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CHLORINATED ORGANIC DERIVATIVES CONTAINING Mo–Hg AND W–Hg BONDS: IMPORTANCE OF THE STERIC EFFECTS IN THEIR STABILIZATION

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Summary

A series of Mo–Hg and W–Hg bonded complexes [RHg–M(CO)$_3$Cp], (R = 2,4,6-$C_6H_2Cl_3$, 2,3,5,6-C_6HCl_4 and C_6Cl_5) have been prepared from ClHgR and the salts Na[M(CO)$_3$Cp]. When R contains only one *ortho* chlorine atom (R = 2,5-$C_6H_3Cl_2$, 2,3,4-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4) a symmetrisation process occurs to give the corresponding HgR_2 and Hg[M(CO)$_3$Cp]$_2$. These results indicate that steric effects are very important in the formation of compounds containing molybdenum- or tungsten–mercury bonds. Complexes of the type [(C_6Cl_5)Hg–M(CO)$_2$(PPh$_3$)Cp] (M = Mo and W) are obtained from [(C_6Cl_5)Hg–M(CO)$_3$Cp] and PPh$_3$ in boiling ethanol.

Introduction

There have been several reports on complexes with Mo–Hg and W–Hg bonds of the type [XHg–M(CO)$_3$Cp] [1] (X = halide or pseudohalide) but surprisingly, only four related bimetallic compounds with organic R groups are known: [RHg–M(CO)$_3$Cp] (M = Mo, R = Ph [2], C_6F_5 [3]; M = W, R = CH_3 [3], $(CH_3)_3SiCH_2$ [4]). There are two reasons for this: (i) the general method for forming [XHg–M(CO)$_3$Cp] (eq. 1) is not applicable for compounds containing the RHg–M

$$\mathrm{Hg[M(CO)_3Cp]_2 + HgX_2 \rightarrow 2[XHg{-}M(CO)_3Cp]} \qquad (1)$$

moiety because no reaction takes place between Hg[M(CO)$_3$Cp]$_2$ and dialkyl- or diaryl-mercury compounds [1], and (ii) compounds of the type [RHg–M(CO)$_3$Cp] usually readily decompose in solution, at room temperature or below, according to eq. 2. This decomposition obviously precludes the isolation of the bimetallic derivatives.

$$2[RHg\text{-}M(CO)_3Cp] \rightarrow HgR_2 + Hg[M(CO)_3Cp]_2 \qquad (2)$$

The stability of the $[XHg\text{-}M(CO)_3Cp]$ towards the symmetrisation process could be attributed to the high electronegativity of X, which removes the excess electron density from the metal–metal bond. However, the spontaneous redistribution of $[(C_6F_5)Hg\text{-}W(CO)_3Cp]$, which contains the very electronegative C_6F_5 ligand, to give $Hg(C_6F_5)_2$ and $Hg[W(CO)_3Cp]_2$ [3], suggests that electronegativity is not always the overriding factor. This agrees with our results on the stability of complexes $[RHg\text{-}PtR(PPh_3)_2]$ [5], $[RHg\text{-}PtCl(PPh_3)_2]$ [6] and $[RHg\text{-}Ir(CO)Cl_2(PPh_3)_2]$ [7] (R = polychlorinated groups). In this series of compounds, steric factors are even more important than electronic factors in the stability of the metal–mercury bonds. In an attempt to prepare complexes containing Mo–Hg and W–Hg bonds, and in order to evaluate the relative influence of steric and electronic effects of the ligands R attached to mercury, the reaction of metal carbonylates $[M(CO)_3Cp]^-$ (M = Mo, W) with ClHgR (R = polychloroaryl group) has been studied, and is the subject of this paper.

