ELSEVIER

Inorganica Chimica Acta 228 (1995) 251–254

Inorganica Chimica Acta

Note

Effects of substitutions on cyclopentadienyl rings in complexes with molybdenum–mercury bonds. ^{95}Mo and ^{199}Hg NMR studies

Mercedes Cano [a], Jose A. Campo [a], Elena Pinilla [a,b], Angeles Monge [b], Roger Pichon [c], Jean-Yves Salaün [c], Paul L'Haridon [d], Jan Szymoniak [e], Marek M. Kubicki [e,*]

[a] *Departamento de Chimica Inorganica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain*
[b] *Laboratorio de Difraccion de Rayos X, Facultad de Ciencias Quimicas, Universidad Complutense and Instituto de Materiales, C.S.I.C., Serrano 113, Madrid, Spain*
[c] *Laboratoire de Chimie, Electrochimie et Photochimie Moléculaires associé au CNRS (URA 322), Université de Bretagne Occidentale, 29287 Brest, France*
[d] *Laboratoire de Chimie Minérale C associé au CNRS (URA 254), Université de Rennes-Beaulieu, 35042 Rennes, France*
[e] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 1685), Université de Bourgogne, 21000 Dijon, France*

Received 4 February 1994; revised 15 June 1994

Abstract

NMR data for ^{95}Mo and ^{199}Hg nuclei have been obtained for new di- and trimetallic complexes Cp'(CO)$_3$MoHgX containing molybdenum–mercury bonds and bulky and/or potentially bifunctional substituted cyclopentadienyl ligands; Cp' = $C_5HMe_2Ph_2$, C_5Me_4Bz, C_5Bz_5, $C_5H_4PPh_2$ and $C_5Me_4PPh_2$ (Bz = $CH_2C_6H_5$; Me = CH_3; Ph = C_6H_5); X = Cp'(CO)$_3$Mo, Cl, Br, I, SCN. They are discussed within the context of our earlier results reported for analogous complexes with the cyclopentadienyl ligands bearing methyl groups. With the exception of phenyl substituted rings, a rather narrow range of ^{95}Mo chemical shifts is found for the compounds with the same number of different substituents on cyclopentadienyl ligands. An outstanding shielding of ^{199}Hg nuclei, observed in complexes bearing the rings with Bz, PPh_2 and Ph substituents instead of the methyls, is assigned to the intramolecular substituent–mercury interactions.

Keywords: Molybdenum complexes; Cyclopentadienyl-substituted complexes; ^{95}Mo NMR; ^{199}Hg NMR

---

1. Introduction

A great number of mono- and poly-substituted cyclopentadienyl systems bearing the donor as well as the acceptor functions has been prepared recently [1]. The effects of varying the Cp substituents on the spectroscopic features, chemical reactivity and stereochemistry have been observed. However, although cyclopentadienyls are a common ligand type, few systematic studies of such effects have been performed [2,3].

We have been interested for some years in the systematic NMR qualitative study of metallic nuclei in Cp'(CO)$_2$LMoHgX molybdenum–mercury bonded complexes bearing different ligands L [4] and differently substituted cyclopentadienyl rings [5]. For Cp'(CO)$_3$MoHgX complexes (Cp' = C_5H_5, C_5H_4Me, C_5HMe_4, C_5Me_5, C_5HPh_4; X = Cl, Br, I, Cp'(CO)$_3$Mo) we concluded that generally (i) the upfield shifts of ^{199}Hg are accompanied by lower field shifts of ^{95}Mo, (ii) the better donors X shield ^{199}Hg and (iii) the better donors Cp' deshield ^{95}Mo. For complexes with Cp' = C_5HPh_4, we suggested that intramolecular interactions may be present in solution between the phenyl groups of the cyclopentadienyl ring and the mercury atom. This last observation inspired us to undertake an analogous study on new related systems bearing bulky and/or potentially bifunctional Cp' ligands like $C_5HMe_2Ph_2$ (series **1**), C_5Me_4Bz (**2**), C_5Bz_5 (**3**),

---

* Corresponding author.

