Bis(cyclopentadienyl) Molybdenum Complexes Containing Mo–Sn σ-Bond

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The reactions of Cp_2MoH_2 with $SnCl_4 \cdot 5H_2O$ and with $SnCl_4$ have been studied. Elimination of HCl and five water molecules has been shown to take place in the case of $SnCl_4 \cdot 5H_2O$ and the product $Cp_2Mo(H)SnCl_3$ (I) formed. In the other case the substance $[Cp_2Mo(H)SnCl_3]_2SnCl_4$ (II) formed as a result of the reaction of Cp_2MoH_2 with $SnCl_4$. It can be treated as the product of Lewis base-acid reaction (I) with $SnCl_4$.

The substances (I) and (II) were investigated by H n.m.r., ^{119}Sn Mössbauer and i.r. spectroscopy methods. On the basis of the spectroscopic data, the structures of (I) and (II) have been suggested.

The existence of terminal hydride in the solid state is characteristic for (I), while the bridge bond Mo–H–Sn occurs in the solution. In the (II) strong $(Mo–H→)_2Sn$ bonding takes place in the condensed phase, and the distruction of the complex (II) during dissolving is observed.

Introduction

The interaction of molybdenocene dihydride with metal halides, being Lewis acids, proceeds as a rule with preservation of Mo–H bonds and produces adducts containing donor–acceptor bond Mo:→M (M = B, Al) [1] or hydrogen bridges

$$Mo\underset{H}{\overset{H}{\diagdown\hspace{-0.3em}\diagup}}M$$

(M = Co, Mo, Cu, Fe, Zn) [2–4]. The known exception is the reaction between Cp_2MoH_2 and mercury (II) halides: elimination of hydrogen halide produces

bimetallic complexes, wherein molybdenum is σ-bonded to mercury [5]. Thus, the products of the reaction of Cp_2MoH_2 — a bifunctional Lewis base — with metal halides are probably determined by the coordination capabilities and acidity of $MHal_n$. A possibility to form Mo–M σ-bond also plays a major role. As is known, molybdenum strongly bonds to elements of the silicon subgroup, to tin in particular, for which a number of tin–molybdenum carbonyl complexes have been prepared [6]. In this respect there is interest in combining Cp_2MoH_2 with chloride of four-valent tin and its solvates, since the latter form a series of Lewis acids of varying strengths.

Experimental

All the procedures were carried out under dry argon. Solvents were dried by boiling and subsequently distilled over lithium aluminum hydride or calcium hydride directly before use. Cp_2MoH_2 and Cp_2MoD_2 were obtained as described in [7]. $SnCl_4$ and $SnCl_4 \cdot 5H_2O$ were analytically pure. The content of molybdenum was determined spectrophotometrically on a SF-4A instrument. The quantity of chloride was calculated following titration with silver nitrate solution with potentiometric indication of the equivalence point. IR-spectra were taken in the region 200–2000 cm^{-1} on a IKS-22V or UR-20 spectrometer; the samples were prepared as suspensions in Nujol. ^{1}H NMR-spectra were recorded on a Varian XL-100 spectrometer operating at 100 MHz. The samples were run as dimethylformamide-d7 solutions. Solvent resonances (1.95, 7.08, 7.22τ) served as standards for reference of proton chemical shifts. The Mössbauer ^{119}Sn spectra were taken on

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TABLE I. Hydrogen-1 NMR Data of Complexes Based on Cp_2MoH_2 and Cp_2WH_2.