Results and discussion

Preparation of [RHg–M(CO)₃Cp] (M = Mo or W)

The compounds $[RHg\text{-}M(CO)_3Cp]$ (M = Mo or W; R = 2,4,6-$C_6H_2Cl_3$; 2,3,5,6-C_6HCl_4 and C_6Cl_5) were prepared by adding an equimolar quantity of $Na[M(CO)_3Cp]$ in THF to a solution of ClHgR in the same solvent under nitrogen (eq. 3). When the starting materials were the organomercury compounds ClHgR

$$ClHgR + Na[M(CO)_3Cp] \rightarrow [RHg\text{-}M(CO)_3Cp] + NaCl \qquad (3)$$

(R = 2,5-$C_6H_3Cl_2$; 2,3,4-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4) it was not possible to isolate the bimetallic compounds containing M–Hg bonds, because, even at −78 °C, a symmetrisation process occurred to give HgR_2 and $Hg[M(CO)_3Cp]_2$. This reaction is easily detected because the complexes with Mo–Hg or W–Hg bonds are white, whereas the trimetallic $Hg[M(CO)_3Cp]_2$ are bright yellow. The reaction of $Na[M(CO)_3Cp]$ to a THF solution of ClHgPh immediately gives $HgPh_2$ and $Hg[M(CO)_3Cp]_2$.

These results indicate that even though the electronegativity is an important factor in determining the stability of the compounds with Mo–Hg or W–Hg bonds, the presence of one or two chlorine atoms in the *ortho* position of the benzene ring can be the determining factor. Thus, the stabilization and isolation of the compounds $[RHg\text{-}M(CO)_3Cp]$ is favoured if R contains two bulky substituents in the *ortho* positions. In the light of the nature of the products formed, our results suggest an associative mechanism to explain the symmetrisation process; the approach of two *ortho* chlorine atoms on R will be strongly disfavoured due to steric congestion, and this may account for the remarkable stability of these species.

Unsymmetrical mercurials RHgX show identical behaviour towards disproportion: thus compounds RHgCl symmetrise in the presence of phenanthroline when R contains only one *ortho* chlorine atom [8].

Analyses, decomposition temperatures, IR and ^1H NMR spectra are given in

Table 1. All the compounds are air-stable as solids and in solution. They are only sparingly soluble in most usual organic solvents. The IR spectra show the bands due to polychlorophenyl groups with very small differences from the corresponding HgR_2 [9]. ν(Cp) appears at approximately the same frequency in all cases (~ 820 cm^{-1}). A high frequency shift of the three ν(CO) bands with respect to $Na[M(CO)_3Cp]$ is observed in all compounds, in accord with an increase of the oxidation state of M. When the symmetrisation occurs, the IR spectrum shows the characteristic bands at 1940–1960 cm^{-1} of the $Hg[M(CO)_3Cp]_2$ derivatives [1].

Preparation of $[(C_6Cl_5)Hg\text{–}M(CO)_2(PPh_3)Cp]$

In order to complete the characterization of the new compounds we attempt to replace one or more of the carbonyl groups by triphenylphosphine. Complexes $[(C_6Cl_5)Hg\text{–}M(CO)_2(PPh_3)Cp]$ were obtained from $[(C_6Cl_5)Hg\text{–}M(CO)_3Cp]$ and a slight excess of PPh_3 in boiling ethanol. The yields were almost quantitative and no symmetrisation reaction was observed. Analyses, IR and ^1H NMR spectra indicate that only one CO group has been replaced, as previously observed for other similar products [10]. The $^{31}P\{^1H\}$ NMR spectrum of the $[(C_6Cl_5)Hg\text{–}Mo(CO)_2(PPh_3)Cp]$ show one signal (δ(P) 70.0 ppm) flanked by ^{199}Hg satellites (natural abundance 16.8%) with $^2J(^{31}P\text{–}^{199}Hg)$ 285 Hz, indicating the presence of a direct Mo–Hg bond. Similarly, the compound $[(C_6Cl_5)Hg\text{–}W(CO)_2(PPh_3)Cp]$ exhibits a singlet at δ(P) 37.9 ppm with $^2J(^{31}P\text{–}^{199}Hg)$ 297 Hz. No $J(^{31}P\text{–}^{183}W)$ coupling was detected due to a poor resolution.

It is believed that both compounds have structures based upon a linear mercury geometry involving *cis* or *trans* substituted pseudo-square-pyramidal molybdenum or tungsten atoms, as recently described for the complex *trans*-$[(CN)Hg\text{–}Mo(CO)_2(AsMe_2Ph)Cp]$ [11]. A distinction between *cis* and *trans* isomers can be drawn from the ^1H NMR spectra, and the doublet of the cyclopentadienyl resonance in the two compounds supports a *trans* geometry. In *cis* complexes ^{31}P coupling to the cyclopentadienyl protons is negligible [12]. Furthermore, the intensity ratio of the ν(CO) absorptions in both complexes is consistent with the *trans* formulation [13]. In no case was a mixture of isomers detected.

