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AN INTRAMOLECULAR SECONDARY Cl⋯Sn BOND; CRYSTAL AND MOLECULAR STRUCTURE OF $(\eta^5\text{-}C_5H_5)_2Mo[(CH_3)_2SnCl]_2$

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Summary

The structure of the trimetallic complex $(\eta^5\text{-}C_5H_5)_2Mo[(CH_3)_2SnCl]_2$ (I) was determined by X-ray analysis. Crystals of I are monoclinic: *a* 30.519(6), *b* 13.953(2), *c* 9.082(2) Å, γ 106.50(1)°, space group $P2_1/n$, $Z = 8$, ρ_{calcd} 2.13 g/cm^3. The structure of I consists of two independent, isolated $Cp_2Mo(Me_2SnCl)_2$ molecules containing Mo–Sn σ-bonds of different lengths (2.740 and 2.706 Å for Ia; 2.733 and 2.717 Å for Ib). The inequivalence of the Mo–Sn distances within the molecule appears to be accounted for by the formation of a secondary intramolecular Sn(1)Cl–Sn(2) bond (*r*(Sn---Sn) 3.616 Å, *r*(Cl---Sn(2)) 2.89 Å). The coordination around the Sn(2) atom is distorted trigonal bipyramidal, while that around the Sn(1) atom is distorted tetrahedral. The considerable contraction of the Mo–Sn interatomic distances (against the sum of the covalent radii of the metals) is assumed to be determined by the increased *s*-contribution of the bond in question.

Introduction

The essential shortening of M–Sn distances (by 0.2–0.35 Å), as compared with the sum of their covalent radii, has been observed in certain bimetallic complexes containing a metal–tin σ-bond [1]. The nature of this effect, either dative interaction [2] or the higher *s*-character of the M–Sn bond [3], has been under discussion to date. It has been shown in ref. 4 that the Mo–Sn distance in the complex $(\eta^5\text{-}C_5H_5)_2Mo(H)SnCl_3$ is 2.652(1) Å, considering that the sum of the covalent radii of these metals is ~ 3.0 Å [5]. One might assume that with decreasing Mo–Sn bond length the acidity of the Sn-containing component of the complex should increase significantly. This fact could confirm whether the hypothesis of dative interaction is correct. To be able to state this more precisely, it is of interest to study the influence of the decrease in the acceptor properties of the SnX_3 group on the Mo–Sn bond length. With this in mind, we undertook an X-ray study of the compound $(\eta^5\text{-}C_5H_5)_2Mo[(CH_3)_2SnCl]_2$, whose synthesis is reported in the present paper. It should also be noted that the study of this compound is of interest in view of the chemistry of dicyclopentadienyl complexes of transition metals on the whole since structural data on wedge-like sandwich compounds involving two bulky $M'X_3$ substituents at the transition metal atom are extremely rare.

TABLE 1

MAIN INTERATOMIC DISTANCES FOR $Cp_2Mo(SnMe_2Cl)_2$ (I)

Distance (Ia)	d (Å)	Distance (Ib)	d (Å)
Mo(1)–Sn(1)	2.740(1)	Mo(2)–Sn(3)	2.733(1)
Mo(1)–Sn(2)	2.706(1)	Mo(2)–Sn(4)	2.717(1)
Sn(1)–Cl(1)	2.476(3)	Sn(3)–Cl(3)	2.459(4)
Sn(2)–Cl(2)	2.468(4)	Sn(4)–Cl(4)	2.462(4)
Sn(1)–C(11)	2.141(10)	Sn(3)–Cl(31)	2.169(9)
Sn(1)–C(12)	2.159(10)	Sn(3)–C(32)	2.163(9)
Sn(2)–C(21)	2.173(13)	Sn(4)–C(41)	2.160(8)
Sn(2)–C(22)	2.157(9)	Sn(4)–C(42)	2.165(12)
Mo(1)–C_{Cp}	2.290(11)	Mo(2)–C_{Cp}	2.294(9)
C–C_{aver}	1.404(11)	C–C_{aver}	1.404(23)
Mo(1)–Cp [a]	1.971(11)	Mo(2)–Cp [a]	1.971(9)
Sn(1)–Sn(2)	3.616(1)	Sn(3)–Sn(4)	3.626(1)
Cl(1)–Sn(2)	2.890(4)	Cl(3)–Sn(4)	3.000(4)

[a] Centres of the Cp rings.