Compound	$\tau H-Cp$	$\Delta\tau H-Cp$	$\tau H-M$	$\Delta\tau H-M$	Ref.
Cp_2MoH_2	5.63	0.0	18.83	0	7
Cp_2WH_2	5.77	0.0	22.30	0	7
$Cp_2Mo\overset{H}{\underset{}{—}}SnMe_3$	5.88	+0.25	22.37	−0.05	8
$Cp_2W\overset{H}{\underset{}{—}}SnMe_3$	5.98	+0.21	22.37	+0.07	8
$Cp_2W\overset{H}{\underset{}{—}}SnPh_3$	5.50	−0.27	22.24	−0.06	9
$Cp_2Mo\overset{H}{\underset{H}{\diagup\diagdown}}ZnCl_2 \cdot DMF$	5.00	−0.63	20.10	+1.27	10
$CpW\overset{H}{\underset{H}{\diagup\diagdown}}ZnCl_2 \cdot DMF$	4.90	−0.87	23.10	+0.80	11
$Cp_2Mo\overset{H}{\underset{}{—}}SnCl_3 \cdot DMF$	4.70	−0.93	20.50	+1.67	this work

a spectrometer of an electrodynamic type in the region of constant accelerations. $Ba^{119m}SnO_3$ served as the source.

Methods of Preparing Cp_2MoH_2 Complexes with Tin Chloride (VI)

Solution of $SnCl_4 \cdot 5H_2O$, $SnCl_4 \cdot 2Et_2O$ ($SnCl_4$) in ether (benzene) was added with stirring to the solution of 0.3–0.4 g (1.5–2 mmol) of Cp_2MoH_2 in 20–50 ml in the same solvent. Since the composition of products was independent of the reagent ratio, 15–20% stoichiometric excess of chloride was introduced into the reaction. After precipitation, the mixture was stirred for an hour, the precipitate was filtered off, washed with a large amount of solvent, and dried *in vacuo*. The compounds were obtained in 90–95% yield. Data of chemical analysis are as follow:

$Cp_2Mo(H)SnCl_3$. Found, %: Mo, 21.2; Cl, 23.5. Calcd. %: Mo, 21.2; Cl, 23.6.

$[Cp_2Mo(H)SnCl_3]_2SnCl_4$. Found, %: Mo, 16.0; Cl, 30.0. Calcd. %: Mo, 16.5; Cl, 30.5.

Results and Discussion

Combining excess of tin chloride pentahydrate (IV) with Cp_2MoH_2 in ether produces crystalline, hydrolytically stable, rosy substances consistent with the formulation as $Cp_2Mo(H)SnCl_3$ (I):

$$Cp_2MoH_2 + SnCl_4 \cdot 5H_2O \xrightarrow[25\,°C]{Et_2O}$$

$$Cp_2Mo(H)SnCl_3\downarrow + HCl + 5H_2O \qquad (1)$$

$$(I)$$
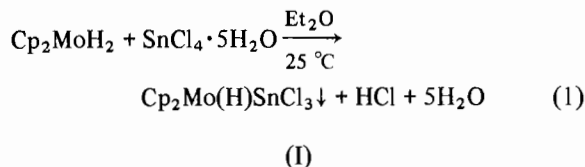
This compound easily oxidizes in air, is insoluble in nonpolar and weakly solvating solvents, but dissolves well in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). It dissolves significantly much less in acetonitrile, where recrystallization yields large red single crystals of (I). Compound (I) slowly interacts with the solvent to give products of unknown composition. Therefore, (I) was crystallized from the solution and ^1H NMR-spectra were recorded immediately after it had been prepared. Hydrogen-1 NMR-spectrum exhibits two signals: one from cyclopentadienyl protons at 4.7 τ, and the other from hydride protons at 20.50 τ with the intensity ratio of 10:1. Satellites near both signals arise from spin–spin interactions of magnetic nuclei ^{117}Sn and ^{119}Sn with hydride proton ($J_{H-Mo-Sn}$ = 300 Hz) and cyclopentadienyl protons ($J_{H-C-Mo-Sn}$ = 20 Hz). The strong spin–spin interaction between C_5H_5-group protons and the tin magnetic nuclei suggests the presence of direct intermetallic Mo–Sn σ-bond ensuring high electron density at the tin nucleus. This is confirmed by the high isomer shift value (IS) in the Mössbauer spectrum of (I) (Fig. 2a). Downfield shift of cyclopentadienyl protons
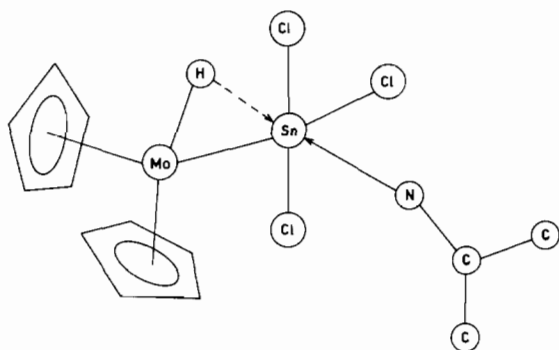
Fig. 1. Structure of complex $Cp_2Mo(H)SnCl_3$ in DMF.

