Molybdenum–mercury bond. NMR (^{199}Hg, ^{31}P, ^{1}H) and IR study on [$(C_5H_5)(CO)_2LMoHgZ$] (L$=$P(4-X-$C_6H_4)_3$ (X$=$F, Cl, Me, OMe), $P(CH_2CH_3)_3$, $P(CH_2CH_2CN)_3$; Z$=$Cl, I, $(C_5H_5)(CO)_2LMo$) complexes

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Abstract

IR and multinuclear NMR studies, and in particular those of ^{199}Hg NMR, have been carried out on the title molybdenum–mercury bonded complexes of the type $Cp(CO)_2$(phosphine)MoHgZ. It is found that the ^{199}Hg chemical shifts correlate well with the pK_a values and with some electronic parameters, like Hammet's σ_p or Bartik's $^{FT}\chi$, for *para*-substituted triphenyl phosphines and for PEt_3. Less basic phosphines give rise to a shielding of mercury nuclei. A particular behaviour of $P(CH_2CH_2CN)_3$ derivatives is ascribed to a possible intramolecular $MoPCH_2CH_2CN \rightarrow Hg$ interaction. The ^2J(HgP) coupling constants do not exhibit a clear dependence either on the nature of the *para*-substituent in triarylphosphines or on the pK_a values of the phosphorus ligand involved but do show a good linear correlation with the values of Tolman's θ cone angles: the higher the cone angle is, the lower is the coupling constant.

Introduction

For some years we have been interested in systematic qualitative NMR studies of metallic nuclei in carbonyl cyclopentadienyl complexes involving transition metal M(^{95}Mo)–heavy metal M′(^{199}Hg, ^{207}Pb) bonds [1–5]. Complexes of the type $Cp'(CO)_2LMo–HgZ$ are very suitable for such a study since they allow one to alter the nature of the ligands present; the Cp ligand can be given different substituents, the CO acceptors may be replaced by donor L ligands and the Z ligand bound to mercury can be varied. Our previous measurements carried out on $Cp'(CO)_3Mo–HgZ$ complexes have shown that generally (i) upfield shifts of ^{199}Hg are accompanied by lower field shifts of ^{95}Mo, (ii) the better donors Z shield the ^{199}Hg (normal halogen dependence) and (iii) the better donors Cp′ deshield the ^{95}Mo. The first statement may indicate that the covalent Mo–Hg bonds are polarized and the last two can be qualitatively explained by an analysis of the paramagnetic contribution to the overall shielding [2, 3, 5–7].

In our earlier study [2] we introduced $P(OMe)_3$ and PPh_3 in place of one carbonyl ligand and observed that both the ^{95}Mo and the ^{199}Hg resonances were shifted dowfield upon these substitutions with respect to the parent tricarbonyl complexes. Here we present an extended study of the effects of such substitutions on ^{199}Hg resonances including the *para*-substituted triphenylphosphines and two trialkyl (ethyl and cyanoethyl) phosphines.

Experimental

All manipulations were carried out under nitrogen by using standard Schlenk tube techniques. Freshly distilled, dried and degassed solvents were used. The compounds were prepared by methods analogous to

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those described in the literature [8]. IR spectra were recorded on a Perkin-Elmer 1300 using KBr pellets.

For determination of ^{199}Hg NMR spectra almost saturated solutions were made up under nitrogen in dried and degassed CH_2Cl_2 containing C_6D_6 as internal lock. The 10 mm NMR tubes were sealed under vacuum. The NMR spectra were recorded on a JEOL FX100 spectrometer at room temperature. A 10-mm multinuclear probe model NM 3980 (operating at 99.60 MHz for ^{1}H, 40.32 MHz for ^{31}P and 17.78 MHz for ^{199}Hg) was used. The 90° pulse was found to be 38 μs for ^{199}Hg. The routine acquisition parameters used for ^{199}Hg were as follows: pulse width 10 μs; acquisition time 0.4 s with the repetition time of 0.5 s, spectral width 20 kHz; data points 16 K; number of scans $\approx 10^5$. Chemical shifts were measured relative to an internal reference of TMS for ^{1}H; 85% H_3PO_4 and neat $HgMe_2$ were used as external references for ^{31}P and ^{199}Hg, respectively.

