studies involving the metal nuclei and we decided to examine the ^{95}Mo and ^{199}Hg resonances in the complexes of the type $Cp(CO)_3MoHgX$ in which the Cp ligand bears either methyl (more electron-releasing than H) or phenyl (more electron-withdrawing than H) substituents, and the results are presented here.

Results and discussion

The compounds investigated in this study are for convenience divided in the following classes determined by the type and by the number of substituents on the cyclopentadienyl ring:



In all these classes the ligands Z are $Mo(CO)_3Cp^*$ (Cp^* denotes whatever cyclopentadienyl ligand is involved), Cl, Br and I. The NMR data are given in Table 1 and a plot of $\delta(^{199}Hg)$ against $\delta(^{95}Mo)$ chemical shifts is shown in Fig. 1. The data for the H5Z class are taken from ref. 1.

^{95}Mo chemical shifts

Chemical shifts for the ^{95}Mo signals (Table 1) lie between -1536 and -1834 ppm, a region characteristic of non-bridged singly bonded cyclopentadienyl molybdenum-metal complexes; cf. -2072 ppm for $(C_5H_5)(CO)_3MoSnMe_3$ [5], -1838 to -2007 ppm for molybdenum-lead compounds [3], and -1856 and -1701 ppm for molybdenum-molybdenum dimers $[(C_5H_{5-n}R_n)(CO)_3Mo]_2$ with $n = 0$ [11] or $n = 5$ [12], respectively. Two principal trends in the ^{95}Mo chemical shifts are apparent from Table 1 and from Fig. 1, viz.: (i) the shifts depend on the substituents in the Cp ligand, and move downfield in the order $H5Z > Me1Z > Me4Z > Me5Z > Ph4Z$; and (ii), within a given class (H5Z and methyl-substituted species) they are far less dependent on Z, and decrease on going from $Z = Mo(CO)_3Cp^*$ from Cl to Br to I.

It is known that the substitution of hydrogen atoms by methyl groups increases the electron donor ability of the Cp ligands [7] and thus the electron density on molybdenum atom. In the case of our complexes this increase in donation effect appears to be shown by IR data for some compounds in the carbonyl stretching region (Table 2). The largest shift towards lower frequencies is observed for complexes belonging to the Me5Z class in accord with their having the highest

Table 1
NMR data for $(C_5H_{5-n}R_n)(CO)_3MoHgZ$ complexes

$C_5H_{5-n}R_n$	Z	$\delta(^1H)$ (ppm)	$\delta(^{95}Mo)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	$\delta(^{199}Hg)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)
$C_5H_5^a$	$Mo(CO)_3(C_5H_5)$	5.42	-1834	160	+236	50
	Cl	5.51	-1826	160	-574	50
	Br	5.51	-1815	180	-759	45
	I	5.49	-1795	120	-1107	35
C_5H_4Me	$Mo(CO)_3(C_5H_4Me)$	5.65 ^b	-1795	80	+229	7
		5.45				
	Cl	5.90 ^b	-1793	50	-577	6
		5.65				
	Br	5.78 ^b	-1775	80	-765	10
		5.50				
I	5.66 ^b	-1756	100	-1135	40	
	5.43					2.00
C_5HMe_4	$Mo(CO)_3(C_5HMe_4)$	5.30	-1666	140	+209	9
		2.07	1.99			
	Cl	5.59	-1635	150	-614	10
		2.11	2.00			
	Br	5.57	-1615	130	-776	40
		2.10	2.00			
I	5.50	-1600	100	-1059	30	
	2.07	1.99				
C_5Me_5	$Mo(CO)_3(C_5Me_5)$	2.05	-1631	140	+192	7
	Cl	2.09	-1567	80	-645	7
	Br	2.09	-1551 ^c	160 ^c	-807 ^c	12 ^c
	I	2.06	-1537	120	-1060	25
C_5HPh_4	$Mo(CO)_3(C_5HPh_4)$	5.98	-1547	150	-4	5
		7.14	7.08			
	Cl	6.60	-1547	150	-685	7
		7.25	7.21			
	Br	6.56	-1536 ^c	270 ^c	-905 ^c	10 ^c
		7.24	7.20			
	I	6.50	-1539	150	-1309	7
		7.25	7.21			

^a Ref. 1. ^b Ref. 27 in DMSO. ^c Without spinning.

donor abilities. On the other hand, although the C_5HPh_4 ligand is regarded as electron-withdrawing [10], it seems from the IR data that the electron donation by complexes of the Ph4Z class are not much different from those of complexes in the H5Z and Me4Z classes, and in no case was the presumably greater electron-withdrawal by the C_5HPh_4 compared to that of the C_5H_5 ligand detected.

