Interaction of Tin Methylchlorides $SnMe_nCl_{4-n}$ with Molybdenum Hydride Bis(cyclopentadienyl)

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Received July 4, 1985

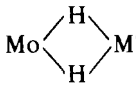
Abstract

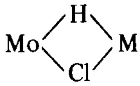
The interaction between Cp_2MoH_2 ($Cp = \eta^5$-C_5H_5) and $SnMe_nCl_{4-n}$ (n = 0–3) proceeds in aprotic solvent with the elimination of HCl and the formation of heterometallic complexes of the composition $Cp_2Mo(H)SnMe_nCl_{3-n}$ (n = 0–3) and $Cp_2Mo(SnMe_2Cl)_2$ which contains an Mo–Sn σ-bond. It has been found that in all studied compounds the length of this bond is 0.20–0.30 Å less than the sum of the covalent radii of the Mo and Sn atoms.

Based on analysis of the geometry of the Mo and Sn environment, the high values of the isomeric shifts (*IS*) in the Mössbauer spectra, the constants of the spin–spin interactions (*SSI*) J^3_{Cp-Sn} and J^2_{HMoSn}, and the considerably decreased values of the J^2_{Me-Sn} constants in ^1H NMR spectra, it was concluded that the decrease in the interatomic distance Mo–Sn is due to the high s-character of this bond. It is suggested that this effect, which is most pronounced in wedge-like complexes, is brought about by changing the orbital hybridization type of the tin atom from sp^3 to s + 3p. This can explain the shorter interatomic distance M–Sn in heterometallic complexes of other types.

Introduction

Molybdenocene dihydride, Cp_2MoH_2 (Cp-η^5-C_5H_5), is known to be a rather strong Lewis base due to the presence of an unshared pair of d-electrons at the Mo atom. Known reactions of this compound with Lewis acids and the halides of transition and non-transition metals can take three distinct pathways, depending on the nature of these metals:

(a) with the retention of the Mo–H bonds and the formation of donor–acceptor type adducts $Cp_2MoH_2MX_n$ (M = B, Al) or chelate type complexes with hydrogen bridges  (M′ = Zn, Fe(II), Cu(II), Cu(I)) [1];

(b) with partial or complete elimination of hydrogen and reduction of the metal atom of the Lewis acid (M′ = Fe(III), Cu(II)), which, in some cases, results in forming structures with an assymetrical heterobridge  [2, 3];

(c) with the elimination of HX (X = Hal, R) and formation of the complexes with an Mo–M′ σ-bond. This type of reaction and its products have been studied in the examples of the interactions of Cp_2MoH_2 with HgX_2 [4] and Cp_2MoH_2 with $SnCl_4$ [5, 6].

This paper concerns further studies of the reactions between Cp_2MoH_2 and organometal Lewis acids $SnMe_nCl_{4-n}$ of 'C' type and establishes the influence of the strength of a Lewis acid on the composition and structure of the resulting heterometallic complexes.

Experimental

All the procedures were carried out under dry argon. Solvents were dried by boiling and subsequently distilled over $LiAlH_4$ (ether, benzene) directly before use. Cp_2MoH_2 and Cp_2MoD_2 were obtained as previously described [7]. Tin chloride and methylchlorides were analytically pure. The complexes of $Cp_2Mo(H)SnCl_3$ (I) and $[Cp_2Mo(H)SnCl_3]_2 \cdot SnCl_4$ (II) were obtained by reacting Cp_2MoH_2 with $SnCl_4$, as previously described [5]. The rest of the complexes were obtained by the following techniques.

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0020-1693/86/$3.50

$Cp_2Mo(H)SnMeCl_2$ (III)

0.2 mmol solution of $SnMeCl_3$ in benzene (or ether) was added to the solution of 0.3–0.4 g (0.15–0.20 mmol) of Cp_2MoH_2 in 30 ml of the same solvent under stirring. This resulted in a yellow precipitate, which was filtered off, washed with ether and dried under vacuum. The compounds were obtained in 95% yield. The resulting $Cp_2Mo(H)SnMeCl_2$ is a crystalline yellow substance, insoluble in benzene and ether, poorly soluble in acetonitrile and THF, and readily soluble in methylene chloride, DMSO and DMFA. *Anal.* Found: Mo, 22.2; Cl, 16.2. Calc. for $(C_5H_5)_2Mo(H)SnMeCl_2$: Mo, 22.20; Cl, 16.21%.

$Cp_2Mo(SnMe_2Cl)_2$ (IV)

0.35–0.45 mmol solution of $SnMe_2Cl_2$ in benzene was added to the solution of Cp_2MoH_2 (0.15–0.20 mmol) in the same solvent under stirring. The completion of the reaction was marked by forming a yellow solution and a white flocculent precipitate V (see below). The precipitate was filtered off, washed with ether and dried under vacuum. Slow evaporation of the yellow solution gave yellow needle-like crystals of $Cp_2Mo(SnMe_2Cl)_2$, readily soluble in benzene and ether. *Anal.* Found: Mo, 16.1; Cl, 11.9. Calc. for $(C_5H_5)_2Mo(Sn(CH_3)_2Cl)_2$: Mo, 16.16; Cl, 11.79%.