Results and discussion

The new complexes are yellow microcrystalline solids, air-stable at room temperature for several weeks but sensitive to light. They are less soluble in common polar solvents than their non-substituted analogues $Cp(CO)_3MoHgZ$ and the halogeno derivatives containing the $P(CH_2CH_2CN)_3$ ligand are practically insoluble. Spectroscopic data are summarized in Table 1. In no case could the ^{95}Mo resonance be clearly detected. Even after prolonged accumulations, only very broad (3000–4000 Hz) weak signals, practically indistinguishable from the background, were observed.

All symmetrical complexes $[Cp(CO)_2LMo]_2Hg$ with *para*-substituted triphenylphosphines exhibit two sets of ^{1}H (Cp) and ^{31}P resonances, indicating that two different conformers are present in solution. Only one ^{1}H (Cp) and one ^{31}P resonance is observed for trialkylsphosphine substituted complexes suggesting either the existence of a sole isomer or a rapid (in relation to the NMR detection) rotation around the Mo–Hg–Mo bonds. The latter may be plausible because the steric hindrance for alkyl phosphines is smaller than for aryl phosphines. The corresponding Tolman's cone angles θ, defined in Fig. 1, are equal to 132° and 145°, respectively [9].

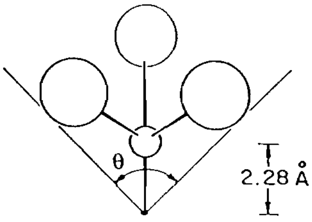

Fig. 1. Cone angle θ as defined by Tolman [9].

IR frequencies in the carbonyl stretching region for cyclopentadienyl–carbonyl complexes depend on donor–acceptor properties (basicity, other electronic factors) of the other ligands and should reflect the electron density on molybdenum or on the bimetallic Mo–Hg unit. Two ν(CO) bands are recorded for chloride and iodide derivatives. The four bands observed for symmetric 'Mo–Mg–Mo' complexes are consistent with the presence of two $Cp(CO)_2LMo$ groups in a skew configuration with respect to the Mo–Hg–Mo linkage [10]. The frequencies of these bands roughly suggest the following order of basicities for the phosphines employed: $P(CH_2CH_3)_3 > P(CH_2CH_2CN)_3 > P(4\text{-}CH_3O\text{-}C_6H_4)_3 > P(4\text{-}CH_3\text{-}C_6H_4)_3 > P(4\text{-}F\text{-}C_6H_4)_3 > P(4\text{-}Cl\text{-}C_6H_4)_3$. Except for the position of $P(CH_2CH_2CN)_3$, which suggests for this phosphine high donor properties, the order observed is consistent with the pK_a values reported in the literature [11]. According to the classification established by Giering and co-workers [12] PEt_3 and all arylphosphines studied here belong to the class of σ-donor ligands, whereas $P(CH_2CH_2CN)_3$ is considered as a σ-donor π-acceptor ligand. Thus, and from the corresponding pK_a values, the ν(CO) frequencies for $P(CH_2CH_2CN)_3$ substituted complexes should be close to those observed for the derivatives with $P(4\text{-}Cl\text{-}C_6H_4)_3$.