TABLE 2

VALENCE ANGLES IN $Cp_2Mo(SnMe_2Cl)_2$ (I)

Angles (Ia)	ω,°	Angles (Ib)	ω,°
Sn–(1)–Mo(1)–Sn(2)	83.2(1)	Sn(3)–Mo(2)–Sn(4)	83.4(1)
Mo(1)–Sn(1)–Cl(1)	102.4(1)	Mo(2)–Sn(3)–Cl(4)	103.4(1)
Mo(1)–Sn(1)–C(11)	123.8(3)	Mo(2)–Sn(3)–C(31)	119.4(2)
Mo(1)–Sn(1)–C(12)	120.9(2)	Mo(2)–Sn(3)–C(32)	124.4(3)
Cl(1)–Sn(1)–C(11)	96.1(3)	Cl(3)–Sn(3)–C(31)	97.4(3)
Cl(1)–Sn(1)–C(12)	97.3(3)	Cl(3)–Sn(3)–C(32)	97.6(3)
C(11)–Sn(1)–C(12)	108.3(4)	C(31)–Sn(3)–C(32)	107.8(4)
Mo(1)–Sn(2)–Cl(2)	114.8(1)	Mo(2)–Sn(4)–Cl(4)	114.7(1)
Mo(1)–Sn(2)–C(21)	122.2(3)	Mo(2)–Sn(4)–C(41)	121.2(3)
Mo(1)–Sn(2)–C(22)	121.0(3)	Mo(2)–Sn(4)–C(42)	121.3(3)
Cl(2)–Sn(2)–C(21)	936(4)	Cl(4)–Sn(4)–C(41)	94.7(3)
Cl(2)–Sn(2)–C(22)	94.3(3)	Cl(4)–Sn(4)–C(42)	94.5(3)
C(21)–Sn(2)–C(22)	104.4(4)	C(41)–Sn(4)–C(42)	104.4(4)
Cp(1)–Mo(1)–Cp(2)	140.8	Cp(3)–Mo(2)–Cp(4)	140.9(2)
C–C–C_{Cp}	108.0(1.6)	C–C–C_{Cp}	108.0(1.8)
Sn(1)–Cl(1)- - -Sn(2)	84.5(2)	Sn(3)–Cl(3)- - -Sn(4)	82.6(2)
Cl(1)- - -Sn(2)–Cl(2)	152.3(2)	Cl(3)- - -Sn(4)–Cl(4)	154.4(2)

Experimental

$Cp_2Mo(SnMe_2Cl)_2$ (I) was prepared by the interaction of Cp_2MoH_2 and $SnMe_2Cl_2$ in the ratio 1/2 in an ether medium. Yellow single crystals of I were grown by slow concentration, by evaporation, of its solution in Et_2O.

The X-ray study was performed using a Syntex P$\bar{1}$ diffractometer (Mo-K_α irradiation, graphite monochromator, $\theta/2\theta$ scanning up to $2\theta < 50°$). Correction for extinction was neglected (μ 36.1 cm^{-1}). Crystals of I are monoclinic: a 30.519(6), b 13.953(2), c 9.082(2) Å, γ 106.50(1)°, space group $P2_1/n$, $Z = 8$, ρ_{calcd} 2.13 g/cm^3. 3348 reflections with $I > 3\sigma(I)$ from a total of 3400 were selected for the calcula-