Fig. 2. Mössbauer spectra: $Cp_2Mo(H)SnCl_3$ (I) (2a); $[Cp_2Mo(H)SnCl_3]_2SnCl_4$ (II) (2b); product precipitating from DMF solution of (II) on addition of THF (2c). T = 80 K. Source $Ba^{119m}SnO_3$.

from Cp_2MoH_2 [7] and $Cp_2Mo\cdots SnMe_3$ [8] should apparently be attributed to deshielding as the electronegative group $SnCl_3$ withdraws electrons from the C_5H_5 group. As is known, the value of geminal coupling constant J_{H-C-Sn} for organotins [12] does not exceed 100 Hz, whereas the directly bonded hydrogen—tin coupling constant J_{H-Sn} for organotin hydrides [13] lies in the range 1500—1950 Hz. Thus, coupling constant $J_{H-Mo-Sn}$ for solution of compound (I) lies between direct and geminal constants, which suggests the formation of an asymmetric bridge $Mo\overset{H}{\diagup\diagdown}Sn$. This conclusion is also supported by an upfield shift ($\Delta\tau$ = 1.7 ppm) of hydride protons relative to the starting Cp_2MoH_2. Table I gives the parameters of ^1H NMR-spectra for a series of Cp_2MoH_2 and Cp_2WH_2 derivatives containing both bridging and terminal metal—hydrogen bonds. As can be seen in the Table, the presence of bridges in $Cp_2Mo(H)_2ZnCl_2$ DMF leads to that shifts τ_{Cp} and τ_{H-Mo} are found upfield relative to initial Cp_2MoH_2 as with (I), while in $Cp_2Mo(H)SnMe_3$ [8], $Cp_2W(H)SnMe_3$ [8], $Cp_2W(H)SnPh_3$ [9] containing terminal M—H bonds and not carrying electron-acceptor substituents at tin, chemical shifts for protons relative to the initial dihydrides change only slightly. The bridge $Mo\overset{H}{\diagup\diagdown}Sn$ probably forms because the tin atom in complex (I) acquires high acidity in solution, while significant electron density makes hydride hydrogen highly basic. The most plausible seems the formation of bridge $Mo\overset{H}{\diagup\diagdown}Sn$ within one molecule, as depicted in Fig. 1. Compound (I) is assumed to be solvated at tin atom which has a coordination number of six. When conducting the reaction in ether or crystallizing complex (I) from THF or acetonitrile it is isolated in the nonsolvated state. The presence of the terminal
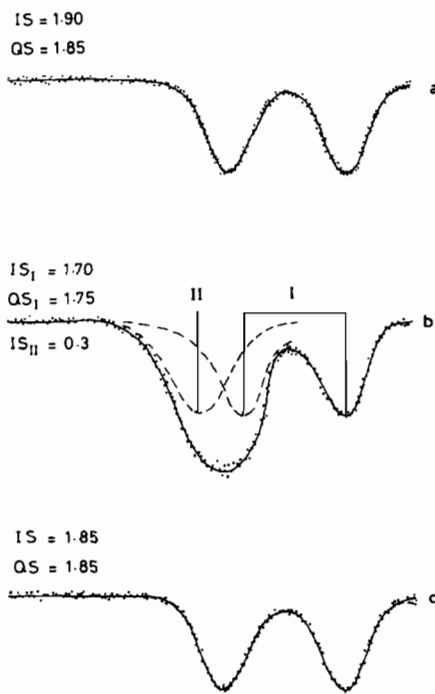
hydride atom is identified by infrared spectroscopy (Nujol mulls). Bands arising from Mo—H vibrations appear at 1840 cm^{-1} (1853 cm^{-1} in the initial Cp_2MoH_2 [7]), whereas the formation of the bridge would significantly decrease the frequency of the vibrations. The band at 720 cm^{-1} corresponds to bending vibrations of hydride hydrogen. The long wavelength region of the spectrum (200—400 cm^{-1}) exhibits two highly intense bands at 331 and 303 cm^{-1}. The first should apparently be attributed to Sn—Cl^t vibrations (similar absorption band in the spectrum of $SnCl_4 \cdot 2L$ lies in the region 330—360 cm^{-1} [14]), while the second probably belongs to bridging Sn—Cl^b vibrations. The Mössbauer spectrum of complex (I) (Fig. 2a) confirms the presence of direct Mo—Sn σ-bond. The magnitudes of isomer shift and quadrupole splitting are characteristic of $GSnCl_3$ complexes, where G is an organometallic group containing a transition metal M = Mo, Fe, Mn of the type π-$Cp(CO)_3Mo$ [15]. This and the nonsolvated state of complex $Cp_2Mo(H)SnCl_3$ in the condensed phase give grounds to suggest that the compound polymerizes during condensation because of the formation of bridges Sn--Cl--Sn. The polymerization probably involves cleavage of the bridge $Mo\overset{H}{\diagup\diagdown}Sn$ and displacement of the solvating

