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TANTALUM DICYCLOPENTADIENYL HYDRIDES CONTAINING THE Ta–Sn σ -BOND. CRYSTAL AND MOLECULAR STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_2\text{Sn}(\text{CH}_3)\text{Cl}_2$

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Summary

Interaction of Cp_2TaH_3 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with $\text{Me}_n\text{SnCl}_{4-n}$ ($n = 0-2$) in benzene leads to heterometallic complexes with the composition $\text{Cp}_2\text{TaH}_2(\text{SnMe}_n\text{Cl}_{3-n})$. The complex $\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$ can be obtained only when the HCl eliminated is fixed with triethylamine. The Mössbauer, IR and ^1H NMR spectroscopy data show that these compounds have a symmetrical structure with two terminal Ta–H bonds and a central Ta–Sn σ -bond. The $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ complex was studied by X-ray analysis. The crystals of this compound are rhombic with the unit cell parameters a 7.736(1), b 10.552(1), c 16.943(3) Å, space group P_{cmn} , $R = 0.0264$, $R_w = 0.0278$. The molecule $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ possesses a mirror symmetry plane which passes through the centers of the Cp cycles and the Ta, Sn, and C atoms of the methyl group: $d(\text{Ta}–\text{Sn})$ 2.752(1), $d(\text{Ta}–\text{H})$ 1.61(10) Å. On the basis of spectroscopic and structural data the Ta–Sn bond is concluded to have increased s character.

Introduction

The study of structural and spectral features of the heterometallic tin-containing complexes of molybdenocene (d^2 base) and rheniocene (d^4 base) with a general formula of $\text{Cp}_2\text{MH}_m(\text{SnMe}_n\text{Cl}_{3-n})$, where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $n = 0-3$; when $\text{M} = \text{Mo}$, $m = 1$ [1–4]; when $\text{M} = \text{Re}$, $m = 0$ [5], revealed that these compounds are characterized by an increased s contribution by the M–Sn bond, much higher than is

normally assumed by sp^3 hybridization of the tin atom. According to refs. 1–5, this feature is the main reason for the shorter M–Sn interatomic distance with respect to the expected value calculated from the covalent radii of the participating metals. However, the degree of contribution, by the lone pairs of the Mo and Re atoms, to the formation and strengthening of the M–Sn bond was not elucidated in the papers mentioned above, although the possibility of dative $\pi(d_M \rightarrow d_{Sn})$ interaction was not altogether disproved. In this connection it is reasonable to investigate tin-containing complexes of metallocenes with the d^0 configuration, such as the derivatives of Cp_2Nb^V and Cp_2Ta^V . Currently only one compound of this type, $Cp_2TaH_2(SnMe_3)$, is known, and is obtained by the reaction of Cp_2TaH_3 with Me_3SnNMe_2 [6]. The present work reports the results of Mössbauer, IR and 1H NMR spectroscopic studies and structural analyses for the complexes obtained on interaction of Cp_2TaH_3 with $SnMe_nCl_{4-n}$.

Experimental

All the procedures, with Cp_2TaH_3 as the initial reagent and compounds synthesized, were carried out in a vacuum or under dry argon. Benzene and triethylamine were dried by boiling and distilling over $LiAlH_4$, dimethylsulfoxide (DMSO) was fractionated in vacuo.

Tantalum dicyclopentadienyl trihydride, Cp_2TaH_3 , was prepared by a published, modified procedure [7] *. Tin methylchlorides and $SnCl_4$ were analytically pure and used without additional purification.

The tantalum content was determined spectrophotometrically in the form of its complex with chromotropic acid in a concentrated H_2SO_4 medium, the chloride content was determined by potentiometric titration with silver nitrate solution.

IR spectra were taken on a UR-20 spectrophotometer; the samples were prepared as suspensions in Nujol. 1H NMR spectra were recorded on a Varian XL-100 instrument operating at 100.1 MHz for DMSO- d_6 solutions (with the signals of the solvent protons as internal standard). The ^{119}Sn Mössbauer spectra were taken on a spectrometer of electrodynamic type equipped with a multichannel analyzer (Nokia). $Ba^{119}SnO_3$ served as the source.