TABLE 3

ATOMIC COORDINATES (for Sn and $Mo_4 \times 10^5$; for Cl and for $C \times 10^4$) IN $Cp_2Mo(SnMe_2Cl)_2$ (I)

Atom	x	y	z
Sn(1)	7051(2)	71687(5)	33999(8)
Sn(2)	19049(2)	74495(6)	40281(9)
Sn(3)	−8034(2)	76168(5)	83944(8)
Sn(4)	−18962(2)	80446(5)	92021(8)
Mo(1)	12072(3)	73071(5)	59322(9)
Mo(2)	−12430(3)	77032(6)	109914(9)
Cl(1)	−74(1)	6994(3)	4353(4)
Cl(2)	1690(1)	7381(4)	1404(4)
Cl(3)	−136(1)	7079(3)	9151(4)
Cl(4)	−1640(1)	8540(3)	6672(4)
C(1)	701(4)	5697(7)	5910(14)
C(2)	1136(3)	5662(6)	5505(11)
C(3)	1441(3)	5963(6)	6653(11)
C(4)	1206(4)	6211(7)	7807(11)
C(5)	745(4)	6057(7)	7386(13)
C(6)	1392(3)	8455(6)	7797(9)
C(7)	928(4)	8386(7)	7340(13)
C(8)	953(4)	8735(7)	5909(14)
C(9)	1410(4)	8994(6)	5432(11)
C(10)	1684(3)	8835(6)	6633(12)
C(11)	−1149(4)	6372(7)	12333(12)
C(12)	−1574(4)	6552(7)	12778(12)
C(13)	−1867(3)	6376(6)	11597(11)
C(14)	−1630(3)	6093(5)	10384(9)
C(15)	−1197(3)	6076(5)	10859(11)
C(16)	−644(3)	8655(7)	12404(12)
C(17)	−1055(4)	8758(7)	12975(10)
C(18)	−1277(3)	9194(6)	11951(11)
C(19)	−984(4)	9399(6)	10271(11)
C(20)	−599(3)	9084(7)	10998(12)
M(11)	521(4)	5868(7)	2026(11)
M(12)	760(3)	8465(7)	2036(11)
M(21)	2242(4)	6279(8)	3826(14)
M(22)	2449(3)	8820(8)	3811(13)
M(31)	−2091(3)	6407(7)	6867(11)
M(32)	−441(3)	8909(7)	7123(11)
M(41)	−2481(3)	6843(7)	8535(12)
M(42)	−2168(4)	9299(7)	9565(12)

tion. The structure was solved by the direct full-matrix least-squares method in the anisotropic (isotropic for H atoms) approximation up to $R = 0.023$. The main interatomic distances and bond angles for molecule I are listed in Tables 1 and 2; the atomic coordinates and thermal parameters are given in Table 3.

Results and discussion

The crystalline structure of I consists of two independent, isolated $(\eta^5\text{-}C_5H_5)_2Mo(SnMe_2Cl)_2$ molecules of similar structure (Fig. 1). Figure 2 shows the conformation of one of the two independent molecules. The distances between the two molecules are not smaller than the usual Van der Waals contacts.

The molybdenum atom is bonded through π-bonds to two cyclopentadienyl rings, and through σ-bonds to the two tin atoms. The cyclopentadienyl rings are planar within the range of 0.01 Å. The average values for the C–C interatomic distances (range of values 1.369–1.452(11) Å), and those for Mo–C (range of values 2.277–2.307(11) Å) (see Table 2), are close to the corresponding values found for the related complex $(\eta^5\text{-}C_5H_5)_2Mo(H)SnCl_3$ (II) (1.39(4) and 2.29(1) Å) [4]. The wedge-like Cp_2Mo entity within I has a staggered conformation [6], which is common to the majority of Cp_2MoX_2 compounds; however, contrary to the usual case, two carbon atoms of the C_5H_5 rings are close to each other. The increased repulsion of the cyclopentadienyl groups is compensated for, in the case at hand, by the less mutual repulsion of the bulky $SnMe_2Cl$ groups and the C_5H_5 rings.