$[Cp_2Mo(SnMe_2Cl)_2H]^+Cl^-$ (V)

The white substance, isolated from the above synthesis in the form of a white flocculated precipitate and insoluble in organic solvents, dissolves in DMSO and DMFA with decomposition. *Anal.* Found: Mo, 15.0; Cl, 17.0. Calc. for $[(C_5H_5)_2Mo(Sn(CH_3)_2Cl)_2H]^+Cl^-$: Mo, 15.23; Cl, 16.90%.

$Cp_2Mo(H)SnMe_2Cl$ (VI)

Under prolonged retention of the precipitate V in a small volume of ether, the solvent turned yellow, yielding needle-like crystals of **VI**, moderately soluble in ether and benzene, and readily soluble in CH_2Cl_2, THF, acetonitrile, DMSO and DMFA. Complex **VI** can also be obtained by reacting Cp_2MoH_2 with $SnMe_3Cl$ at the ratio Mo:Sn = 1:2 according to the technique described for the complex $Cp_2Mo(H)SnMe_3$. *Anal.* Found: Mo, 23.2; Cl, 8.6. Calc. for $(C_5H_5)_2Mo(H)Sn(CH_3)_2Cl$: Mo, 23.33; Cl, 8.64%.

$Cp_2Mo(H)SnMe_3$ (VII)

1 mmol of triethylamine was added to the solution of Cp_2MoH_2 in benzene (0.15–0.20 mmol) under stirring; then 0.2 mmol solution of $SnMe_3Cl$ in the same solvent (the ratio Mo:Sn:Et_3N = 1:1:5) was added to the reaction mixture under stirring. The solution was stirred for 5–6 h, and gave a pale-gray flocculent precipitate of $Et_3N \cdot HCl$. The solution became turbid and turned an intensive yellow color. It was filtered, and after slow evaporation, yellow foliated crystals of $Cp_2Mo(H)SnMe_3$ were isolated. To obtain big crystals suitable for X-ray analysis, complex **VII** was recrystallized from pentane or hexane. This was a yellow crystalline substance, readily soluble even in alkanes. *Anal.* Found: Mo, 24.6; Cl, 0.0. Calc. for $(C_5H_5)_2Mo(H)Sn(CH_3)_3$: Mo, 24.61%.

Measurements

The contents of molybdenum was determined spectrophotometrically. The quantity of chlorine was calculated by titration with silver nitrate solution with potentiometric indication of the equivalence point. IR spectra were taken on UR-20 and IKS-22B instruments. The samples were prepared as suspensions in Nujol. ^1H NMR spectra of the solutions in d^7-DMFA and CD_2Cl_2 were recorded on Varian-XL100 and Varian-FT80 spectrometers. Solvent resonances served as standards for references of proton chemical shifts. The Mössbauer ^{119}Sn spectra were taken on a spectrometer of an electrodynamic type. $Ba^{119m}SnO_3$ served as the source.

The X-ray study was performed using a Synthex $P\bar{1}$ diffractometer (Mo k_α irradiation, graphite monochromator, 2θ-scanning up to $2\theta \leqslant 54°$).

The crystals of **VI** are monoclinic: $a = 8.848(2)$, $b = 11.702(2)$, $c = 14.727(3)$ Å, $\gamma = 114.59(1)°$, space group $P2_1/b$, $Z = 1$, $\rho_c = 1.96$ g cm^{-3}. The crystals of **VII** are monoclinic: $a = 8.944(2)$ $b = 11.845(2)$, $c = 26.275(5)$ Å, $\gamma = 91.86(2)°$, space group $P2_1/n_1$, $Z = 8$, $\rho_c = 1.87$ g cm^{-3}. 2002 reflections for **VI** and 3468 for **VII** with $I > 3\sigma(I)$ were used for the calculations. The correction for absorption was made: $\mu^{VI} = 28.4$ cm^{-1}, crystal size, 0.2 × 0.3 × 0.4 mm, $\mu^{VII} = 26.6$ cm^{-1}, crystal size 0.2 × 0.2 × 0.14 mm.

The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic (isotropic for H atoms) approximation up to $R^{VI} = 0.019$ and $R^{VII} = 0.022$ ($R_w{}^{VII} = 0.029$), respectively. **VII** showed two crystallographically independent molecules, **1a** and **1b**. Atomic coordinates for complexes **VI** and **VII** are listed in Tables I and II, and the most important structural characteristics are listed in Table III.

Results and Discussion

In all cases the interaction between Cp_2MoH_2 and tin methylchlorides $SnMe_nCl_{4-n}$ was accompanied by the elimination of HCl and the formation of complexes with an Mo–Sn σ-bond. However, the composition of the final reaction products depends both on methylchloride acidity and on the basicity of the complex $Cp_2Mo(H)SnMe_nCl_{3-n}$.