solvent from the coordination sphere of tin. Association of bimetallic compounds of similar type *via* halogen bridges is rather common and is known for Cp_2MoH_2 complexes with CuI and $FeBr_2$ [10, 16]. Strongly solvating solvent splits bridges M--HaI--M' to produce solvated molecules [17].

Combining Cp_2MoH_2 with non-aqueous $SnCl_4$ in ether, in which the latter exists as $SnCl_4 \cdot 2Et_2O$, gives (according to IR data) a substance identical to complex (I). In both cases, the complex $SnCl_4 \cdot$ 2L undergoes ligand displacement by the stronger Lewis base Cp_2MoH_2 followed by HCl elimination to produce a Mo–Sn σ-bond. It is of interest that $Cp_2Mo(H)SnCl_3$, though it carries a lone electron pair is, in contrast to Cp_2MoH_2, not protonated by Bronsted acids, in particular by HCl released in reaction (1). Since tin does not form a π-dative bond, this phenomenon could be attributed either to steric hindrance or to a decrease in basicity of molybdenum caused by introducing an electron-accepting substituent.

The reaction of Cp_2MoH_2 with non-aqueous $SnCl_4$ in benzene is more intricate and produces a yellow substance formulated as $[Cp_2Mo(H)SnCl_3]_2SnCl_4$ (II). It rapidly oxidizes in air and, as distinct from (I), is sensitive to hydrolysis. The compound is insoluble in common organic solvents but dissolves on heating in DMF and DMSO with the preliminary swelling characteristic of bulk polymers. The Mössbauer spectrum of (II) visualizes superposition of two components: a doublet and s singlet (Fig. 2b). The doublet component belongs to tin σ-bonded to molybdenum, and its parameters are close to the parameters of compound (I) spectrum. Isomer shift of the singlet component (0.3 mm/s) corresponds to $SnCl_4$ coordination bonded to donor ligands. Repeated washing of (II) with benzene and benzene–ether mixture easily dissolving $SnCl_4$ and its solvates does not decrease the singlet intensity, which points to a coordination bonding between the two components. The IR-spectrum of (II) in the region of stretching vibrations of M–H bonds visualizes an intense band at 1588 cm^{-1} (1173 cm^{-1} for the deutero-analog) and two weak bands at 1810 and 1954 cm^{-1}, which do not shift on deuteration. A considerable (250 cm^{-1}) shift of frequency of Mo–H vibrations to the higher wavelengths, as compared to (I), unambiguously confirms the presence in (II) of