The Mo–Sn bond lengths within I are noticeably different for the two tin atoms: 2.740(1) and 2.706(1) Å (Ia), and 2.733(1) and 2.717(1) Å (Ib); nevertheless, in both cases the bond lengths are noticeably less than the sum of the covalent radii of these metals (~ 3.0 Å [5]). The geometry of the coordination environment for the two tin

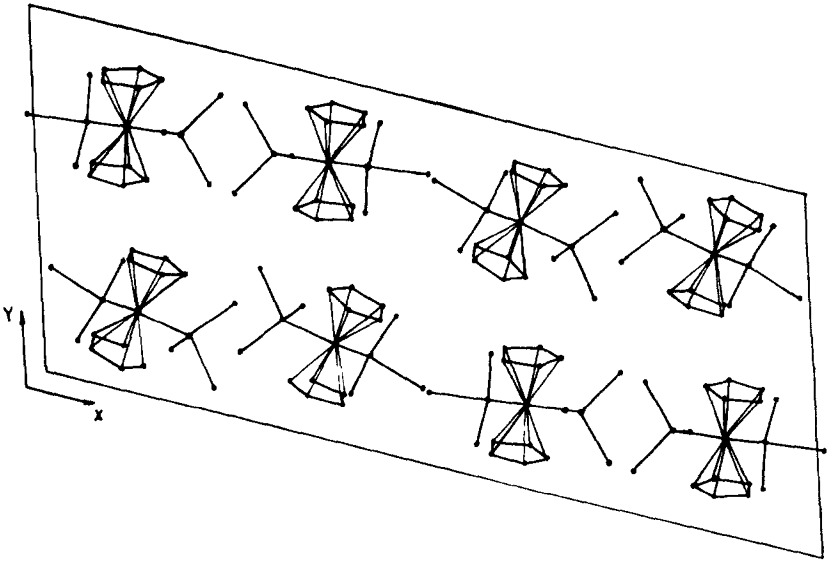

Fig. 1. Projection of $Cp_2Mo(SnMe_2Cl)_2$ onto the XY plane.

atoms is also distinctly different, and in both cases is highly distorted compared with a tetrahedral one. The average Sn–C distance (2.16 Å) is close to the sum of the covalent radii (2.17 Å [7,8]) and to the Sn–C distances within the uncoordinated tin methyl chlorides $(CH_3)_2SnCl_2$ (2.21(8) Å) [9] and $(CH_3)_3SnCl$ (2.12 Å) [10]. At the same time, the average Sn–Cl distance (2.47(1) Å) is considerably larger than *r*(Sn–Cl) within II (2.28 (1) Å) [4] and within the tin methyl chlorides $(CH_3)_2SnCl_2$ (2.40(4) Å) [9] and $(CH_3)_3SnCl$ (2.43(1) Å) [10]. The mutual orientation of the $SnMe_2Cl$ groups within I (the Sn–Cl bonds situated practically within the bisector plane of the wedge-like sandwich are directed towards one side with respect to the symmetry axis of the Cp_2Mo wedge-like sandwich, resulting in one pyramidal $SnMe_2Cl$ group being as though "embedded" in the other one) is distinctly different from that of the $SnMe_3$ groups within the complex $(C_6H_5CH_3)_2Hf(SnMe_3)_2$ (III). In this complex the $SnMe_3$ pyramids are adjoined through the edges whereas the Sn–C bonds situated within the bisector plane are directed along different sides with respect to the C_2 symmetry axis [11]. Despite such a considerable distinction, the non-bond contact Sn ··· Sn within I (3.62(1) Å) is just less than the Sn ··· Sn distance within III (3.84(1) Å).

