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STRUCTURAL INVESTIGATIONS OF HETEROMETALLIC COMPLEXES WITH Re–Sn σ-BOND. MOLECULAR STRUCTURES OF $(\eta^5\text{-}C_5H_5)_2ReSn(CH_3)_2Cl$ AND $(\eta^5\text{-}C_5H_5)_2ReSnCl_3$

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Summary

Heterometallic complexes with an Re–Sn σ-bond, in $Cp_2ReSnCl_3$ (I), $Cp_2ReSnMeCl_2$ (II) and $Cp_2ReSnMe_2Cl$ (III), have been synthesized and studied by means of X-ray diffraction analysis. In all the three complexes a marked shortening of the Re–Sn interatomic distance (2.61 (I), 2.63 (II), 2.66 Å (III)) was noted compared to the sum of the covalent radii of the metals ($\sim$ 2.95 Å) and a sharp deviation of the $SnMe_nCl_{3-n}$ fragment structure from the tetrahedral. The peculiarities observed in the structures of I–III are explained as primarily resulting from the Re–Sn bonds *s*-character.

Introduction

A marked shortening of the M–Sn σ-bond length compared to the sum of covalent radii, which can be observed for all known transition metal heterometallic complexes having such a bond [1–6], is explained in the literature in two ways; dative π-interaction between the unshared pair of *d* electrons of the transition metal atom and the vacant *d* orbital of the tin atom [2] or the predominant, high, *s*-character of this bond [4]. It is convenient to ascertain the nature of this effect on bicyclopentadienyl heterometallic complexes with the general formula of $Cp_2M(L)_mSnX_nR_{3-n}$, where M is a transition metal of Groups III–VIII, $m = 0$–2, $n = 0$–3, X = Hal, R = alkyl, aryl, L = H or CO having a similar structure but

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differing substantially in the bacisity of the M atom. The structurally characterized complexes of such type are; niobium compounds $(Me\text{-}Cp)_2Nb(CO)SnCl_3$ and $Cp_2Nb(CO)SnPh_3$ [3] and molybdenum compounds $Cp_2Mo(H)SnCl_3$ [5] and $Cp_2Mo(SnMe_2Cl)_2$ [6], where transition metal atoms have d^2 configuration (one nonbonding d electron pair). It was of interest to determine the M–Sn bond length and its variation in the series of complexes $Cp_2ReSnX_nR_{3-n}$ ($n = 0$–3), where the Re^{III} atom has d^4 configuration and, therefore, higher bacisity than the Mo and Nb atoms. It may be expected that an even greater reduction of the Re–Sn bond length, as compared with the bond lengths found in molybdenum and niobium complexes, would be a strong point in favour of the dative π-interaction hypothesis.

Experimental

All the operations on the synthesis of $Cp_2ReSnMe_nCl_{3-n}$ ($n = 0$ (I), 1 (II), 2 (III)) complexes were performed under dry argon or in vacuo. The solvents were dried by boiling over $LiAlH_4$ (Et_2O, NEt_3) or P_2O_5 (CH_3CN) and distilled before use. Rhenium bicyclopentadienylhydride was obtained as in ref. 7 and purified by sublimation in vacuo. Anhydrous tin chloride and methyl chloride of "chemically pure" grade were used.

Synthesis of $Cp_2ReSnMe_nCl_{3-n}$ *complexes*

Complexes I–III were synthetized as shown in eq. 1:

$$Cp_2ReH + SnMe_nCl_{4-n} \xrightarrow{NEt_3} Cp_2ReSnMe_nCl_{3-n} + Et_3NH^+\ Cl^- \qquad (1)$$

in the presence of triethyl amine ($NEt_3/Cp_2ReH = 5$) by conventional procedure. 0.11–0.14 mmol of tin chloride or methyl chloride solution in the same solvent (5–10% excess over stoichiometry) was added with stirring to 0.3–0.4 g Cp_2ReH (0.1–0.13 mmol) solution in a corresponding solvent (acetonitrile for complex I, diethyl ether for complexes II and III). The solution turned red ($SnCl_4$) or yellow (tin methyl chlorides). In the latter case, the Et_3NHCl precipitate, insoluble in ether, was filtered off. The solution was then slowly evaporated in vacuo up to the formation of the crystalline phase. The precipitated crystals were separated, washed with the solvent and dried in vacuo. As a result, red tabular crystals of $Cp_2ReSnCl_3$, yellow tabular crystals of $Cp_2ReSnMeCl_2$ and yellow cicular crystals of $Cp_2ReSnMe_2Cl$ were obtained.