TABLE I. Atomic Coordinates for the Complex $Cp_2Mo(H)SnMe_2Cl$ (VI)

Atom	x	y	z	U_{eq}
Sn	0.8204(1)	0.2359(1)	0.1621(1)	0.049(1)
Mo	0.5081(1)	0.2106(1)	0.1348(1)	0.035(1)
Cl	0.8839(2)	0.0869(2)	0.0706(1)	0.110(1)
C(1)	0.2517(5)	0.0784(4)	0.1824(3)	0.063(2)
C(2)	0.3344(5)	0.0031(4)	0.1624(3)	0.062(2)
C(3)	0.4653(5)	0.0337(4)	0.2224(3)	0.058(2)
C(4)	0.4673(5)	0.1304(4)	0.2787(3)	0.058(2)
C(5)	0.3340(6)	0.1594(5)	0.2550(3)	0.065(2)
C(6)	0.3665(5)	0.2314(5)	0.0135(3)	0.065(2)
C(7)	0.4831(6)	0.1896(4)	−0.0204(3)	0.061(2)
C(8)	0.6391(5)	0.2838(5)	−0.0044(3)	0.063(2)
C(9)	0.6211(6)	0.3820(4)	0.0407(3)	0.068(2)
C(10)	0.4514(6)	0.3506(5)	0.0517(3)	0.070(2)
C(11)	0.8961(7)	0.1983(6)	0.2932(4)	0.098(3)
C(12)	1.0267(6)	0.4002(5)	0.1130(4)	0.093(3)
H(0)	0.6011(64)	0.3353(50)	0.1987(36)	0.071(18)^a

^{a}Isotropic heat parameter of the atom.

TABLE II. Atomic Coordination for the Complex $Cp_2Mo(H)SnMe_3$

Atom	x	y	z	U_{eq}
Sn1	0.7605(1)	0.2382(1)	0.4413(1)	0.038(1)
Sn2	0.0074(1)	0.2642(1)	0.6723(1)	0.041(1)
Mo1	0.4579(1)	0.2622(1)	0.4561(1)	0.036(1)
Mo2	0.3065(1)	0.2605(1)	0.6971(1)	0.035(1)
C(11)	0.3165(6)	0.2221(5)	0.5250(2)	0.061(2)
C(12)	0.3520(7)	0.3400(5)	0.5252(2)	0.065(2)
C(13)	0.5038(7)	0.3540(5)	0.5325(2)	0.063(2)
C(14)	0.5673(6)	0.2470(5)	0.5365(2)	0.056(2)
C(15)	0.4501(7)	0.1646(5)	0.5314(2)	0.057(2)
C(16)	0.4717(6)	0.1791(5)	0.3755(2)	0.056(2)
C(17)	0.4354(7)	0.2926(5)	0.3705(2)	0.063(2)
C(18)	0.2958(8)	0.3074(5)	0.3941(2)	0.073(2)
C(19)	0.2504(6)	0.2003(6)	0.4147(2)	0.071(2)
C(110)	0.3607(7)	0.1238(5)	0.4025(2)	0.067(2)
C(111)	0.8441(6)	0.0771(4)	0.4684(2)	0.049(2)
C(112)	0.8499(7)	0.2483(7)	0.3646(2)	0.068(3)
C(113)	0.9029(7)	0.3605(6)	0.4811(3)	0.069(2)
C(21)	0.2907(9)	0.1075(5)	0.7494(3)	0.072(3)
C(22)	0.4404(7)	0.1312(5)	0.7367(3)	0.074(3)
C(23)	0.4577(7)	0.1141(5)	0.6853(3)	0.070(3)
C(24)	0.3187(8)	0.0808(4)	0.6650(3)	0.066(2)
C(25)	0.2168(6)	0.0749(4)	0.7043(3)	0.063(2)
C(26)	0.2326(7)	0.4432(5)	0.7136(3)	0.077(3)
C(27)	0.3097(8)	0.4032(5)	0.7560(3)	0.081(3)
C(28)	0.4563(8)	0.3810(5)	0.7408(3)	0.078(3)
C(29)	0.4223(8)	0.4222(6)	0.6987(4)	0.085(3)
C(210)	0.3312(8)	0.4448(5)	0.6730(3)	0.081(3)
C(211)	−0.0696(8)	0.4111(6)	0.6313(3)	0.080(3)
C(212)	−0.1385(7)	0.2579(6)	0.7375(2)	0.077(3)
C(213)	−0.0829(8)	0.1287(7)	0.6247(3)	0.082(3)
HMo1	0.5435(54)	0.3900(40)	0.4442(18)	0.054(16)^a
H1o1	0.9545(90)	0.2882(65)	0.3631(29)	0.143(28)^a

^{a}Isotropic heat parameter of the atom.

As shown in [5], the reaction between Cp_2MoH_2 and $SnCl_4 \cdot 5H_2O$ or $SnCl_4 \cdot 2Et_2O$ solvates results in the complex $Cp_2Mo(H)SnCl_3$ (I). The interaction between Cp_2MoH_2 and unsolvated $SnCl_4$, which is a stronger electrophyl than the complexes $SnCl_4 \cdot 2L$, goes deeper and yields $[Cp_2Mo(H)SnCl_3]_2SnCl_4$ (II). The data of the IR, ^1H NMR and Mössbauer spectroscopy testify to the adduct nature of this compound, where two molecules of **I** coordinate the molecule of $SnCl_4$ by Mo–H → Sn bridges [5].