SSDI 0020-1693(94)04172-R

$C_5H_4PPh_2$ (**4**) and $C_5Me_4PPh_2$ (**5**) ($Bz=CH_2C_6H_5$; $Me=CH_3$; $Ph=C_6H_5$).

2. Experimental

The new complexes were prepared by methods analogous to those described in the literature, starting from $Mo(CO)_6$ and the corresponding cyclopentadienides [6] and $Hg(CN)_2$, followed by reactions of the resulting trimetallic complexes $[Cp'(CO)_3Mo]_2Hg$ with a stoichiometric amount of HgX_2. The products were recrystallized from dichloromethane/hexane or acetone solutions. Correct elemental analyses were obtained from Elemental Micro-Analysis Ltd. Laboratories (Devon, UK).

For determination of NMR spectra, the solutions close to saturation were made up under nitrogen in dried and degassed CH_2Cl_2 containing C_6D_6 as internal reference and these were sealed in a 10 mm tube. NMR spectra were recorded on a JEOL FX 100 spectrometer at ambient temperature as described elsewhere [5]. Aqueous Na_2MoO_4 (2 M) at pH 11 and neat $HgMe_2$ were used as external references.

3. Results and discussion

NMR data for complexes **1**–**5** with X=Cl, Br, I, SCN and $Cp'(CO)_3Mo$ are given in Table 1. In order to give a better idea of electronic and steric effects exerced by the Cp′ ligands on metallic nuclei selected results from our earlier publication [5] are as follows: ^{95}Mo and ^{199}Hg chemical shift data (ppm) for trimetallic complexes $[Cp'(CO)_3Mo]_2Hg$: $Cp'=C_5H_5$ (**6**-Mo) −1834, +236; C_5H_4Me (**7**-Mo) −1795, +229; C_5HMe_4 (**8**-Mo) −1666, +209; C_5Me_5 (**9**-Mo) −1631, +192; C_5HPh_4 (**10**-Mo) −1547, −4.

The ^{95}Mo chemical shifts for the new compounds lie between −1542 and −1794 ppm, well in the region observed in related cyclopentadienyl molybdenum complexes with a single Mo–M′ (M′=Hg, Sn, Pb, Mo) bond [5,7]. For a given Cp′ ligand, the ^{95}Mo chemical shifts depend not only on its nature but also on that of X, running upfield in the order $SCN < I < Br < Cl < Mo(CO)_3Cp'$.

The ^{199}Hg chemical shifts lie between +139 and −1169 ppm. A similar range has been observed in other related transition metal–Hg derivatives [4,5,8]. The ^{199}Hg chemical shifts for complexes with the same Cp′ ligand decrease to higher fields in the order $Cp'(CO)_3Mo < SCN < Cl < Br < I$, which is the same as that reported for HgX_2 and MeHgX compounds [9].

Table 1
NMR data for new $Cp'(CO)_3MoHgX$ complexes

Cp′	X	Complex	^1H (ppm)	^{95}Mo (ppm)	$\Delta\nu_{1/2}$ (Hz)	^{199}Hg (ppm)	$\Delta\nu_{1/2}$ (Hz)
$C_5HMe_2Ph_2$	Mo [a]	**1**-Mo	2.06 5.37	−1641	200	+98	25
	Cl	**1**-Cl	2.13 5.80	−1621	100	−644	25
	Br	**1**-Br	2.12 5.75	−1604	100	−827	10
	I	**1**-I	2.10 5.67	−1583	75	−1169	25
	SCN	**1**-S	2.17 5.81	−1585	75	−504	70
C_5Me_4Bz	Mo [a]	**2**-Mo	2.05 2.09 3.90	−1636	100	+139	15
	Cl	**2**-Cl	2.10 2.13 3.89	−1585	50	−665	12
	Br	**2**-Br	2.09 2.12 3.88	−1572	30	−809	12
	I	**2**-I	2.06 2.08 3.86	−1560	50	−1064	35
	SCN	**2**-S	2.13 2.17 3.94	−1542	70	−506	35
C_5Bz_5	Mo [a]	**3**-Mo	3.92	−1619	200	+49	40
	Cl	**3**-Cl	3.89	−1598	160	−672	55
	Br	**3**-Br	3.88	−1594	40	−852	20
	I	**3**-I	3.85	−1563	75	−1169	25
	SCN	**3**-S	3.92	[b]	[b]	−523	50
$C_5H_4PPh_2$	Mo [a]	**4**-Mo		−1794	140	+109 [c]	75
$C_5Me_4PPh_2$	Mo [a]	**5**-Mo	1.50 1.54	−1624	95	+27 [d]	18
	Cl	**5**-Cl	1.53 1.56	−1582	228	−676 [e]	25
	I	**5**-I	1.51 1.55	−1562	310	−1141 [f]	52