Heterometallic complexes of tantalum and tin were prepared by allowing stoichiometric amounts of Cp_2TaH_3 and Me_nSnCl_{4-n} to react in benzene.

$Cp_2TaH_2(SnMe_nCl_{3-n})$ ($n = 0, 1$)

A 0.1 M solution of $SnCl_4/MeSnCl_3$ (1 : 1) in benzene (10 ml) was added with stirring to a solution of 0.3 g (~ 1 mmol) of Cp_2TaH_3 in 30 ml of benzene. The microcrystalline precipitate was filtered off, washed with 5 ml of benzene, and dried in vacuo. The following complexes were obtained:

$Cp_2TaH_2(SnCl_3)$ (I) (yellow, 80% yield). Found: Ta, 31.6; Cl, 20.3. $C_{10}H_{12}TaSnCl_3$ calcd.: Ta, 33.62; Cl, 19.76%.

$Cp_2TaH_2(SnMeCl_2)$ (II) (white, 70% yield). Found: Ta, 34.3; Cl, 16.2. $C_{11}H_{15}TaSnCl_2$ calcd.: Ta, 34.95; Cl, 13.69%.

* All the previously published procedures for the preparation of Cp_2TaH_3 , including that of ref. 7, proved to be either irreproducible or, at best, afforded only 2–5% yields. In the very near future, we intend to publish a new procedure for the synthesis of Cp_2TaH_3 providing a sure 12–15% yield.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\text{\AA}^2 \times 10$) FOR $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ta	3840(1)	2500	4206(1)	29(1)
Sn	4502(1)	2500	2610(1)	43(1)
Cl	2980(4)	4195(3)	1926(1)	73(1)
C(1)	6924(15)	2500	4290(7)	71(5)
C(2)	6342(12)	3565(8)	4689(6)	65(3)
C(3)	5413(11)	3155(8)	5332(5)	58(3)
C(4)	1064(15)	2500	3618(6)	59(5)
C(5)	1136(10)	3575(8)	4114(5)	53(3)
C(6)	1358(9)	3151(8)	4885(5)	55(3)
C(7)	6826(20)	2500	1941(8)	73(5)
H(1)Ta	3894(122)	3889(114)	3817(60)	108(40)

$\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$ (III). To a solution of 0.3 g (~ 1 mmol) of Cp_2TaH_3 in 30 ml of benzene, then 0.2 ml of triethylamine was added, and finally 10 ml of a 0.1 *M* solution of Me_2SnCl_2 in benzene was added with stirring. A precipitate of $\text{NEt}_3 \cdot \text{HCl}$ was filtered off and washed on the filter, with 5 ml of benzene. The filtrate was concentrated by evaporation to ~ 10 ml. The resulting precipitate was filtered off and dried in vacuo to give 0.3 g of a white substance. Found: Ta, 36.5; Cl, 9.1. $\text{C}_{12}\text{H}_{18}\text{TaSnCl}$ calcd.: Ta, 36.37; Cl, 7.13%.

A similar reaction, but without triethylamine, produced at the beginning a grey muddy precipitate (about 30% of the weight of the initial Cp_2TaH_3) containing, by Mössbauer spectroscopy data, no tin. The composition of this compound corresponds to the formula $\text{Cp}_2\text{TaCl}_2\text{H}$ (found: Cl, 17.0; H, 3.1; C, 30.0; Ta (as for the rest), 49.9. $\text{Cp}_2\text{TaCl}_2\text{H}$ calcd.: Cl, 18.51; H, 2.87; C, 31.33; Ta, 47.26%). Complete evaporation of the solvent affords a mixture of the complexes $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ and $\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$ in an approximately 9:1 ratio. Incomplete evaporation of the solvent yields large hexahedral crystals of $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$, which were employed for X-ray analysis, while the solution was enriched with the more soluble $\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$.