Experimental

The reactions were performed in a Schlenk-type flask under dry nitrogen. Solvents were distilled under nitrogen from sodium benzophenone-ketyl prior to use. Chemical analyses were carried out at the Institut de Bio-Orgànica de Barcelona. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 Fourier Transform Spectrometer for $CDCl_3$ solutions using 85% H_3PO_4 as external reference. PRM spectra were recorded on a Perkin–Elmer R-12A at 60 MHz. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer.

Starting materials. $Na[Mo(CO)_3Cp]\cdot DME$, $Na[W(CO)_3Cp]\cdot DME$ were prepared according to [14], and the compounds RHgCl were prepared by refluxing an equimolar solution of HgR_2 [9] and $HgCl_2$ in xylene.

Preparation of $[RHg\text{–}M(CO)_3Cp]$. All these were prepared by the following general method: A THF solution of $Na[M(CO)_3Cp]\cdot DME$ (1.0 mmol) was added to a suspension of RHgCl (1.0 mmol) in THF at −78°C. After a few minutes, the

TABLE 1

ANALYTICAL DATA AND PROPERTIES OF COMPLEXES

[RHg-M(CO)$_3$Cp]		Decomposition temperatures (°C)	IR spectra [a] ν(CO) cm^{-1}	NMR spectra [b] (ppm)	Analyses (found(calcd.) (%))	
M	R				C	H
Mo	C_6Cl_5	230–235	1980(vs) 1885(sh) 1865(vs)	δ(Cp) 5.40	24.1 (24.19)	0.6 (0.72)
Mo	2,3,5,6-C_6HCl_4	235–240	1975(vs) 1890(sh) 1865(vs)	δ(Cp) 5.40	25.3 (25.45)	0.9 (0.91)
Mo	2,4,6-$C_6H_2Cl_3$	238–240	1975(vs) 1880(sh) 1860(vs)	δ(Cp) 5.40	26.8 (26.85)	1.0 (1.12)
W	C_6Cl_5	215–220	1970(vs) 1890(vs) 1880(vs) 1860(vs)	δ(Cp) 5.50	21.5 (21.47)	0 6 (0.64)
W	2,3,5,6-C_6HCl_4	225–230	1970(vs) 1885(s) 1860(vs)	δ(Cp) 5.50	22.2 (22.46)	0.8 (0.94)
W	2,4,6-$C_6H_2Cl_3$	235–240	1970(vs) 1885(s) 1860(vs)	δ(Cp) 5.50	23.5 (23.54)	0.9 (0.98)
[(C_6Cl_5)Hg-Mo(CO)$_2$(PPh$_3$)Cp]		170–180	1890(s) 1820(vs)	δ(Cp) 4.95 [c] δ(^{31}P) 70.0	93.7 (40.06)	2.0 (2.16)
[(C_6Cl_5)Hg-W(CO)$_2$(PPh$_3$)Cp]		200–210	1880(s) 1805(vs)	δ(Cp) 5.0 [d] δ(^{31}P) 37 9	36.3 (36 60)	1.9 (1.98)

[a] KBr disks. [b] PMR reference TMS; $^{31}P\{^1H\}$ NMR reference H_3PO_4 85%. PMR at 200 MHz. [c] $^3J(^1H-^{31}P)$ 1.0 Hz. [d] $^3J(^1H-^{31}P)$ 1.2 Hz. $^2J(^1H-^{183}W)$ 1.2 Hz.

solution was evaporated to dryness and the residue was recrystallized from benzene/hexane. (Yield about 70–80%).

Preparation of $[(C_6Cl_5)Hg{-}M(CO)_2(PPh_3)Cp]$. A mixture of $[(C_6Cl_5)Hg{-}M(CO)_3Cp]$ (1.0 mmol) and PPh_3 (1.1 mmol) in ethanol was refluxed for 4 h. After cooling, the solid obtained was washed with hexane to remove the excess of PPh_3 (Yield about 95%).

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