[a] $Mo=Mo(CO)_3Cp'$.
[b] Not observed.
[c] Triplet J(Hg–P)=45 Hz, δ $^{31}P=-17.8$ ppm.
[d] Triplet J(Hg–P)=28 Hz, δ $^{31}P=-17.0$ ppm.
[e] Doublet J(Hg–P)=37 Hz, δ $^{31}P=-13.3$ ppm.
[f] Doublet J(Hg–P)=24 Hz; δ $^{31}P=-18.1$ ppm.

A representative plot of $\delta(^{199}Hg)$ against $\delta(^{95}Mo)$ chemical shifts for trimetallic complexes with Mo–Hg–Mo linkage (compounds **1**–Mo to **10**–Mo, Table 1, see above) is shown in Fig. 1. Examination of Fig. 1 shows the following features: (i) a narrow range of ^{95}Mo chemical shifts for complexes with five substituents on the C_5 ring; a similar observation can be made for compounds with a single substitution on the cycle, but only two complexes belong to this class (**4**-Mo and **7**-Mo); (ii) a shielding of ^{199}Hg nuclei in complexes bearing the rings with Bz, PPh_2 and Ph substituents instead of methyls; (iii) a deshielding of ^{95}Mo in the presence of Ph groups (**1**-Mo and **10**-Mo).

The applications and the effectiveness of substituted cyclopentadienyl rings arise from a contribution of steric and electronic factors, as often invoked in phosphine

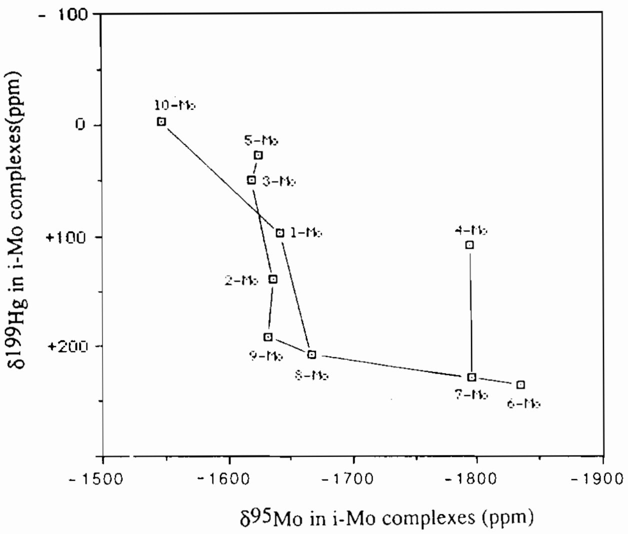

Fig. 1. $\delta(^{199}Hg)$ vs. $\delta(^{95}Mo)$ chemical shifts in trimetallic Mo–Hg–Mo bonded complexes (i-Mo).