TABLE 2

MAIN INTERATOMIC DISTANCES *d* AND BOND ANGLES ω FOR $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$

Bond	<i>d</i> (Å)	Angle	ω (°)
Ta–Sn	2.752(1)	Cp–Ta–Cp ^a	140.1
Ta–H	1.61(1)	H–Ta–Sn	65.9(40)
Ta–C _{av.} (Cp(I))	2.38(1)	H–Ta–H'	131.4(50)
Ta–C _{av.} (Cp(II))	2.36(1)	Ta–Sn–Cl	112.2(1)
Ta–Cp(I) ^a	2.07	Ta–Sn–C _{CH₃}	133.0(4)
Ta–Cp(II) ^a	2.04	Cl–Sn–Cl'	94.6(1)
Sn–Cl	2.435(3)	Cl–Sn–C _{CH₃}	98.9(3)
C–C _{av.} (Cp(I))	1.38(2)	α	39.9
C–C _{av.} (Cp(II))	1.45(2)		

^a Center of the cycle.

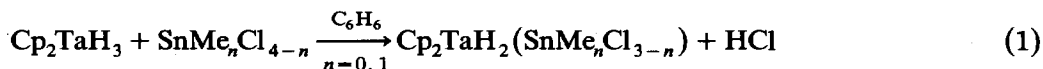
TABLE 3
SPECTROSCOPIC DATA FOR THE COMPLEXES $\text{Cp}_2\text{TaH}_2(\text{SnMe}_n\text{Cl}_{3-n})$, $\text{Cp}_2\text{TaH}_2(\text{ZnCp})_k$ AND $\text{Cp}_2\text{MoH}(\text{SnMe}_n\text{Cl}_{3-n})$

Compound	Mössbauer (mm s^{-1})		$^1\text{H NMR}$ (ppm)						IR (cm^{-1}) $\nu(\text{Ta-H})$	Reference
	IS	QS	$\tau(\text{Cp})$	$\tau(\text{Me})$	$\tau(\text{Ta-H})$	$^3J(\text{Cp-Sn})$	$^2J(\text{Me-Sn})$	$^2J(\text{H-Ta-}^{117,119}\text{Sn})$		
Cp_2TaH_3	-	-	4.79	-	12.45 13.40	-	-	-	1735	8
$\text{Cp}_2\text{TaH}_2(\text{SnCl}_3)$	1.94	1.94	4.25	-	12.17	23	-	578, 555	1730	this work
$\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$	1.77	3.18	4.45	9.09	13.17	18	19	410, 391	1745	this work
$\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$	-	-	4.65	9.50	13.94	5	29	308, 294	1740	this work
$\text{Cp}_2\text{TaH}_2(\text{SnMe}_3)$	-	-	5.53	9.50	14.63	-	36	-	1750	6
$\text{Cp}_2\text{TaH}_2(\text{ZnCp})$	-	-	5.59	-	18.26	-	-	-	-	10
$\text{Cp}_2\text{TaH}(\text{ZnCp})_2$	-	-	5.62	-	17.35	-	-	-	-	10
$\text{Cp}_2\text{MoH}(\text{SnCl}_3)$	1.90	1.85	4.70	-	20.50	20	-	318, 300	1850	4
$\text{Cp}_2\text{MoH}(\text{SnMeCl}_2)$	1.80	3.35	5.05	-	20.04	14.1	24.8	238, 228	1840	4

For $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$, a crystal of dimensions $0.1 \times 0.1 \times 0.2$ mm was placed in a glass capillary and X-ray analysis was performed using an automatic Syntex P1 diffractometer (Mo- K_α irradiation, a graphite monochromator and $\theta/2\theta$ scanning up to $2\theta \leq 54^\circ$). The crystals of II are orthorhombic: a 7.736(1), b 10.552(1), c 16.943(3) Å, V 1383.3(3) Å³, space group P_{cmn} , $Z = 4$, $\rho_{\text{calcd.}}$ 2.49 g cm⁻³. 1278 reflections with $I > 3\sigma(I)$ were used for the calculations. The correction for absorption was μ 104.9 cm⁻¹. The structure was resolved by the direct method and refined by full matrix least squares with a weighting factor of $w = 1/(\sigma^2(F))$ in the anisotropic (isotropic for hydrogen atoms) approximation up to $R = 0.0246$ ($R_w = 0.0278$). Hydrogen atoms were determined in a difference Fourier synthesis. The atomic coordinates and thermal parameters are listed in Table 1; the main interatomic distances and bond angles are given in Tables 2 and 3.