In this light it appears that shifts to lower field of the ^{95}Mo signals upon ring substitution exclude the influence of inductive effects on the overall screening, and suggest that this influence is exerted through the paramagnetic contribution σ_{para} . Moreover, it has been observed previously that the substitution of methyl groups for hydrogen atoms on cyclopentadienyl or arene rings always lead to a deshielding of the metal nucleus linked to those ligands [11-18]. The paramagnetic contribution to

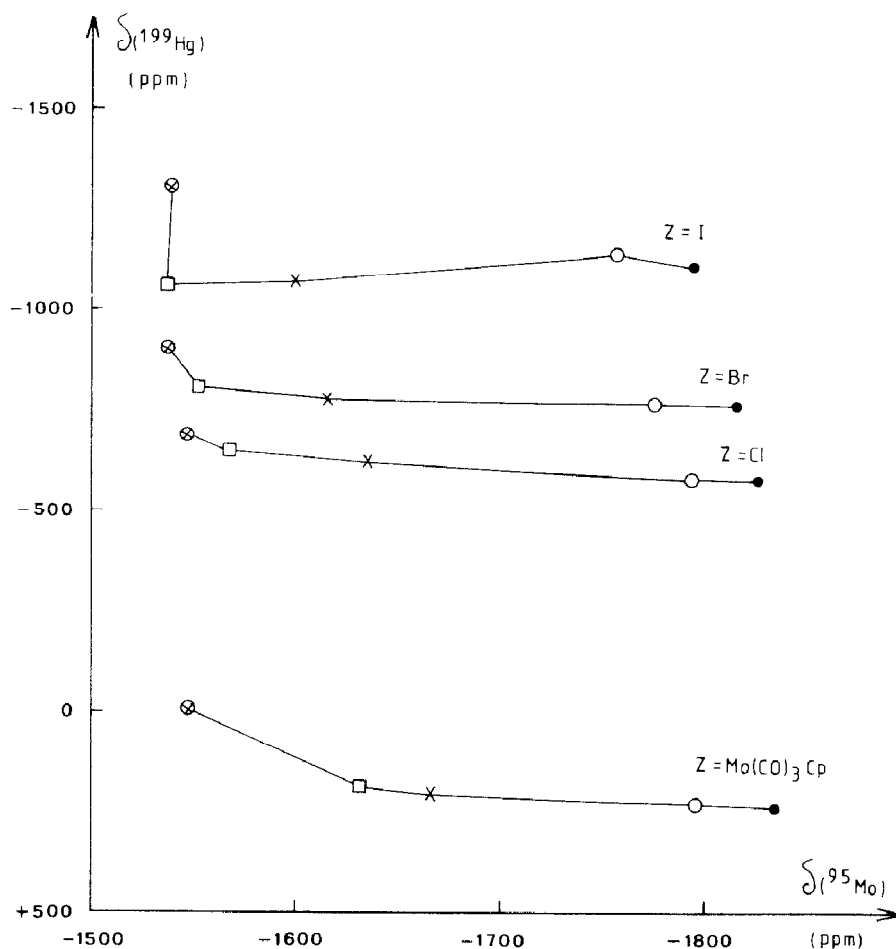


Fig. 1. $\delta(^{199}\text{Hg})$ vs. $\delta(^{95}\text{Mo})$ chemical shifts for the various classes: ● H5Z; ○ Me1Z; × Me4Z; □ Me5Z and ⊗ Ph4Z.

the overall shielding ($\sigma = \sigma_{\text{dia}} + \sigma_{\text{para}}$) (eq. 1) includes three terms, representing the mean HOMO-LUMO gap ΔE , the distance of the valence p - or d -electrons from

$$\sigma_{\text{para}} = -\text{const} \overline{\Delta E}^{-1} (\langle r^{-3} \rangle_{np} Q_p + \langle r^{-3} \rangle_{nd} Q_d) \quad (1)$$