X-ray diffraction study

Air-sensitive monocrystals of complexes I–III, packed into a capillary tube, were analyzed on a Syntex-P$\bar{1}$ automatic diffractometer (Mo-K_α-radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta \leqslant 50°$). The structure of complexes I and III was interpreted using the Patterson method and ascertained in anisotropic approximation for all the non-hydrogen atoms. The coordinates of hydrogen atoms were calculated from geometrical considerations and included in the ascertainment with fixed positions and thermal parameters. The numer of reflections with $I \geqslant 3\sigma(I)$, participating in the calculations, amounted to 2434 for complex I and 2568 for complex III. A correction for absorption was introduced (μ 121.7 (I) and 115.4 cm^{-1} (III)). The crystals of complex I are monoclinic, a 6.268(2), b 12.987(4), c 16.207(4)

TABLE 1

INTERATOMIC DISTANCES (Å) IN COMPLEXES Cp$_2$ReSnCl$_3$, (I) AND Cp$_2$ReSnMe$_2$Cl, (III) [a]

Cp$_2$ReSnCl$_3$		Cp$_2$ReSnMe$_2$Cl	
Re–Sn	2.609(1)	Re–Sn	2.655(1)
Sn–Cl(1)	2.376(3)	Sn–Cl	2.451(5)
Sn–Cl(2)	2.375(3)	Sn–C(1)	2.14(1)
Sn–Cl(3)	2.370(4)	Sn–C(2)	2.14(2)
Re–C$_{mean}$	2.23(1)	Re–C$_{mean}$	2.23(1)
Re–Cp	1.88	Re–Cp	1.88
C–C$_{mean}$	1.41(2)	C–C$_{mean}$	1.42(2)

[a] Cp = η^5-C$_5$H$_5$.

TABLE 2

VALENCE ANGLES (°) IN COMPLEXES Cp$_2$ReSnCl$_3$, (I) AND Cp$_2$ReSnMe$_2$Cl, (III)

Cp$_2$ReSnCl$_3$		Cp$_2$ReSnMe$_2$Cl	
Cp–Re–Cp	148.0	Cp–Re–Cp	150.8
Cp(1)–Re–Sn	105.9	Cp(1)–Re–Sn	104.4
Cp(2)–Re–Sn	106.1	Cp(2)–Re–Sn	104.7
Re–Sn–Cl(1)	122.2(1)	Re–Sn–Cl	107.5(1)
Re–Sn–Cl(2)	122.7(1)	Re–Sn–C(1)	123.3(4)
Re–Sn–Cl(3)	117.0(1)	Re–Sn–C(2)	123.6(4)
Cl(1)–Sn–Cl(2)	97.4(1)	C(1)–Sn–Cl	93.8(4)
Cl(1)–Sn–Cl(3)	94.6(2)	C(2)–Sn–Cl	98.1(5)
Cl(2)–Sn–Cl(3)	96.8(2)	C(2)–Sn–C(1)	103.4(5)
angle between Cp planes	34.1	angle between Cp planes	30.8

TABLE 3

ATOMIC COORDINATES FOR Cp$_2$ReSnCl$_3$ (I)

Atom	x	y	z	$U_{(equiv)}$
Re	0.2594(1)	0.7550(1)	0.3547(1)	0.0060(1)
Sn	0.1542(1)	0.7450(1)	0.5104(1)	0.0046(2)
Cl(1)	0.2357(7)	0.8822(2)	0.6037(2)	0.0103(7)
Cl(2)	0.2526(6)	0.6080(2)	0.5977(2)	0.0114(15)
Cl(3)	−0.2153(5)	0.7357(4)	0.5418(3)	0.0034(23)
C(1)	0.2639(3)	0.8687(8)	0.2527(9)	0.0168(62)
C(2)	0.4004(25)	0.9077(9)	0.3141(12)	−0.0153(64)
C(3)	0.2865(34)	0.9226(8)	0.3856(10)	0.0025(69)
C(4)	0.0676(29)	0.8959(10)	0.3698(11)	0.0487(73)
C(5)	0.0549(24)	0.8614(9)	0.2868(9)	0.0221(65)
C(6)	0.2149(26)	0.5833(6)	0.3701(9)	0.0016(48)
C(7)	0.1663(25)	0.6083(8)	0.2902(10)	0.0118(61)
C(8)	0.3595(26)	0.6507(8)	0.2544(9)	0.0626(66)
C(9)	0.5204(23)	0.6553(8)	0.3185(10)	0.0335(60)
C(10)	0.4239(23)	0.6111(7)	0.3917(10)	0.0241(50)