Results and discussion

Treating Cp_2TaH_3 with SnCl_4 and MeSnCl_3 in benzene (with a 1 : 1 ratio of the reagents) proceeds with elimination of HCl to give; the complex $\text{Cp}_2\text{TaH}_2(\text{SnCl}_3)$ (I), which is insoluble in aromatic hydrocarbons, ether, and THF, and the poorly soluble complex $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ (II) (eq. 1).



The reaction between Cp_2TaH_3 and Me_2SnCl_2 proceeds in a more complicated manner to give an insoluble compound of a conventional $\text{Cp}_2\text{TaCl}_2\text{H}$ composition, and a mixture of the soluble complexes $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ and $\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$ (III). This difference in the nature of interaction between Cp_2TaH_3 and $\text{Me}_n\text{SnCl}_{4-n}$ is, perhaps somehow related to the increase in sensitivity of the Ta-Sn bond towards the eliminated HCl in the order III > II > I (similar dependence, on n , of M-Sn bond stability towards HCl, was also observed for the complexes $\text{Cp}_2\text{MoH}(\text{SnMe}_n\text{Cl}_{3-n})$ [4] and $\text{Cp}_2\text{ReSnMe}_n\text{Cl}_{3-n}$ [5]). Binding the HCl eliminated with triethylamine, however, prevented formation of " $\text{Cp}_2\text{TaCl}_2\text{H}$ " and resulted in the formation of relatively pure $\text{Cp}_2\text{TaH}_2(\text{SnMe}_2\text{Cl})$ (eq. 2).



At the same time, the formation of complex II formed during the reaction between Cp_2TaH_3 and Me_2SnCl_2 can only be explained by eq. 3, which, as is shown below, is caused by the change in the character of the Sn-C bond in the heterometallic complex.



Both the pure form of Me_3SnCl and that formed in reaction 3, do not react with Cp_2TaH_3 even in the presence of NEt_3 . A reaction similar to the last is described in ref. 4 (eq. 4). However, if Cp_2MoH_2 reacts only with Me_3SnCl ; Cp_2TaH_3 seems to react with both Me_2SnCl_2 and MeSnCl_3 , which is suggested by the increased chlorine content in all samples of II and III.



All the compounds obtained in this work were investigated using Mössbauer, IR and ^1H NMR spectroscopic methods (Table 4). The large value of the isomeric shift (IS) for I and II indicates unambiguously the presence of a covalent Ta–Sn bond in these compounds. The absorption bands in the region of $1730\text{--}1745\text{ cm}^{-1}$ in the IR spectra correspond to vibrations of the terminal Ta–H bonds (1735 cm^{-1} for initial Cp_2TaH_3 [8]). The ratio of signal intensities of the cyclopentadienyl and hydride protons in the ^1H NMR spectrum (10 : 2), and a singlet character of the spectrum, suggest that the complexes I–III have a similar structure and that these can be regarded as derivatives of Cp_2TaH_3 [8], in which the central atom of hydride hydrogen is replaced by the stannyl group. This suggestion was confirmed by X-ray analysis complex II.

Crystals of II are composed of isolated $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ molecules separated by the usual Van der Waals contacts (Fig. 1). The $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$ molecule possesses a mirror symmetry plane, which is normal to the bisector plane of the wedge-like sandwich Cp_2Ta and contains the Ta, Sn, C(1), C(4), and C(7) atoms. The Cp–Ta–Cp angle in II is practically identical with that in Cp_2TaH_3 (140°) [9] and close to that in $\text{Cp}'_2\text{TaH}(\text{ZnCp})_2$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_3$) (137.5°) [10]. However, since one of the C_5H_5 cycles in II interacts with a methyl group, and the second cycle (Cp(II)) interacts with two chlorine atoms, interatomic distances in the Ta–Cp(I) and Ta–Cp(II) systems are essentially different (Table 2). Thus, the Ta–C and Ta–Cp(I) distances in Cp(I) are close to those as found in Cp_2TaH_3 (2.39(1) and 2.07 Å, respectively [9]). At the same time, the Ta–C and Ta–Cp(II) distances for the Cp(II) cycle are ~ 0.02 Å shorter. This leads to elongation of the C–C bond in the Cp(II) cycle by 0.07(7) Å (Table 2). Taking the large error of determination into account, the Ta–H distance in II is close to that in Cp_2TaH_3 (1.77(1) Å [9]) and $\text{Cp}'_2\text{TaH}(\text{ZnCp})_2$ (1.52(9) Å [10]). The values of the H–Ta–Sn and H–Ta–H' bond angles (63 and 126° , respectively) in the planar moiety $\text{Ta}(\text{H})_2\text{Sn}$ of molecule II are close to those in Cp_2TaH_3 [9], despite the fact that the hydrogen atom is replaced by