An anomalous behaviour of $[Cp(CO)_2\{P(CH_2CH_2CN)_3\}Mo]_2Hg$ (**6**-Mo) seems to be also reflected in its ^{199}Hg and ^{31}P NMR spectra. Unfortunately for further comparison this is the sole compound with this phosphine that is sufficiently soluble for NMR measurements. The ^{199}Hg resonance is shifted upfield by about 360 ppm with respect to $[Cp(CO)_2(PEt_3)Mo]_2Hg$ (**5**-Mo) and by some 230–260 ppm with respect to the $[Cp'(CO)_3Mo]_2Hg$ complexes [5]. We have already shown that any phosphine or phosphite substitution for one carbonyl ligand leads to a deshielding of the ^{199}Hg nuclei, so the high field resonance of ^{199}Hg in **6**-Mo is unexpected. In the case of all σ-donor phosphines the coordination chemical shifts Δ_c of ^{31}P resonances ($\Delta_c = \delta^{31}$P complex $- \delta$ ^{31}P free phosphine) are found, for symmetrical compounds **1** to **5**-Mo, in the range of 70 to 82 ppm. For $P(CH_2CH_2CN)_3$ (complex **6**-Mo) this coordination chemical shift is smaller and is equal to 63 ppm

A reasonable explanation for such a behaviour of the ^{199}Hg and ^{31}P resonances and at the same time for the low frequencies of ν(CO) vibrations for **6**-Mo may be found in the supposition that in the complexes with $P(CH_2CH_2CN)_3$ there exists a relatively strong intramolecular interaction between the nitrogen atom of the cyano group and the mercury atom and that such an interaction does not markedly change the linear

TABLE 1. Spectroscopic data for the complexes Cp(CO)$_2$LMoHgZ together with the pK_a [11] and χ [15] values for ligands L

Complex	L	Z	IR, ν(CO) (cm^{-1})	^{1}H(Cp) (ppm)	J(P–H) (Hz)	^{31}P (ppm)	^2J(P–Hg) (Hz)	^{199}Hg (ppm)	$\Delta\nu_{1/2}$ (Hz)	pK_a	χ
1-Mo	P(4-Cl-C$_6$H$_4$)$_3$	[Mo]^a	1970s, 1885s	4.98	0.9	73.6	204			1.03	16.80
			1860s, 1815vs	4.97	0.9	72.4	244				
1-Cl		Cl	1925s, 1845vs	5.03	1.2	69.2	414	−523	10		
1-I		I	1910s, 1832vs	5.01	1.2	70.2	382	−959	20		
2-Mo	P(4-F-C$_6$H$_4$)$_3$	[Mo]	1980m, 1880sh	4.97	0.9	71.9	212			1.97	15.70
			1860s, 1805vs			70.7					
2-Cl		Cl	1925s, 1850vs	5.05	1.0	67.4	415	−519	7		
2-I		I	1915s, 1840vs	5.01	1.2	68.3	381	−950	20		
3-Mo	P(4-CH$_3$-C$_6$H$_4$)$_3$	[Mo]	1965m, 1885s	4.97	0.9	68.6	210			3.84	^{b}
			1855s, 1805vs	4.95	0.9	67.3	245				
3-Cl		Cl	1928s, 1850vs	5.00	1.0	64.2	414	−512	12		
3-I		I	1910s, 1835vs	4.98	1.0	65.1	393	−902	30		
4-Mo	P(4-CH$_3$O-C$_6$H$_4$)$_3$	[Mo]	1960s, 1880s	4.98	1.0	66.8	208			4.59	10.50
			1855s, 1795vs	4.97	1.2	64.9	270				
4-Cl		Cl	1925s, 1855vs	5.01	1.2	62.4	414	−508	15		
4-I		I	1915s, 1840vs	5.01	1.2	62.5	366	−893	25		
5-Mo	P(CH$_2$CH$_3$)$_3$	[Mo]	1878sh, 1868s	5.15		50.3	210	+316	20	8.69	6.30
			1820sh, 1800vs	(br)							
5-Cl		Cl	1915s, 1832vs	5.19	1.2	46.1					
5-I		I	1905s, 1820vs	5.11	1.2	46.9	408	−866	25		
6-Mo	P(CH$_2$CH$_2$CN)$_3$	[Mo]	1955m, 1855s	5.43		40.2	263	+43.3	5	1.36	22.35
			1800vs, 2245s(ν_{CN})								
6-Cl		Cl	1852s, 1798vs								
			2240(ν_{CN})								
6-I		I	1855s, 1800vs								
			2240(ν_{CN})								
7-I	PPh$_3$^{c}	I	1930s, 1860vs	5.00	1.3	67.8	390	−921	45	2.73	13.25
8-I	P(OMe)$_3$^{c}	I	1940s, 1872vs	5.25	1.3	189.6	457	−914	20	2.60	24.10