TABLE 4

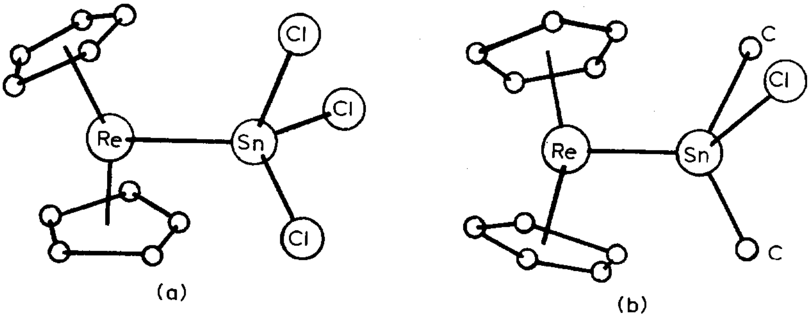
ATOMIC COORDINATES FOR $Cp_2ReSnMe_2Cl$ (III)

Atom	x	y	z	$U_{(equiv)}$
Re	0.4955(1)	0.3040(1)	0.3705(1)	0.0334(1)
Sn	0.1830(1)	0.2562(1)	0.3328(1)	0.0506(2)
Cl	0.1117(4)	0.4169(4)	0.4146(4)	0.1552(27)
C(1)	0.5160(12)	0.3550(10)	0.2238(6)	0.0561(37)
C(2)	0.5145(12)	0.4657(9)	0.2748(7)	0.0562(38)
C(3)	0.6562(11)	0.5083(8)	0.3309(6)	0.0527(33)
C(4)	0.7416(10)	0.4266(9)	0.3158(7)	0.0535(35)
C(5)	0.6551(12)	0.3315(9)	0.2501(7)	0.0599(41)
C(6)	0.5229(11)	0.3165(10)	0.5198(6)	0.0571(38)
C(7)	0.3607(12)	0.2264(10)	0.4997(6)	0.0564(39)
C(8)	0.3712(13)	0.1191(9)	0.4491(7)	0.0624(38)
C(9)	0.5404(14)	0.1435(10)	0.4395(7)	0.0674(46)
C(10)	0.6343(11)	0.2654(10)	0.4830(6)	0.0589(40)
C(11)	0.0218(12)	0.0922(12)	0.3853(9)	0.0904(54)
C(12)	0.0999(16)	0.2836(14)	0.2026(10)	0.1083(68)

Å, γ 92.41(2)°, V 1318.1(6) Å^3, space group $P2_1/b$, ρ 2.73 g cm^{-3}, $Z = 4$. The crystals of complex III are monoclinic, a 8.841(3), b 11.165(4), c 14.876(4), γ 113.66(3)°, V 1345 Å^3, space group $P2_1/b$, ρ 2.47 g cm^{-3}, $Z = 4$. The final R-factor value for complexes I and III was equal to 0.042 and 0.028, respectively. The principal interatomic distances and valence angles for complexes I and III are shown in Tables 1 and 2, and the coordinates of atoms and the thermal parameters are shown in Tables 3 and 4. Because of the poor quality of crystals, it proved impossible to perform a complete interpretation of the structure of complex II, only the distance between heavy Re and Sn atoms, equal to 2.63(1) Å, was determined.

Results and discussion

The crystals of complexes I and III are made up of isolated monomeric molecules separated by the usual Van der Waals contacts (Fig. 1). The isostructurality of the complex $Cp_2ReSnMeCl_2$ (II) to the $Cp_2Ta(H)_2SnMeCl_2$ complex, whose structure is similar to that of I and III [8], allows us to be certain that II also belongs to the same type of compound. The rhenium atom in complexes I and III is bonded with two



(a) (b)

Fig. 1. Molecular structures of $(\eta^5\text{-}C_5H_5)_2ReSnCl_3$ (a) and $(\eta^5\text{-}C_5H_5)_2ReSnMe_2Cl$ (b).

TABLE 5

M-Sn BOND LENGTHS AND THE DEVIATION OF TIN ATOM GEOMETRY FROM THE TETRAHEDRAL IN Re, Mo AND Nb COMPLEXES; $Cp_2M(L)SnR_nCl_{3-n}$ (L = H, CO; R = Me, Ph)

Complex	n	d(M–Sn) (Å)	Δ [a] (Å)	$\Sigma_i^{Sn} \lvert W_i - 109 \rvert$ (°)	Reference
$Cp_2ReSnCl_3$	0	2.609	0.31	73	this work
$Cp_2ReSnMeCl_2$	1	2.63	0.29	–	this work
$Cp_2ReSnMe_2Cl$	2	2.655	0.26	62	this work
$Cp_2Mo(H)SnCl_3$	0	2.652	0.32	74.4	5
$Cp_2Mo(SnMe_2Cl)_2$	2	2.740	0.23	58	6
		2.706	0.26	65	
$Cp_2Nb(CO)SnCl_3$	0	2.764	0.31	75	3
$Cp_2Nb(CO)SnPh_3$	3	2.825	0.24	40	3

[a] $\Delta = \Sigma r(\text{cov.}) - d(\text{M–Sn})$.