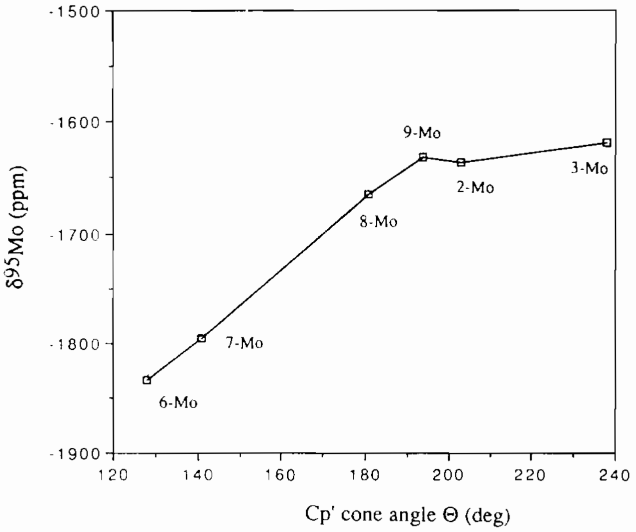

Fig. 2. $\delta(^{95}Mo)$ chemical shifts vs. Cp′ cone angles Θ in selected Mo–Hg–Mo (i-Mo) complexes.

complexes [10]. The size of the Cp′ ligand is certainly a factor which influences the geometry of the molecule and consequently may be responsible for a stabilization or destabilization of the atomic orbitals of the metallic center involved in the bonding. An evaluation of the sizes of differently substituted Cp rings has been proposed recently by Coville et al. [3]. The reported cone angles (Θ) are 128° (C_5H_5), 141° (C_5H_4Me), 194° (C_5Me_5) and 150° (C_5H_4Bz), from which the values of 181°, 203° and 238° are derived for C_5HMe_4, C_5Me_4Bz and C_5Bz_5 rings, respectively. A roughly linear correlation between the ^{95}Mo chemical shifts and the cone angles Θ is observed for methyl substituted rings. It is shown for trimetallic complexes (**i**-Mo) in Fig. 2. However, this correlation no longer holds for the compounds with benzyl substituted rings. The cone angle values are much larger now, but the fields of ^{95}Mo resonances are close to the values observed for complexes with a permethylated (C_5Me_5) ring. This suggests that the steric effects of the benzyl substituent are negligible and that the electronic influences of the CH_3 and CH_2Ph substituents are similar. The electronic factor therefore seems to determine the shielding of ^{95}Mo in our complexes.

Moreover, the preliminary results obtained by extended Hückel calculations on $Cp'(CO)_3MoHgCl$ complexes show a systematic decrease of ΔE (taken as the HOMO–LUMO energy gap) parameter [1] on going from $Cp' = C_5H_5$ (**6**-Cl, 2.205 eV) through C_5H_4Me (**7**-Cl, 2.187 eV), C_5HMe_4 (**8**-Cl, 2.164 eV) to C_5Me_5 (**9**-Cl, 2.158 eV) [11]. Even in the absence of calculations for complexes bearing the benzyl substituted rings, it seems reasonable to conclude that the ^{95}Mo chemical shifts are more sensitive to the electronic nature of the Cp′ ring than to its steric influence. Better electron donors increase the electron density on the molybdenum atom and the energies of the occupied molecular orbitals. Consequently, the LUMO–HOMO energy gap decreases, and the absolute value of paramagnetic contribution σ_p increases, leading to a low field resonance of the molybdenum nucleus.

We mentioned that for a given number of substituents the ^{95}Mo resonances vary little, but that those of ^{199}Hg are shifted to higher fields in the presence of Ph, Bz and PPh_2 substituents. It has been observed, that the ^{199}Hg nuclei resonate at higher fields in donor solvents than in the inert ones for compounds $HgMe_2$, RHgX [12] and $[Cp(CO)_3Mo]_2Hg$ (+115 ppm in DMSO [13] versus +236 ppm in $CHCl_3$ [4a]). The stronger shielding of ^{199}Hg is due to a donor (solvent)–acceptor (Hg) interaction. By analogy with these solvent–mercury interactions, we suggest that the higher fields of the ^{199}Hg resonances observed in complexes **1**–**5** are due to the intramolecular donor (substituent)–acceptor (Hg) effects. Such intramolecular interactions may be considered as the through-space ones. This seems to be confirmed by the phosphorus–mercury couplings of 24 to 45 Hz observed in complexes **4** and **5** (Table 1). Moreover, an inspection of the data given in Table 1 shows that the ^{199}Hg nuclei are more sensitive to the electronic effects of substituents in trimetallic complexes with Mo–Hg–Mo linkage (more than 200 ppm region is covered in the presence of tetra- and penta-substituted rings) than in chlorides, where the overall range of ^{199}Hg does not exceed 70 ppm. This observation would confirm the through-space nature of the intramolecular interactions. They are stronger in trimetallic Mo–Hg–Mo complexes, where two Cp′ ligands may give rise to the interactions with mercury atom, than in dimetallic