the nucleus $\langle r^{-3} \rangle$, and the degree of ground state imbalance Q in the LCAO coefficients of the orbitals taking part in electronic transitions. The modified energies of Cp^* orbitals [6,19] should in turn influence the set of molecular orbitals involved in the Cp^*-Mo bonding, and the expected decrease in ΔE should lead to an increase in the paramagnetic term and so to deshielding of the molybdenum nucleus. Because there is a systematic decrease of molybdenum shieldings on going from H5Z to Me5Z complexes, the increase in the electron donor ability of the substituted Cp^* ligands must be the predominant influence of the overall screening. As was mentioned above, any introduction of a methyl group on the ring increases the electron density at the molybdenum nucleus, and in consequence there is increased metal-carbonyl $d_{\pi}-p_{\pi}$ back bonding (Table 2), which lowers the C-O bond order but at the same time enlarges the metal-carbon (CO)- π -bond order. This

Table 2

Infrared data for $(C_5C_{5-n}R_n)(CO)_3MoHgZ$ complexes in the carbonyl stretching region (Nujol cm^{-1})

Z	R_n				
	H_5	Me_1^a	Me_4	Me_5	Ph_4
$Mo(CO)_3(C_5H_{5-n}R_n)$	2000s		1982vs	1963sh	1980vs
	1970vs	1950vs	1952s	1933vs	1946s
	1908sh	1886s	1892m	1881s	1897s
	1865s	1870vs	1876s	1856s	1880vs
Cl	2002s	2000vs	1993vs	1984vs	2000s
	1940s	1930sh	1924sh	1917s	1937sh
	1910vs	1916vs	1910s	1901vs	1916vs

^a In KBr, ref. 27.

satisfactorily accounts for the observed deshielding of the ^{95}Mo signal. A $d_{\pi}-p_{\pi}$ interaction should lead to a decrease of ΔE and to an increase of the Q term in the paramagnetic contribution σ_{para} . The role of the $\langle r^{-3} \rangle$ term in this equation is probably less clear, because the π interactions would be expected to enlarge the valence shell dimensions, but on the other hand the fact that the bonds are shorter may lead to the opposite effect.

We have mentioned above that in H5Z and methyl substituted classes the ^{95}Mo shifts are dependent on Z. The high field shifts of the resonances decrease in the order $Z = Cl > Br > I$, which is the inverse of the usual halogen dependence, and for structurally analogous halogenides $(C_5H_5)(CO)_3MoZ$ there is a normal halogen dependence [5]. This indicates that in the complexes studied here the electronic influence of ligands Z on molybdenum nucleus is reduced or even fully inhibited by the mercury atom.

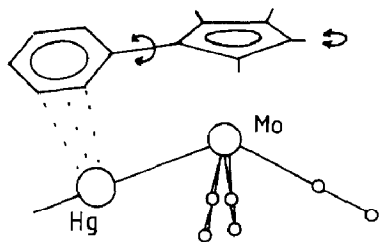
The ^{95}Mo resonances for the Ph4Z class are unusual in the constancy of the shifts. The variations of the ^{95}Mo shifts for this class (11 ppm) with the half-height values of about 150 Hz (23 ppm) are insignificant, whereas for the other classes the shifts vary by 39 to 94 ppm. This suggests that the electronic structure of the central Mo atom in the complexes of the Ph4Z class is protected against external influences by the bulky and probably highly-buffering C_5HPh_4 ligand. Thus, it is likely that the chemical behaviour of the molybdenum centre in complexes of the Ph4Z class will be virtually independent of Z.

^{199}Hg chemical shifts

Within a given class the ^{199}Hg chemical shifts (to higher fields) increase in the order $Z = Mo(CO)_3Cp^* < Cl < Br < I$. In the case of halogenides the trend is the same as that for the compounds HgZ_2 (-1497 , -2152 and -3106 ppm) and $HgZMe$ (-814 , -915 and -1097 ppm for $Z = Cl, Br,$ and I , respectively) [20], and so there is a normal halogen dependence. Apparently, the ^{199}Hg shifts are little affected by the substituents on the C_5 rings. For a given Z they remain roughly constant for the three classes with methyl substituents and for the unsubstituted class H5Z.