The fact that the Cl(1)---Sn(2) and Cl(3)---Sn(4) distances (2.89 and 3.00 Å, respectively) are essentially less than the sum of the Van der Waals radii (~ 3.8 Å), [7,12] though being greater than the sum of the covalent radii (~ 2.4 Å) [7,8],

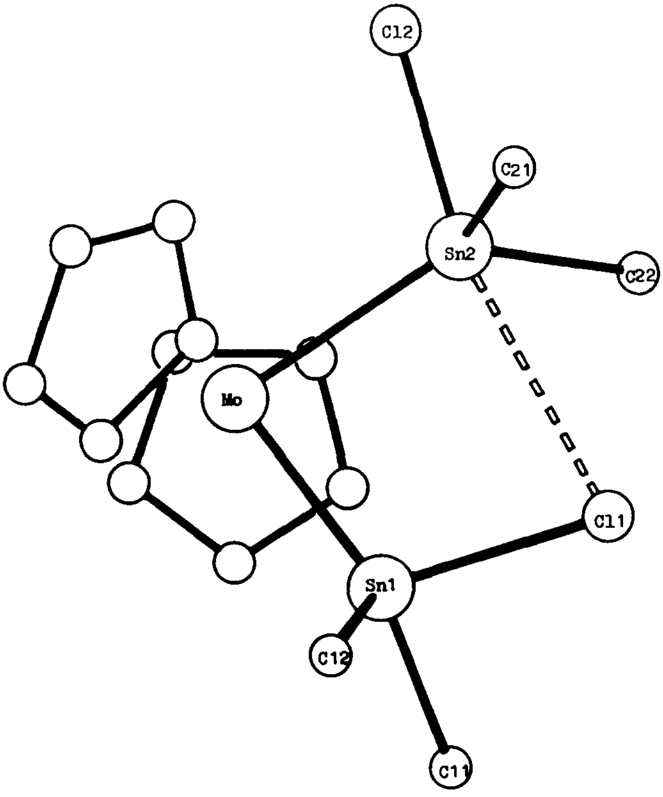

Fig. 2. Structure of one of the independent $Cp_2Mo(SnMe_2Cl)_2$ molecules.

deserves special attention. This appears to stem from the formation of an intramolecular secondary Mo$\cdots$Sn ($n \to \pi^*$) bond. A similar type of bonding is assumed for the molecule (bipy)(CO)$_3$Mo(Cl)SnCl$_2$Me (IV) (r(Sn–Cl) 2.81 Å) [2], for the Br–Sn bond within Cp$_2$Mo(Br)SnBr$_3$ (V) (r(Sn–Br) 3.41 ± 0.01 Å) [13] and for the intermolecular one in the polymeric chain [(CH$_3$)$_2$SnCl$_2$]$_n$ (r(Sn$\cdots$Cl) 3.54(5) Å) [9] and [(CH$_3$)$_3$SnCl]$_n$ (r(Sn$\cdots$Cl) 3.27(1) Å) [10]. If this bonding is taken into account, the coordination polyhedron around the Sn(2) and Sn(4) atoms, as well as for compounds IV (2), V [13] and [(CH$_3$)$_3$SnCl]$_n$ [10], is a distorted trigonal bipyramid in which the axial positions are occupied by chlorine atoms. The angle Cl(1)- - -Sn(2)–Cl(2) (Cl(3)- - -Sn(4)–Cl(4)) is 152.3° (154.4°). For compounds IV, V and [(CH$_3$)$_3$SnCl]$_n$, the angle between the axial bonds in the bipyramid equals 168 [2], 152 [13] and 150° [10], respectively. At the same time, the Sn–Cl–Sn angles for I (84.5 and 82.6°) are significantly larger than the corresponding angles in complexes IV (62.2°) and V (58° [13]), the former angles approaching the values established for complexes involving the usual M–Cl–M bridging bond (90° [14]).