[a] [Mo] = Cp(CO)$_2$LMo. [b] Not given. [c] Ref. 2.

hybridization of mercury. This last atom may lie in the shielding region due to magnetic anisotropy of a cyano group [13]. Consequently, the electron density on the Mo–Hg unit and the $d_\pi(Mo)–p_\pi(CO)$ backbonding should be enhanced. Such secondary intramolecular interactions between the terminal donor atom of the ligand and mercury have already been observed in a number of mercury compounds [14].

In all cases the resonances of the mercury nuclei are observed at higher fields in iodides than in chlorides (normal halogen dependence). Among the complexes with σ-donor phosphines there are regular changes of ^{199}Hg chemical shifts with a number of electronic parameters like Tolman's χ_i [9] and Bartik's $^{FT}\chi$ [15] contributions, Hammet's σ_p field and resonance effects [16], Bodner's substituent parameters σ [17] as well as with the pK_a values [11] of the phosphines involved. There is less evident dependence of δ^{199}Hg on the Taft's resonance interaction with a π-system ($\sigma^0{}_R$ constant) and polar or inductive effects (σ_I constant) [18]. Because the σ_I is a combination of through-bond and through-space field effects (the last one is considered to be more important for σ_I) we think that the influence of through-space interactions on ^{199}Hg resonances is of little or no importance in the complexes studied here. The representative plots of δ^{199}Hg versus pK_a values and Bartik's $^{FT}\chi$ contributions for iodides are given in Fig. 2. Nearly linear correlations are observed for *para*-substituted phenyl phosphines (complexes **1** to **4-I**). The points corresponding to **5-I** (PEt_3) fall slightly off the straight lines. This is not surprising in view of the differences in the steric effects of PEt_3 and aryl phosphines. A slightly higher field for complex **5-I** than would be expected from the straight line may be explained by some destabilization of the HOMO leading to a decrease of the ΔE term in the paramagnetic contribution to the overall shielding. This may be due to an easier transmission of the donor strength in the case of PEt_3 ($\theta = 132°$) than in the case of aryl phosphines ($\theta = 145°$).

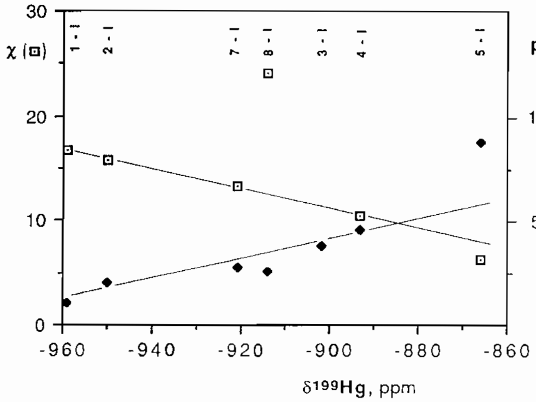

Fig. 2. ^{199}Hg chemical shifts for iodides vs. pK_a values and Bartik's χ contributions, with the numbering of complexes (**1-I** to **8-I**) as in Table 1.