Irrespective of the solvent nature, the interaction between Cp_2MoH_2 and tin methylchloride is described by the eqn. 1. The resulting $Cp_2Mo(H)SnMeCl_2$ (III), as well as complex **I**, is not protonated by evolving HCl. Unlike the reaction between Cp_2MoH_2 and $SnCl_4$, the methyl-substituted analog of complex **II** is not formed in the excess of $SnMeCl_3$. This can be due to lower acidity of methylchloride as compared to $SnCl_4$.

$$Cp_2MoH_2 + SnMeCl_3 \longrightarrow Cp_2Mo(H)SnMeCl_2 + HCl \qquad (1)$$

TABLE III. Interatomic Distances and Valent Angles in the Complexes $Cp_2Mo(H)SnMe_2Cl$ (VI) and $Cp_2Mo(H)SnMe_3$ (VII)

$Cp_2Mo(H)SnMe_2Cl$				$Cp_2Mo(H)SnMe_3$					
Bond	d (Å)	Angle	ω (°)	Bond	d (Å)			ω (°)	
					1a	1b		1a	1b
Mo–Sn	2.700(1)	CpMoCp	144.6	Mo–Sn	2.758(1)	2.755(1)	CpMoCp	146.1	146.6
Mo–Cp	1.985(5)	HMoSn	72.7(2)	Mo–Cp	1.955(2)	1.945(2)	HMoSn	67.6(3)	69.5(3)
Mo–H	1.64(5)	C–C–C	108	Mo–H	1.60(5)	1.51(6)	C–C–C	108	108
$C–C_{mean}$	1.40(2)	MoSnCl	111.8(2)	$C–C_{mean}$	1.40(2)	1.39(2)	$MoSnC_1$	114.1(1)	117.5(2)
Sn–Cl	2.499(2)	$MoSnC_1$	120.5(2)	$Sn–C_1$	2.191(2)	2.177(2)	$MoSnC_2$	119.1(2)	113.5(2)
$Sn–C_1$	2.149(6)	$MoSnC_2$	120.2(2)	$Sn–C_2$	2.169(3)	2.155(3)	$MoSnC_3$	114.8(2)	117.6(2)
$Sn–C_2$	2.157(5)	$ClSnC_1$	99.4(2)	$Sn–C_3$	2.166(3)	2.169(3)	C_1SnC_2	102.4(2)	102.4(3)
		$ClSnC_2$	95.0(2)				C_1SnC_3	102.4(2)	100.7(3)
		C_1SnCl_2	105.1(2)				C_2SnC_3	101.8(2)	102.9(3)

The reaction between Cp_2MoH_2 and $SnMe_2Cl_2$ in diethyl ether or benzene results in the mixture of soluble $Cp_2Mo(SnMe_2Cl)_2$ (**IV**) and insoluble $[Cp_2Mo(H)(SnMe_2Cl)_2]^+Cl^-$ (**V**). In the presence of triethylamine the same reaction gives complex **IV** alone (eqn. 2). This suggests that **V** is the product

$$Cp_2MoH_2 + 2SnMe_2Cl_2 \xrightarrow{Et_3N} Cp_2Mo(SnMe_2Cl)_2 + Et_3N{\cdot}HCl \qquad (2)$$

of protonating complex **IV** (eqn. 3), and that it possibly has an ionic structure. This is confirmed by their chemical properties and the IR and Mössbauer

$$Cp_2Mo(SnMe_2Cl)_2 + HCl \rightleftharpoons [Cp_2Mo(H)(SnMe_2Cl)_2]^+Cl^- \qquad (3)$$

spectroscopic data (IS = 1.66 mm/s, QS = 2.90 mm/s for **V** are similar to the same parameters for the complex **IV** (Table IV). However, the IR spectrum of **V** shows a broad band of low intensity for ν_{Mo-H} at 1660–1720 cm^{-1}, which, in terms of its form and frequency, is different from ν_{Mo-H} in Cp_2MoH_2). Thus, **V** dissociates in ether according to the eqn. 4 to give $Cp_2Mo(H)SnMe_2Cl$ (**VI**). Dissolved in DMSO

$$\underset{\text{solid}}{Cp_2Mo(H)(SnMe_2Cl)_2{}^+Cl^-} \rightleftharpoons \underset{\text{solution}}{Cp_2Mo(H)SnMe_2Cl + SnMe_2Cl_2} \qquad (4)$$

and DMFA, complex **V** gives NMR signals which correspond to the complexes **IV**, **VI**, Cp_2MoH_2 and $SnMe_2Cl_2{\cdot}nL$. Thus, **V** is decomposed in strongly solvating solvents according to eqns. 5 and 6.

$$\underset{\text{solid}}{[Cp_2Mo(H)(SnMe_2Cl)_2]^+Cl^-}$$

$$\xrightarrow{+L} \underset{\text{solution}}{Cp_2MoH_2 + Cp_2Mo(SnMe_2Cl)_2 + 2SnMe_2Cl_2{\cdot}nL} \qquad (5)$$

$$\xrightarrow{+L} \underset{\text{solution}}{Cp_2Mo(H)SnMe_2Cl + SnMe_2Cl_2{\cdot}nL} \qquad (6)$$