---

[1] The paramagnetic contribution (σ_p) to the overall shielding of nuclei in polyelectronic atoms is given by the relation: $\sigma_p(A) \approx -\Delta E^{-1}\langle r^{-3}\rangle Q$.

Mo–Hg–X systems in which only one Cp′ ligand is present.

The crystal structures of two complexes with phenyl substituted rings ($[(C_5HMe_2Ph_2)(CO)_3MoHgI]$ (**1**-I) and $[(C_5HPh_4)(CO)_3Mo]_2Hg$ (**10**-Mo)) have been determined by X-ray diffraction[2]. The shortest mercury–carbon(phenyl group) distances are rather long (about 4 Å). However, the ring substituent–mercury intramolecular interactions may exist even in the solid state, because the anisotropic magnetic currents associated with unsaturated ligands operate at long distances [14]. These interactions should be stronger in solution, where rotations of both the cyclopentadienyl and the phenyl rings are allowed.

Further theoretical and NMR studies on $Cp'(CO)_2LMoHgX$ complexes with electron-withdrawing substituents on C_5 rings are currently in progress.

4. Supplementary material

ORTEP drawings, atomic coordinates and selected bond distances and angles for both structures are available from author M.M.K. on request.

References

[1] N.J. Coville, K.E. du Plooy and W. Pickl, *Coord. Chem. Rev., 116* (1992) 1, and refs. therein.

[2] (a) M.D. Rausch, W.M. Tsai, J.W. Chambers, R.D. Rogers and H.G. Alt, *Organometallics, 8* (1989) 816; (b) D.L. Lichtenberger, S.K. Renshaw, F. Basolo and M. Cheong, *Organometallics, 10* (1991) 148; (c) P.G. Gassman, P.A. Deck, C. H. Winter, D.A. Dobbs and D.H. Cao, *Organometallics, 11* (1992) 959; (d) R.J. Hoobler, M.A. Hutton, M.M. Dillard, M.P. Castellani, A.L. Rheingold, A.L. Rieger, P.H. Rieger, T.C. Richards and W.E. Geiger, *Organometallics, 12* (1993) 116; (e) C. Saadeh, S.B. Colbran, D.C. Craig and A.D. Rae, *Organometallics, 12* (1993) 133; (f) L.D. Field, A.F. Masters, M. Gibson, D.R. Latimer, T.W. Hambley and I.E. Buys, *Inorg. Chem., 32* (1993) 211; (g) M. Arthurs, J.C. Bickerton, G. Kubal, J. O'Sullivan, C. Piper, G. Hogharth and D.A. Morton-Blacke, *J. Organomet. Chem., 467* (1994) 135.

[3] N.J. Coville, M.S. Loonat, D. White and L. Carlton, *Organometallics, 11* (1992) 1082.

[4] (a) M.M. Kubicki, R. Kergoat, J.Y. Le Gall, J.E. Guerchais, J. Douglade and R. Mercier, *Aust. J. Chem., 35* (1982) 1543; (b) M. Cano, J.A. Campo, J.Y. Le Gall, R. Pichon, J.Y. Salaün and M.M. Kubicki, *Inorg. Chim. Acta, 193* (1992) 207.

[5] M.M. Kubicki, J.Y. Le Gall, R. Pichon, J.Y. Salaün, M. Cano and J.A. Campo, *J. Organomet. Chem., 348* (1988) 349.