One sees from the correlations given in Fig. 2 that the better donors L give rise to the ^{199}Hg resonances shifted to higher frequencies and that the highest fields are observed in the case of the least basic $P(4\text{-}Cl\text{-}C_6H_4)_3$. Similar trends of ^{199}Hg resonances have already been observed in the butyl and *para*-substituted phenyl phosphine adducts of mercury(II) salts of the type $HgX_2(PR_3)_n$ with direct mercury–phosphorus bonds [19–21]. We have included into the plots of Fig. 2 and in Table 1 the parameters of the complexes $Cp(CO)_2LMoHgI$; $L = PPh_3$ (**7-I**), $L = P(OMe)_3$ (**8-I**) [2]. The ^{199}Hg resonance for **8-I** falls outside the lines defined by σ-donor phosphines and is observed at lower field than any value predicted on the basis of various electronic parameters. In this case the different behaviour of the mercury nuclei is consistent with the properties of a $P(OMe)_3$ ligand which is thought to be a strong π-acceptor and is designated by Giering as a σ-donor/π-acceptor ligand. Because it is now established that in structurally analogous compounds the lower field resonances may reflect some π-bonding, it is possible that there is some of this type of interaction in $Cp(CO)_2P(OMe)_3MoHgI$ with π-donation going from I through Hg to Mo and $P(OMe)_3$. Such a π-type interaction is well illustrated by the ^{197}Pt chemical shifts in the electron rich d^8 $[PtCl_3L]^-$ complexes where the lowest field signal (−3496 ppm) is observed for $L = P(OMe)_3$ followed by that of $L = PPh_3$ −3513 ppm and the highest one at −3540 ppm for $L = PEt_3$ [22].

We have already mentioned that it was not possible to record any ^{95}Mo resonance for the complexes studied here. However, it is worth noting that in the carbonyl derivatives of $Mo(0) - d^6$ of the type $Mo(CO)_5L$ there is no overall correlation of the ^{95}Mo chemical shifts with the basicity of phosphines L and that the fields of these resonances decrease in the order $P(OMe)_3 > PEt_3 > PEt_2Ph > PPh_3$ [23–25]. The same trends have been observed for δ^{51}V in $V(-I) - d^6$ carbonyl anions $V(CO)_5L^-$ and in $V(I) - d^4$ carbonyl cyclopentadienyl complexes $CpV(CO)_{4-n}L_n$ [26]. In these vanadium complexes the ^{51}V chemical shifts were tentatively interpreted in terms of the relative stabilizations of the σ and π orbitals and of the relative strengths of the metal–phosphorus bonds but the separation of σ- and π-type orbitals cannot be carried out unambiguously. One may conclude for the $Mo(II) - d^4$ complexes with molybdenum–mercury bonds that the δ^{95}Mo should be observed at higher fields for PEt_3 than for the triphenyl phosphines. It is in a good agreement with our earlier observations that the higher fields of ^{95}Mo resonances correspond to the lower ones of ^{199}Hg. The interpretation of the metallic chemical shifts in the presence of $P(OMe)_3$ remains more obscure and certainly needs more theoretical treatment. It seems, at least for the metals directly bound to PR_3 ligand, that the chemical shift values are related to the M–P bond strengths that themselves depend on steric factors (Tolman's cone angles: phosphites < alkyl phosphines < phenyl phosphines). ^{95}Mo resonances have been reported for some *para*-substituted benzyl complexes $Cp(CO)_3MoCH_2C_6H_4X$ [27]. These compounds are formally analogous to those studied here as regards the number of bonds separating the molybdenum atom from the X substituent on the phenyl group (Mo-A-C_6H_4X, A = CH_2 or P). The trend in chemical shift variations for these benzyl complexes is: X = Cl −1566 ppm; X = F −1577 ppm; X = Me −1583 ppm and X = OMe −1587 ppm. A similar trend for ^{95}Mo chemical shifts may be expected for the complexes studied here, in which the dependence of ^{199}Hg resonances on the nature of X is reversed. Thus, this observation provides an indirect confirmation of our statement that the lower field shifts of ^{95}Mo are accompanied by the higher field ones of ^{199}Hg. This suggests a different magnetic behaviour of the molybdenum (open valence shell) and of the mercury (formally closed shell) nuclei.