Treatment of **IV**, **V** and **VI** with an excess of HCl results in breaking of the Mo–Sn bond and the complete substitution of stannyl groups at the molybdenum atom for the atoms of hydrogen, for example, according to eqn. (7).

$$[Cp_2Mo(H)(SnMe_2Cl)_2]^+Cl^- \xrightarrow{HCl} [Cp_2Mo(H)_2SnMe_2Cl]^+[SnMe_2Cl_3]^- \xrightarrow{HCl} [Cp_2MoH_3]^+[SnMe_2Cl_3]^- + SnMe_2Cl_2 \qquad (7)$$

TABLE IV. Spectroscopic Parameters of the Complexes $Cp_2Mo(H)SnMe_nCl_{3-n}$ and $Cp_2Mo(SnMe_2Cl)_2$

Compound	^1H NMR spectroscopy						^{119}Sn NGR		IR spectroscopy		
	Cp	Me	HMo	$^3J_{Cp-Sn}$ (Hz)	$^2J_{Me-Sn}$ (Hz)	$^2J_{HMoSn}$ (Hz)	IS (mm/s)	QS (mm/s)	Sn–Cl (cm^{-1})	Mo–H (cm^{-1})	Mo–Sn (cm^{-1})
Cp_2MoH_2[a]	5.63		18.83							1850	
$Cp_2Mo(H)SnCl_3$ (**I**)[b]	4.70		20.50	20		318, 300	1.90	1.85	331, 303	1850	225
$Cp_2Mo(H)SnMeCl_2$ (**III**)[b]	5.05	9.02	20.04	14.8	24.8	238, 228	1.80	3.35	300, 290	1850	223
$Cp_2Mo(H)SnMe_2Cl$ (**VI**)[a]	5.42	9.50	19.73	7.9	32.2	198, 189	1.70	3.17	296, 278	1828	221
$Cp_2Mo(SnMe_2Cl)_2$ (**IV**)[a]	5.28	9.38		8.9	35.8		1.66	2.90	286, 275		220
$Cp_2Mo(H)SnMe_3$ (**VII**)[a]	5.57	10.04	19.09	4.9	35.1	148, 138	1.34	0.5		1829	218

[a] ^1H NMR spectra were obtained in CD_2Cl_2. [b] ^1H NMR spectra were obtained in DMFA-d^7, chemical shifts were determined based on solvent resonances.

$Cp_2Mo(H)SnMe_3$ (**VII**) is formed only in the presence of Et_3N. In contrast to **V**, the protonated complex **VII** is unstable and is decomposed by eqn. 8. This explains why **VII** can not be obtained in the absence of Et_3N. The increase in the Sn:Mo ratio to 2:1 does not result in forming the disubstituted complex $Cp_2Mo(SnMe_3)_2$, as happens with **IV**.

$$Cp_2Mo(H)SnMe_3 + HCl \longrightarrow \{[Cp_2Mo(H)_2SnMe_3]^+Cl^-\} \longrightarrow Cp_2MoH_2 + SnMe_3Cl \qquad (8)$$

The reaction occurring is untypical for tin alkylhalides (eqn. 9) and involves the redistribution of a methyl group between tin atoms. The fact that this

$$Cp_2MoH_2 + 2SnMe_3Cl \xrightarrow{Et_3N} \{Cp_2Mo(H)SnMe_3 + Me_3SnCl\} \longrightarrow Cp_2Mo(H)SnMe_2Cl + SnMe_4 \qquad (9)$$

reaction proceeds in mild conditions indicates a considerable weakening of the Sn–C bond in the complex **VII** as compared to tin methylchlorides.

Thus, our experimental data suggest that Cp_2MoH_2 interacts with $SnMe_nCl_{4-n}$ by the general Scheme 1. Apparently, the reaction of Cp_2MoH_2 with $SnMe_nCl_{4-n}$ starts by forming donor–acceptor complexes with Mo–H → Sn or Mo: → Sn bonds, followed by the production of the ionic complex, whose stability depends on the basic properties of $Cp_2Mo(H)SnX_3$ and determines equilibrium points in **2** and **3**. At $n < 2$, when the complexes $Cp_2Mo(H)SnX_3$ have no basic properties, the equilibrium in **3** is completely shifted to the right. At $n = 2$ the basicity of $Cp_2Mo(H)SnMe_2Cl$ grows, and the second hydrogen atom is substituted for $SnMe_2Cl$ group giving the ionic complex **V**. Finally, at $n = 3$ the basicity becomes so high that the interaction between $Cp_2Mo(H)SnMe_3$ and the evolving HCl results in splitting the complex and shifting the equilibrium **2** to the left. Triethylamine always shifts equilibrium **3** to the right.