However, the complexes of the Ph4Z class give signals at higher fields than those from the other classes. In particular, the shifts are increased by more than 200 ppm for $Z = Mo(CO)_3(C_5HPh_4)$ or I. Because all the complexes studied here are

structurally analogous, the different behavior of the ^{199}Hg nuclei in the Ph4Z class must be attributed to the presence of phenyl substituents on the C_5 ring. It has been shown that in the crystal structure of octaphenylferrocene the dihedral angles between phenyl planes and C_5 planes vary from 15.3 to 77.1° [9]. Different tilt angles between the C_5 cyclopentadienyl rings and the planes of the phenyl groups they carry have been also observed in $(\eta^5\text{-C}_5\text{Ph}_5)\text{Co}(\text{CO})_2$ [10]. It is possible, that for our Ph4Z complexes there is an orientation of one (or more) of the phenyl group that favours its intramolecular interaction with the mercury atom. A diagrammatic representation of such an interaction is shown in 1.



(1)

Examples of π -interaction between the mercury atom, and aromatic rings are known [21–23]. Such “donor”-mercury secondary interaction may lead to increased shielding of the mercury nucleus. For example, for HgMe_2 and HgClMe the signals appear at higher fields for solutions in the good donor solvent DMSO than for those in the fairly neutral solvent CH_2Cl_2 [20], as is the case for one of the complexes we examined $[(\text{C}_5\text{H}_5)(\text{CO})_3\text{Mo}]_2\text{Hg}$, for which the shift is $+236$ ppm in CH_2Cl_2 (Table 1) compared with $+115$ ppm in DMSO [24]. However, further information on the shielding of ^{199}Hg in compounds containing aromatic rings is needed for a better understanding of such weak π interactions and of the role of the magnetic anisotropy of phenyl groups involved therein.

Conclusion

The results indicate that any substitution on cyclopentadienyl ring leads to deshielding of metallic nucleus to which it is attached. From the fact that the ^{95}Mo chemical shifts are little affected by the changes in Z and that those of ^{199}Hg show little variation upon ring substitution, we conclude that the electronic effects are not readily transferred through a metal–metal bond. Transmetallation reactions (replacement of HgZ ligands by other metallic ligands) by the $\text{Cp}^*(\text{CO})_3\text{Mo}$ moieties are thus to be expected. The ^{199}Hg chemical shifts values are closer to those for MeHgZ ($Z = \text{Me}, \text{Cl}, \text{Br},$ and I) than those for HgZ_2 ($Z = \text{Cl}, \text{Br}$ and I) compounds, indicating a covalent nature for the molybdenum–mercury bond. However, because the lower field shifts for ^{199}Hg are accompanied by higher field shifts for ^{95}Mo within a given class (Ph4Z is a special case) and for a given Z, these bonds must be polarized.

Experimental

All manipulations were carried out under nitrogen by standard Schlenk tube techniques. Freshly distilled, dried and degassed solvents were used. Known com-

plexes with C_5H_5 and C_5H_4Me ligands made as previously described [25,26]. The new ones with C_5HMe_4 , C_5Me_5 and C_5HPh_4 ligands were prepared by analogous methods starting from $Mo(CO)_6$ and the corresponding lithium cyclopentadienides [9,27] and $Hg(CN)_2$, followed by reactions of the resulting trimetallic complex $[Cp^*(CO)_3Mo]_2Hg$ with a molar proportion of HgX_2 . The products were recrystallized from acetone or from CH_2Cl_2 /hexane.

For determination of NMR spectra almost saturated solutions were made up under nitrogen in dried and degassed CH_2Cl_2 containing C_6D_6 as internal reference and these were sealed in 10-mm tube.

The NMR spectra were recorded on a JEOL FX 100 spectrometer at room temperature. A 10-mm multinuclear probe model NM 3980 (operated at 6.44 MHz for ^{95}Mo and at 17.78 MHz for ^{199}Hg) was used. The 90° pulse was found to be 80 μs for ^{95}Mo and 38 μs for ^{199}Hg . The routine acquisition parameters used were as follows: pulse width 40 μs (^{95}Mo) and 10 μs (^{199}Hg); acquisition time 5×10^{-2} with the repetition time of $7-9 \times 10^{-2}$ s for ^{95}Mo and 0.4 s and 0.5 s, respectively, for ^{199}Hg ; spectral width 20 kHz; data points 2 k (^{95}Mo) and 16 k (^{199}Hg); number of scans 5×10^4 to 6×10^5 (^{95}Mo) and $\approx 10^5$ (^{199}Hg) depending on the solubility of the compounds. Aqueous Na_2MoO_4 (2 M) at pH 11 and neat $HgMe_2$ were used as external references.

Infrared spectra were recorded on a Perkin-Elmer 1430 Ratio Recording Infrared Spectrophotometer.

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