$$\underset{\text{bridges Mo}}{\overset{H}{\diagup}} \underset{\text{Sn.}}{\diagdown}$$

bridges Mo   Sn. Thus, hydride atoms are donor ligands at tin, to which belongs the singlet component in the Mössbauer spectrum of (II). Comparing the IR-spectra of (II) and its deutero-analog produced from Cp_2MoD_2 allowed us to assign bands at 736 and 810 cm^{-1} to bending vibrations of Mo–H bonds (537 and 585 cm^{-1} for the deutero-analog). The
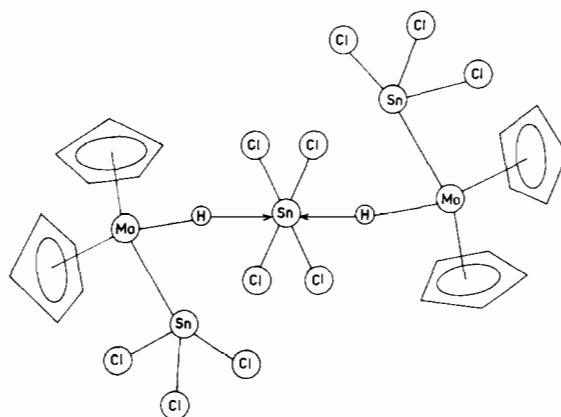

Fig. 3. Structure of a fragment of polymeric chain $[Cp_2$-$Mo(H)SnCl_3]_2SnCl_4$ (II).

IR-spectrum of (II) in the region of stretching vibrations of Sn–Cl bonds exhibits bands at 332 and 304 cm^{-1} characteristic of (I) and also a band at 351 cm^{-1} corresponding to $\nu(Sn–Cl^t)$ in coordination bonded $SnCl_4$. The ^1H NMR-spectrum of compound (II) in DMF is representative of the mixture of substances. The region of cyclopentadienyl protons shows five types of signals, while the hydride region displays three. From this it follows that dissolution of (II) is accompanied with its decomposition by the solvent. The most intense signals at 4.7 and 20.50 τ should apparently be attributed to complex (I): $Cp_2Mo(H)SnCl_3 \cdot DMF$ (Fig. 1). The intensity of other peaks is rather low, and we failed to perform their assignments. The addition of acetonitrile or THF to the solution of (II) in DMF leads to precipitation of a rosy substance, the Mössbauer spectrum of which is identical to that recorded for (I) (Fig. 2a and c). This confirms the destruction at dissolution of polymeric complex (II). The reaction of Cp_2MoH_2 with nonsolvated $SnCl_4$ probably proceeds *via* formation of complex (I) by the reaction (I) followed by complexation with excess $SnCl_4$ by means of Mo–H → Sn bridges. Compound Cp_2-$Mo(H)SnCl_3$ is basic enough to produce a complex with a strong Lewis acid, nonsolvated $SnCl_4$, but still insufficiently basic to displace H_2O or Et_2O from $SnCl_4$ hydrate or etherate. The physical properties of compound (II) are characteristic of polymers. Its polymerization apparently proceeds *via* formation

$$\underset{\text{of bridges Sn}}{\overset{Cl}{\diagup}} \underset{\text{Sn.}}{\diagdown}$$

of bridges Sn   Sn. From the spectral data we suggest the structure of the polymeric fragment depicted in Fig. 3. The suggested model explains the sensitivity of (II) to hydrolysis and its possible destruction by the solvent to produce (I).

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