The ^2J mercury–phosphorus coupling constants (Table 1) are greater for chlorides than for iodides and the lowest values are observed for symmetrical complexes **1** to **6**-Mo. The higher ^1J(Hg–P) couplings for chlorides than for iodides have been observed in many metal–phosphorus bonded compounds and interpreted in terms of an increase in the metal 's' orbital contribution to the M–P bonds with an increase in the electronegativity of the anionic ligands [28]. Such an interpretation is valid for our complexes with P–Mo–Hg–Z (Z = Cl, I) linkage because the presence of better electron-withdrawing chloride should prevent a molybdenum to phosphorus backdonation and reduce a potential (if there is any) π-interaction in the Mo–Hg bond. Thus, the two- bond phosphorus–mercury interactions should have higher 's' character in chlorides than in iodides. It has been stated that greater ^1J(Hg–P) coupling constants are observed for more deshielded mercury nuclei [29]. However, in the complexes studied here we observe the lowest coupling constants for symmetrical complexes in which the mercury nuclei are most deshielded. This result shows that the bonding in Mo–Hg–Mo and Mo–Hg–Z (Z = Cl, I) complexes is different. Both, the lower field resonances of ^{199}Hg and the lower coupling constants ^2J(Hg–P) in complexes **1** to **6**-Mo indicate that the π-bonding is present in the trimetallic unit (ΔE influence on the paramagnetic contribution σ_p to the overall shielding and on the Fermi contact term K dominating the coupling constants [4]). It has been also stated that in the complexes of Hg(II), Cd(II), Sn(IV) with tertiary phosphines the largest phosphorus–heavy metal coupling constants are observed with the most basic phosphines reflecting their σ-donor strengths [28, 30, 31]. In our complexes the ^2J(Hg–P) values are greater for more basic PEt_3 than for the less basic aryl phosphines, but the dependence of J upon the pK_a values cannot be extended to phosphites. The highest ^2J(Hg–P) coupling constants are recorded for π-acceptor $P(OMe)_3$. However, a good linear correlation exists between the ^2J(Hg–P) and the Tolman's cone angle (θ) values (Fig. 3) indicating the importance of steric factors in the couplings observed in our complexes. The smaller cone angle of $P(OMe)_3$ allows this ligand to move closer to the metal giving a shorter and stronger Mo–P bond and a better stabilization of the HOMO (higher ΔE value), while with bulkier phenyl phosphines the Mo–P bonds should be longer and weaker leading to smaller ΔE values and thus smaller couplings. Moreover, the lone electron pair on sp^3 hybridized phosphorus in free phosphines has higher 'p' and smaller 's' participation in less pyramidal phosphines, i.e. in those with larger cone angles.

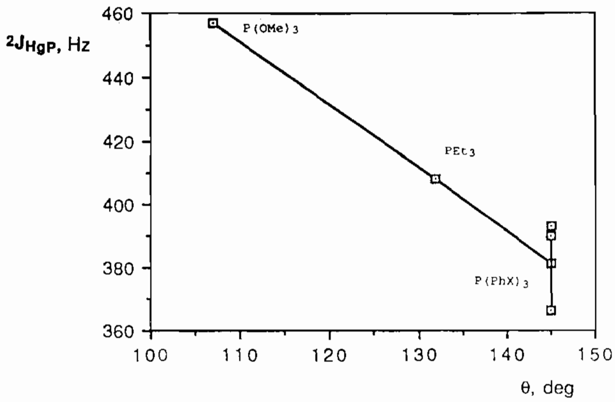

Fig. 3. ^2J(HgP) coupling constants for iodides vs. Tolman's cone angle θ. The mean value of ^2J(HgP) for aryl phosphines $P(PhX)_3$ is equal to 382.4 Hz and lies on the straight line defined by $P(OMe)_3$ (**8-I**) and PEt_3 (**5-I**) complexes.

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