All the compounds obtained were characterized by IR, ^1H NMR and the Mössbauer spectroscopic data (Table IV). X-ray studies of complexes **I** [6], **IV** [8], **VI** and **VII** showed that all these compounds have similar molecular structures of the $Cp_2Mo(SnX_3)Y$ type, where Y–H (**I**, **VI**, **VII**) or SnX_3 (**IV**) (Fig. 1). Basic structural parameters of all these compounds are listed in Table V. As is seen from Table V, the parameters characterizing the bond Mo–η^5-C_5H_5 (r_{Mo-Cp}, r_{Mo-C}, r_{C-C}) are the same for all the complexes and close to those found for other complexes of the Cp_2MXX' type [9, 10]. At the same time, the length of the Mo–Sn bond is markedly shorter than the sum of covalent radii of Mo (1.53 Å [11]) and Sn (1.40 Å [12]). This difference is about 0.2–0.3 Å. Similar shortening of the Mo–Sn bond is observed for tin-containing complexes of niobium [13], manganese and iron [14, 15]. This usually indicates the increase in bond multiplicity and is due to π-dative interaction between the unshared electron pair of the transition metal and the vacant d-orbitals of the tin atom. This is evidenced by the increase in r_{M-Sn} with the decrease in the acceptor strength of stannyl group SnX_3 in the series $CpFe(CO)_2SnPh_nCl_{3-n}$ [14, 15], $Cp_2Nb(CO)ShPh_nCl_{3-n}$ [13] and $Cp_2Mo(H)SnMe_nCl_{3-n}$ (Table V). The hypothesis of dative interaction agrees with the fact that the angles CpMoCp and HMoSn grow with the increase in the occupation of non-bonding orbitals $1a_1$ of Cp_2Mo fragment (Table V). However, the analysis of all spectral (Table IV) and structural (Table V) data shows that shortening of the interatomic distance Mo–Sn can not be ascribed only to dative interaction. Indeed, even for

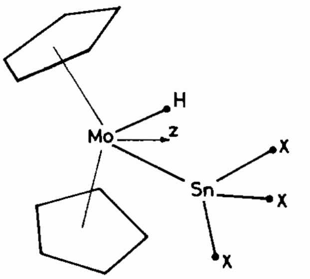
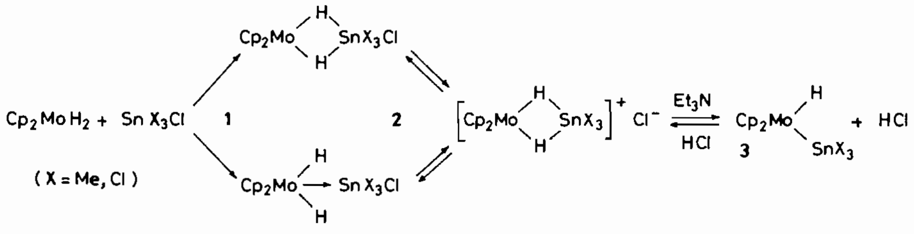


Fig. 1. Molecular structure of the complexes $Cp_2Mo(SnX_3)Y$ ($Y = H$ or $SnMe_2Cl$, X = Me or Cl).



Scheme 1.

TABLE V. Structural Parameters for the Complexes $Cp_2Mo(SnX_3)Y$ (Y = H or $SnMe_2Cl$, X = Me or Cl)

Compound		CpMoCp ω (°)	SnMoY ω (°)	ZMoH ω (°)	ZMoSn ω (°)	Mo–Y d (Å)	Mo–Sn d (Å)	Cp–Mo d (Å)	Mo–C_{mean} d (Å)	C–C_{mean} d (Å)	$\Sigma_i^{Sn}\omega_i$ ω (°)	References
Cp_2MoH_2		145.8	75.5	37.7	37.8	1.685(3)		1.94	2.29	1.42		[9]
$Cp_2Mo(H)SnCl_3$	(I)	141.3	79.2	53.2	26.0	1.74(7)	2.652(1)	1.96	2.29	1.39	74.4	[6]
$Cp_2Mo(H)SnMe_2Cl$	(VI)	144.6	72.7	43.9	28.8	1.64(4)	2.700(1)	1.96	2.28	1.40	53.0	This paper
$Cp_2Mo(SnMe_2Cl)_2$	(IV_a)[a]	140.8	83.2			2.740(1)	2.706(1)[b]	1.97	2.29	1.40	58.6, 65.7	[8]
	(IV_b)	140.9	83.4			2.733(1)	2.717(1)[b]	1.97	2.29	1.40	55.6, 63.6	[8]
$Cp_2Mo(H)SnMe_3$	(VII_a)[a]	146.1	67.6	38.5	29.1	1.60(5)	2.758(1)	1.96	2.27	1.40	41.4	This paper
	(VII_b)	146.6	69.5	39.6	29.9	1.51(6)	2.755(2)	1.95	2.26	1.39	42.6	

[a] The complex contains two independent molecules 'a' and 'b'.

[b] For tetrahedral tin atom: $\Sigma_i^{Sn}\omega_i$ = the sum of the moduli of the differences in tetrahedral angle and all the six valence angles at the tin atom.

the complexes $Cp_2Mo(H)SnMe_3$ and $Cp_2Nb(CO)SnPh_3$ [13], where the stannyl group is virtually a non-acceptor, $r_{M–Sn}$ is about 0.2 Å shorter than the sum of the covalent radii. Besides, the occupation of tin d-orbitals in donor–acceptor complexes of $SnX_4 \cdot 2L$ type results in decreasing *IS* in the Mössbauer spectrum due to the shielding of s-electron density. Hence, the value of *IS* for the complexes $Cp_2Mo(H)SnMe_nCl_{3-n}$ should increase with the growth of '*n*' due to the decrease in dative interaction. The real situation is quite the opposite (Table IV). Moreover, occupation of d-orbitals in the complexes $SnMe_nCl_{4-n} \cdot 2L$ results in increasing of the s-character of the Sn–C bonds, and, hence, in increasing *SSI* constants $^2J_{H–C–Sn}$ [16]. At the same time, the value of $^2J_{H–C–Sn}$ in the complexes with M–Sn bonds is 2–2.5 times lower than that in the corresponding methylchlorides. All these data do not agree with the hypothesis of π-dative interaction and testify to the fact that the shortening of the bond is caused by some other factor, which needs more detailed discussion.