η^5-C_5H_5 groups (planar within the limits of 0.1 Å) and the tin atom, it has distorted trigonal coordination. The structure of Cp_2Re clinosandwiches in both complexes is practically the same. The mean length of Re–C bond (2.23(1) Å) and the mean Re–Cp distance (1.88 Å) coincide, but the angles of inclination of Cp rings differ (148.0 for I and 150.8° for III). The tin atom in I and III is located in the bisectoral plane of the clinosandwich, and is only slightly out of the plane passing through the centres of Cp rings and the rhenium atom (the angle between the Re–Sn line and the Cp(1)ReCp(2) plane is 1.2 in I and 3.2° in III).

Substitution of chlorine atoms by methyl groups in the SnX_3 group results in a monotonic elongation of the Re–Sn bond by approximately 0.02 Å. The length of this bond is shorter than that found in molybdenum and niobium complexes (Table 5). However, from the comparison of M–C bond lengths in similar molybdenum and rhenium complexes; 2.29 for $Cp_2Mo(H)SnCl_3$ [5] and $Cp_2Mo(SnMe_2Cl)_2$ [6], 2.23 for I and III, 2.28 for $(Cp_2MoH_2 \cdot CuI)_2$ [9], 2.24 for $(Cp_2Re(H) \cdot CuI)_2$ [10], 2.32 for $Cp_2MoCl_2^+\ BF_4^-$, 2.31 for Cp_2MoCl_2 and 2.26 Å for $Cp_2ReBr_2^+\ BF_4^-$ [11], it can be concluded that the covalent radius of rhenium is ~ 0.05 Å shorter than that of molybdenum, and, if $r(\text{cov.Mo}) = 1.56$ Å [12] is taken as the reference point, it amounts to ~ 1.51 Å. This value coincides with the one cited in [12], obtained on a smaller amount of qualitatively different material. From this it follows that the value of M–Sn bond shortening, in comparison with the sum of covalent radii ($\Delta = \Sigma r(\text{cov.}) - d(\text{M–Sn})$), for the complexes with a trichlorostannyl group, Table 5, remains practically unchanged in going from Nb and Mo to a more basic Re atom. In our opinion, this is convincing proof of the shortening of M–Sn bond being determined not by π-dative M → Sn interaction, but by the predominantly s-character of this bond, which presupposes the absence of sp^3 hybridization in the atomic orbitals (AO) of the tin atom. This conclusion is confirmed by analyzing the geometry of the ligand environment of the tin atom. In going from the tetrahedral sp^3 hybridization of tin atom to the non-hybridized orbitals, with AO of predominantly p-character, participating in the formation of Sn–X bond and an AO of s-character, participating in the formation of Sn–M bond, there occurs a change in the valence angles at the tin atom from tetrahedral; 109.47° to (in the limit) angles of 90° (X–Sn–X) and 125.26° (M–Sn–X). One can use as a quantitative criterion for this change the value of $\Sigma_1^6 \lvert 109.47 - W_i \rvert$ (the sum of the moduli of the differences in tetrahedral angle and all the six valence angles at the tin atom). Table 5 shows that, although the values of $\Sigma_1^6 |109.47° - W_i|$ do not reach the limiting value ($\sim 106°$), they are sufficiently high and are indicative of a noticeable deviation of the geometry from the tetrahedral. The degree of distortion in this case is well correlated with the M–Sn bond length; the greater the distortion the stronger the bond.

The steric factor does not seem to play an important part in the phenomenon in question, since with a decrease in $\Sigma_1^6 |109.47° - W_i|$ (i.e. when the $ReSnMe_nCl_{3-n}$ group geometry approaches the tetrahedral) one might expect a decrease in the Cp–Re–Cp angle. In actual fact, in complex III, with the smallest sum of deviations, we observe an increase in this angle, as compared with complex I.

The structural features of the heterometallic complexes of $Cp_2ReSnMe_nCl_{3-n}$ composition are thus best of all explained from the point of view of the heightened *s* character of Re–Sn bond, with π-dative interaction playing a secondary part.

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