The formation of the intramolecular bridging secondary bond Cl$\cdots$Sn in the molecule I, which results in electron transfer along the Mo–Sn–Cl$\cdots$Sn chain, accounts for the elongation of the Mo–Sn(1) (Mo–Sn(3)) distance as compared with that for the Mo–Sn(2) (Mo–Sn(4)) distance, as well as for that of the Sn(1)–Cl(1) (Sn(3)–Cl(3)) distances as compared with Sn(2)–Cl(2) (Sn(4)–Cl(4)). This fact also affects the values of the Mo–Sn–Cl(1) (Mo–Sn–Cl(3)) angles, which are considerably decreased (102.4 and 103.4°) compared with the analogous angles MoSnCl, while being formed by the terminal chlorine atoms (114.7°) (118.9° for complex II, [4]). The Sn(2)–Cl(2) and Sn(4)–Cl(4) distances observed for I correlate with the r(Sn–Cl) values for the axial positions within tin complexes with the trigonal-bipyramidal coordination: 2.43 Å for IV [2] and 2.49 Å for Me$_2$SnCl$_2$ · TMU (TMU = tetramethylurea) [15].

It is of interest that the two independent molecules of I differ noticeably from each other structurally. The Cl$\cdots$Sn bond for Ia is somewhat stronger (i.e. shorter by about 0.1 Å) than that for Ib, and both chlorine atoms are situated within the one plane together with the MoSn$_2$ moiety. The latter fact results, as a consequence of mutual repulsion, in the considerable distortion of the geometry of the SnMe$_2$Cl groups; in particular, the Sn–C distances vary within the range 2.141–2.173 Å (Table 2). At the same time, the Cl(3) atom of molecule Ib is displaced from the MoSn$_2$ plane by 0.28(1) Å, which leads, on the one hand, to weakening of the Cl(3)- - -Sn(4) bond, while, on the other hand, to the decrease in the mutual repulsion of the SnMe$_2$Cl groups (range for the Sn–C bond in Ib, 2.160–2.169 Å). Furthermore, the cyclopentadienyl rings within Ib are situated symmetrically with respect to the Mo(2)Sn(3)Sn(4) plane (the angles between the corresponding planes being equal; Cp(III)/SnMoSn 19.4°, Cp(IV)/SnMoSn 19.8°), while for Ia this symmetry is broken and the angles Cp(I)/SnMoSn and Cp(II)/SnMoSn are noticeably different (18.9 and 20.3°).

The IR spectroscopic data confirm the conclusion on the formation of the intramolecular secondary bridging bond Sn–Cl$\cdots$Sn within I. As compared with the IR spectra of compounds of the composition Cp$_2$Mo(H)SnMe$_n$Cl$_{3-n}$, which lack the possibility of forming such bonds, the IR spectrum of I exhibits an increase in the number of the ν(Sn–Cl) absorption bands, as well as their shift into the long-wavelength region. A similar phenomenon was observed on comparison of the spectra of solutions of monomeric Me_nSnCl_{4-n} with those of the crystalline compounds [16], which are subject to polymerization via Sn–Cl–Sn bridges [9,10]. The absorption band at 286 cm^{-1} in the spectrum of I is apparently attributed to the ν(Sn–Cl^{term}), whereas the bands at 275 and 262 cm^{-1} are attributed to vibrations involving the bridging chlorine atoms.

Comparison of the molecular structures for compounds I and II [4] shows that the values of the ClSnX and MoSnX angles, which characterize the Mo–Sn bond [16], are close to each other for both compounds (97.1 and 96.8°, 117.3 and 120.8°, respectively). Due to substitution of the Sn–Cl bonds for the Sn–C ones, the latter having a more pronounced *s*-character [17], and location of the two bulky SnX_3 moieties at the one molybdenum atom, the average Mo–Sn distance for I (2.72 (1) Å) is somewhat larger than that for II (2.65 (1) Å) [4]. This variation, however, is rather small as compared with the sharp drop in the acceptor strength of the SnX_3 moiety in I relative to that in II, which indicates that it is the increase in the *s*-character of the transition metal–tin bond that contributes mainly to the strengthening of this bond, and not the dative interaction.

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