The complexes **I–VII** show high values of *SSI* constants $^2J_{H–Mo–Sn}$ and $^3J_{Cp–Sn}$. Both *IS* and *SSI* constants always correlate with the change in $r_{Mo–Sn}$. The influence of chemical environment of the state of the nucleus in nuclear spectroscopic methods is manifested only by changes in s-electron density, which is non-zero near the nucleus. Hence, high *SSI* and *IS* constants in the complexes **I–VII** are due to a considerable increase in the s-electron density of the Mo–Sn bond and tin atom nucleus. This suggests that the basic reason for the shortening of the M–Sn bond in heterometallic complexes is its increased s-character, and, correspondingly, its higher overlapping integral. Based on this concept, let us consider the changes in spectroscopic and structural characteristics in the series of $Cp_2Mo(H)SnMe_nCl_{3-n}$ compounds.

SSI constants $^2J_{H–C–Sn}$ for these complexes are markedly lower than those found for $SnMe_nCl_{4-n}$ ($n = 1$, 100 Hz; $n = 2$, 71.0 Hz; $n = 3$, 58.1 Hz; $n = 4$, 54.0 Hz), *i.e.*, the s-character of Sn–C bond in heterometallic complexes becomes less pronounced. This can be due to the redistribution of s-electron density mainly to the Mo–Sn bond. This affects both the frequencies of valent vibrations $\nu_{Sn–Cl}$ and $\nu_{Mo–Sn}$ in the IR spectra (Table V) and the lengths of Sn–C, Sn–Cl and Mo–H bonds (Tables III, V). Besides, since the main contribution to the *SSI* constant is due to contact Fermi interaction proportional to s-electron density on the bond between interacting nuclei, the increase in '*n*' brings about a quite explanable decrease in the *SSI* constants $^2J_{HMoSn}$ and $^3J_{Cp–Sn}$ (Table IV). The increase in the s-character of the M–Sn bond suggests a decrease in the mixing of s- and p-atomic orbitals

(A.O.) of the tin atom and the domination of s-orbital in forming the Mo–Sn bond. This rearrangement should lead to the changes in the valent angles (ω) at the tin atom from tetrahedral (sp^3-hybridization) to (in the limit) $\widehat{XSnX} = 90°$ and $\widehat{MSnX} = 125.26°$ (the angle $\widehat{ClSnCl}$ in the completely rehybridized ionic complex $CsSnCl_3$ is 89.8° [17]). The parameter $\Sigma\omega = \Sigma|\omega_i - 109.47°|$ can be used as a quantitative criterion of this change. As is seen from Table V, the values of $\Sigma\omega$ are approaching the limit of 106° and change in proportion to *IS*, $^2J_{HMoSn}$ and $^3J_{Cp-Sn}$. Complexes **I** and **VII** are extreme cases of maximally non-hybridized (**I**) and hybridized (**VII**) orbitals, although in the latter case $\Sigma\omega$ is high enough, and the values of $^2J_{HMoSn}$ and $^3J_{Cp-Sn}$ are quite considerable.

As it can be seen from the Table IV the transition from the complex **VI** to **VII** leads to the uneven decrease of *IS*. This might be due to the sharp growth of s-electron screening by p-electrons, when the last Sn–Cl bond with markedly pronounced p-character (maximal value of r_{Sn-Cl} in the series of $Cp_2Mo(H)SnMe_nCl_{3-n}$ complexes and minimal frequences ν_{Sn-Cl}) is replaced by the non-polar Sn–C bond.

Structural characteristics of $Cp_2Mo(H)SnMe_nCl_{3-n}$ indicate that these complexes are typical d^2 systems with ligands located in the plane bisecting the wedge-like sandwich Cp_2Mo. However, unlike Cp_2MoH_2 and Cp_2MoCl_2, these compounds are characterized by a considerable difference between the volume of hydride-ligand and SnX_3-groups. As a result they become non-symmetrical with respect to *z* axis (Fig. 1).