[6] (a) R.D. Fisher and K. Noack, *J. Organomet. Chem., 16* (1969) 125; (b) P. Yates, N. Yoda, W. Brown and B. Mann, *J. Am. Chem. Soc., 80* (1958) 202; (c) H. Schumann, C. Janiak and H. Khani, *J. Organomet. Chem., 330* (1987) 347; (d) F. Mathey and J.P. Lampin, *Tetrahedron, 31* (1975) 2685; (e) J. Szymoniak, J. Besançon, A. Dormond and C. Moïse, *J. Org. Chem., 55* (1990) 1429; (f) M.J. Mays and J.D. Robb, *J. Chem. Soc. A,* (1968) 329.

[7] (a) J.Y. Le Gall, M.M. Kubicki and F.Y. Petillon, *J. Organomet. Chem., 221* (1981) 287; (b) C.G. Young, M. Minelli, J.H. Enemark, G. Miessler, N. Janietz, H. Kauerman and J. Wachter, *Polyhedron, 5* (1986) 407; (c) M.M. Kubicki, J.Y. Le Gall, R. Kergoat and L.C. Gomes de Lima, *Can. J. Chem., 65* (1987) 1292; (d) M. Minelli, J.H. Enemark, R.T.C. Brownlee, M.J. O'Connor and A.G. Wedd, *Coord. Chem. Rev., 68* (1985) 169.

[8] (a) M.J. Albright and J.P. Oliver, *J. Organomet. Chem., 172* (1979) 99; (b) M.M. Kubicki, R. Kergoat, J.Y. De Vanssay, J.Y. Le Gall and J.E. Guerchais, *Polyhedron, 3* (1984) 1984; (c) J.D. Cotton and E.A. Miles, *Inorg. Chim. Acta, 173* (1990) 129.

[9] R.G. Kidd and R.J. Goodfellow, in R.K. Harris and B.E. Mann (eds.), *NMR and the Periodic Table*, Academic Press, London, 1978, pp. 266–278.

[10] (a) C.A. Tolman, *Chem. Rev., 77* (1977) 313; (b) S.P. Nolan and C.D. Hoff, *J. Organomet. Chem., 290* (1985) 365; (c) A.G. Orpen and N.G. Connelly, *Organometallics, 9* (1990) 1206; (d) E.C. Alyea, S.A. Dias, G. Ferguson and R.J. Restivo, *Inorg. Chem., 16* (1977) 2329; (e) E.C. Alyea and S. Song, *Inorg. Chem., 31* (1992) 4909.

[11] M.M. Kubicki and P. Boudot, unpublished results.

[12] R.J. Goodfellow, in J. Mason (ed.), *Multinuclear NMR*, Plenum, New York, 1987, Ch. 21, p. 581.

[13] M.J. Albright, M.D. Glick and J.P. Oliver, *J. Organomet. Chem., 161* (1978) 221.

[14] (a) E.F. Kiefer and W. Gericke, *J. Am. Chem. Soc., 90* (1968) 5131, and refs. therein; (b) J. Ronayne and D.H. Williams, *J. Chem. Soc., Chem. Commun.,* (1966) 712.

---

[2] $(C_5HMe_2Ph_2)(CO)_3MoHgI$ (**1**-I): triclinic, $P\bar{1}$, $a=7.431(4)$, $b=10.966(3)$, $c=13.763(10)$ Å, $\alpha=75.73(9)$, $\beta=83.58(7)$, $\gamma=82.88(7)^\circ$, $Z=2$, $D_x=2.330$ g cm^{-3}, $R=0.060$, Mo–Hg$\,=2.686(3)$ Å); $[(C_5HPh_4)(CO)_3Mo]_2Hg$ (**10**-Mo): monoclinic, $C2/c$, $a=27.291(7)$, $b=9.338(3)$, $c=22.708(9)$ Å, $\beta=96.14(3)^\circ$, $Z=4$, $D_x=1.500$ g cm^{-3}, $R=0.047$, Mo–Hg$\,=2.722(1)$ Å. See also Section 4.