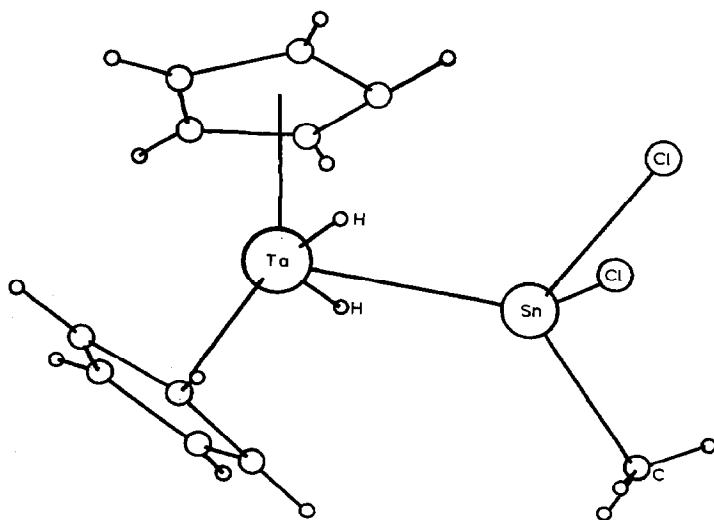


Fig. 1. Molecular structure of the complex $\text{Cp}_2\text{TaH}_2(\text{SnMeCl}_2)$.

the more bulky stannyl group. It is noteworthy that in the case of an even more bulky substituent, ZnCp, in $\text{Cp}'_2\text{TaH}(\text{ZnCp})_2$, the Zn–Ta–Zn angle is unaffected ($62.89(1)^\circ$) but owing to increased repulsion between the Cp and Cp' cycles the H–Ta–Zn angle decreases to $54(3)^\circ$ [10].

The non-bonding contact $\text{H} \cdots \text{Sn}$ in II is 2.55 \AA , this value is slightly less than the sum of the non-bonding radii for H and Sn, 0.87 [9] + 1.82 [11] = 2.7 \AA . Taking into account a small downfield shift of the signals of hydride protons in I relative to the starting Cp_2TaH_3 , it can be asserted that the hydride hydrogens in I–III do not contribute to Ta–Sn bonding. At the same time the $\text{H} \cdots \text{Zn}$ contact in $\text{Cp}'_2\text{TaH}(\text{ZnCp})_2$ [10] is markedly less than the non-bonding one, which, together with an upfield shift of the signal of the hydride protons, indicates that the hydride atom contributes to the bonding with one of the zinc atoms via a $\overline{\text{Ta}}-\text{H} \rightarrow \overline{\text{Zn}}$ bridge. This, however, does not lead to the essential difference in the two Ta–Zn distances.