Binding of the Cp_2Mo fragment with the ligands is described by the molecular orbitals (M.O.) scheme suggested in [18] (Fig. 2a). It is natural to assume that the diffuse 5s-orbital of tin will interact with the most symmetrically similar $2a_1$ orbital of Cp_2Mo. Then the fact that the SnX_3-group is located near the *z* axis provides for maximal overlapping of the orbitals and minimal contact with Cp-ligands. This might be the reason why the *z*MoSn angle in the series of $Cp_2Mo(H)SnMe_nCl_{3-n}$ compounds is changed by as little as 4° (Table V). However, slight changes in the *z*MoSn angle bring about much greater changes in the other component of HMoSn angle, that is, the angle *z*MoH (about 14°) (Table V). In complex **I** this angle is 53°, whereas for Cp_2MoH_2 it is 37.8°. In the latter case it provides for minimal interaction between the H atom and the $1a_1$ orbital of Cp_2Mo occupied by the undivided electron pair, and, accordingly, high d-basicity of Cp_2MoH_2. As the s-character of the tin orbital involved in the Mo–Sn bond in $Cp_2Mo(H)SnMe_nCl_{3-n}$ complexes increases, so the energy minimum at the Wolsh diagram [18] shifts towards big angles, which results in a considerable deviation of the hydride atom from the *z* axis. Naturally, the big deviation of the H atom from the *z* axis should increase its antibonding interaction with the $1a_1$ orbital and its destabilization (Fig. 2b). Apparently, this explains the fact that complexes **I** and **III** lose basic properties, and complexes **VI** and **VII** acquire such properties. This type of interaction results in a significant elongation of the Mo–H bond in **I** and its progressive shortening in the series **I** > **III** > **VI** > **VII**. One can suggest direct antibonding interaction of the $1a_1$ orbital with the difffuse 5s-orbital of tin, since the SnX_3-group is not located on the *z* axis, and the total overlapping is other than zero.

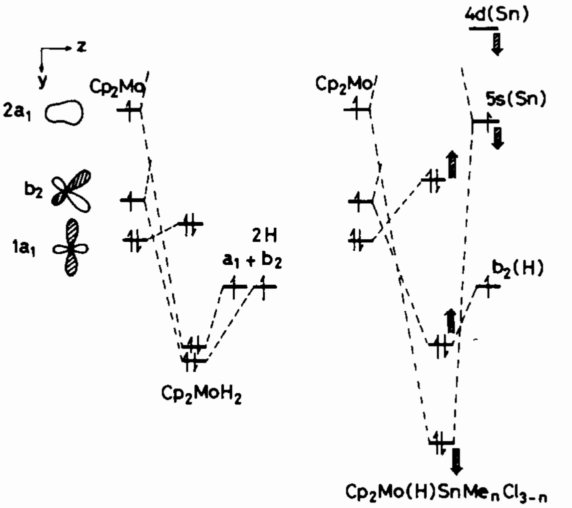


Fig. 2. The schemes of molecular orbitals for Cp_2MoH_2 (a) and $Cp_2Mo(H)SnMe_nCl_{3-n}$ (b).

As is seen from Fig. 2b, the complexes with the Mo–Sn σ-bonds show an increase in the energy of the $1a_1$ orbital with a decrease in '*n*'. For complex **I** the difference in the energies of the $1a_1$ and d-orbitals of tin will be minimal, which can bring about π-dative interaction. Such interaction, however, will be the cause, rather than the effect, of shortening the interatomic distance Mo–Sn, and its contribution to this shortening should be quite low, if any, decreasing with the decrease in '*n*'.

All this strongly suggests that the decrease in the interatomic distances between the transition metal and tin atoms with respect to the sum of the covalent radii in all heterometal complexes, where there is some correlation between r_{M-Sn} and the values *IS* and $^2J_{H-C-Sn}$, is due to the high s-character of this bond. However, in the case of bicyclopentadienyl compounds, all the effects which accompany this phenomenon are much more pronounced than, for instance, in carbonyl complexes. Thus, the value $^2J_{H-C-Sn}$ for the complexes $GSnMe_3$ is decreased in the series G = Cl (58.1 Hz) [16, 19] > $Co(CO)_4$ (52.6 Hz) > $MoCp(CO)_3$ (49.0 Hz) > $Mn(CO)_5$ (48.3 Hz) [19] ≫ Cp_2MoH (35.1 Hz), which indicates that the s-character of the M–Sn bond is increased.

The value of *IS* for the complexes $GSnCl_3$ grows in the series $G = Cl$ (0.85 mm/s) $\ll Mn(CO)_5$ (1.73 mm/s) $< FeCp(CO)_2$ (1.77 mm/s) [14, 15] $< Nb(Me\text{-}Cp)_2(CO)$ (1.90 mm/s) $\approx Cp_2MoH$, and Σw grows accordingly. One can suggest that the s-character of the Mo–Sn bond in biscyclopentadienyl complexes is higher due to specific localization of metal valent orbitals, providing for better overlapping with the 5s-orbital of tin.

In conclusion it should be noted that the observed shortening of the M–Sn bond in heterometal complexes of transition metals is determined primarily by the hybridization character of tin A.O., and, to a much lesser extent, by the nature and environment of the transition metal. Depending on the ligand environment of the tin atom, the length of the M–Sn bond can vary in a wide range; these bonds reach their maximum value in the case of sp^3-hybridization.

Thus, there are no grounds to consider that the shortening of the intermetallic bond as compared to Σr_{cov} is always brought about by higher multiplicity. In discussing this question one should take into account the character of the A.O. and M.O. involved in the intermetallic bond. The changes in the character of these orbitals can bring about changes in both the orbital overlapping integral and the length of the M–M′ bond.

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