The value of $r(\text{Ta}-\text{Sn})$, which in II (as in similar complexes of Mo and Re) is $0.1\text{--}0.25 \text{ \AA}$ less than the sum of the covalent radii, is of interest. Unfortunately, if the value of $r_{\text{Sn}}^{\text{cov}}$ is determined with sufficient accuracy (1.40 \AA) [12], then the value of $r_{\text{M}}^{\text{cov}}$ in metallocenes, including $r_{\text{Ta}}^{\text{cov}}$, can merely be roughly estimated. Thus, estimating the covalent radius from the Ta–Cp bond length, which is practically identical for all known complexes of tantalocene ($2.38_{\text{av.}}$), and taking $r_{\text{C}}^{\text{cov}} \approx 0.77 \text{ \AA}$, gives a value of $\sim 1.60 \text{ \AA}$. On the other hand, starting from a Ta–Cl bond length (2.44 \AA) in $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Ta}^{\text{IV}}\text{Cl}_2$ [13] leads to a $r_{\text{Ta}}^{\text{cov}}$ value of $\approx 1.46 \text{ \AA}$. The latter value seems more plausible since it was deduced from the bond length of a frontal ligand, and is somewhat less than the metallic radius of tantalum (1.49 \AA). Since there are no lone pairs and there is no $\text{H} \cdots \text{Sn}$ contact in complex II, the interatomic distance of M–Sn decreases in the same order, in the series of complexes with $\text{M} = \text{Mo}, \text{Re}, \text{Ta}$ and is convincing evidence in favour of the suggestion given in refs. 3–5, 14, where the decrease is explained by the high s contribution of the M–Sn bond. The M–M' distances in a few examples of structurally characterized complexes of metallocenes such as $\text{Cp}_2\text{MoHMgBr} \cdot \text{THF}$ (2.73 \AA) [15], $\text{Cp}_2\text{Mo}(\text{HgSC}_2\text{H}_5)_2$ (2.68 \AA) [16], $(\text{Cp}_2\text{MoH})_2\text{PbAc}_2$ (2.81 \AA) [17], $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{NbH}_3(\text{InCl})_2$ ($2.82_{\text{av.}} \text{ \AA}$) [18], $\text{Cp}_2\text{Nb}(\text{CO})\text{SnPh}_3$ (2.76 \AA) [19], and particularly in the complexes with a $d^0\text{--}d^{10}$ configuration $\text{Cp}_2\text{TaH}(\text{ZnCp})_2$ (2.59 \AA) [10] and $\text{Cp}_2\text{NbH}_2\text{ZnCp}$ (2.54 \AA) [20] (taking into account the accuracy of the $r_{\text{M}}^{\text{cov}}$ values and additional M–H–Zn interaction in the last two compounds) are found. Since some of these complexes lack non-bonding d electrons, and others lack vacant orbitals, this decrease in length is most likely to be caused by increased s contribution of the M–M' bond. Thus, the effect under consideration is not only inherent in the compounds involving the M–Sn bonds, but appears to be of a more general nature.

Comparing IS values in Mössbauer spectra of tantalocene (Table 3) and molybdenocene complexes [4] it can be seen that they practically coincide. This fact indicates a high s -electron density around the Sn nuclei in these compounds. At the same time ^1H NMR spectral data (Table 3) show that the s character of the M–Sn bond decreases from Ta to Re. Thus the $^3J(\text{Cp}-\text{Sn})$ and $^2J(\text{Me}-\text{Sn})$ values, for which s character can be ascribed, can be more appropriately applied to Ta complexes than to Mo and Re complexes. It especially concerns the value of $^2J(\text{H}-\text{Ta}-\text{Sn})$ which, for complex I is close to that of $^1J(\text{H}-\text{Sn})$ ($\sim 1000 \text{ Hz}$).

Decreasing s character of the M–Sn bond in the series $\text{Cp}_2\text{TaH}_2\text{SnX}_3 - \text{Cp}_2\text{MoHSnX}_3 - \text{Cp}_2\text{ReSnX}_3$, becomes more evident when looking at the change in ${}^2J(\text{Me-Sn})$ values. These values are in proportion only to the s character of Sn–C bonds and, correspondingly, inversely proportional to the s character of the M–Sn bond. As can be seen from Table 3, in this series of similar compounds, the minimum value of ${}^2J(\text{Me-Sn})$ is observed for the tantalocene complexes and the maximum value for rhenocene complexes [4,5].

This makes the reason of reaction 3 occurring clear, leading to the exchange of one of the methyl groups for a chlorine atom. This reaction occurs when Cp_2MoH_2 is treated with an excess of Me_3SnCl [4], and for tantalum derivatives it is observed only when stoichiometric quantities of both Me_2SnCl_2 and MeSnCl_3 are used. This does not take place for $\text{Cp}_2\text{ReSnMe}_n\text{Cl}_{3-n}$ complexes as it has the highest s character of Sn–C bonds in this series.

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