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# Reactions of Tantalocene Trihydride $(\eta^5\text{-}C_5H_5)_2TaH_3$ with the Second Group Metal Halogenides. Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_2TaH(\mu_2\text{-}H)_2ZnCl_2\cdot C_4H_8O$

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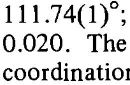
## Abstract

An interaction of $Cp_2TaH_3$ ($Cp = \eta^5\text{-}C_5H_5$) with the group II metal halogenides led to heterometallic complexes $Cp_2TaH_3\cdot ZnCl_2\cdot Et_2O$ (**I**), $Cp_2TaH_3\cdot ZnCl_2\cdot THF$ (**II**), $Cp_2TaH_3\cdot ZnI_2\cdot Et_2O$ (**III**), $Cp_2TaH_3\cdot ZnI_2\cdot THF$ (**IV**), $Cp_2TaH_3\cdot CdI_2$ (**V**), $Cp_2TaH_3\cdot MgI_2$ (**VI**). According to the IR and NMR data the binding in solution is accomplished via the ordinary hydrogen bridge Ta–H–M, whereas in the crystal state this is effected via the double hydrogen bridge

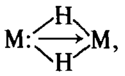


The interaction of $Cp_2TaH_3$ with $BeCl_2$ and $MgCl_2$ in THF proceeds as a redox reaction to give $Cp_2TaCl_2$ as one of the reaction products.

Complex **II** has been studied by X-ray analysis. Crystals of **II** are triclinic: $a = 8.960(1)$, $b = 8.100(1)$, $c = 12.469(2)$ Å, $\alpha = 93.62(1)°$, $\beta = 82.22(1)°$, $\gamma = 111.74(1)°$; space group $P\bar{1}$; $Z = 2$; $R = 0.019$, $R_w = 0.020$. The zinc atom in **II** possesses an unusual coordination number equal to 5. The coordination polyhedron of the zinc atom is an essentially distorted trigonal bipyramid.

## Introduction

In the majority of known heterometallic hydride complexes of transition metals $L_nMH_mM'X_k$ the intermetallic linkage between M and M′ is effected via the nucleophilic bridging hydrogen $M–H \rightarrow M'$ (or $M \leftarrow H–M'$) [1]. However, when M bears lone pairs and M′ possesses vacant orbitals the binding between them may be effected also through the dative–acceptive interaction $M\!: \rightarrow M'$, as for example in the $d^4$-complex $[(\eta^5\text{-}C_5H_5)_2ReHCuI]_2$ [2] ($\eta^5\text{-}C_5H_5$ = Cp), or in the $d^2$-complex $Cp_2MoH_2AlCl_3$ [3]. The most complex linkage type is realized when both types of interactions may coexist in one molecule



as for example in the heterometallic $d^2$-complexes of $Cp_2MoH_2$ with copper [4, 5], iron and nickel [6, 7], and zinc [8] halogenides, in which the interatomic distances are close to the sums of covalent radii of both metals, or even less. The linkage $M–H \rightarrow M'$ in these compounds is unambiguously detected by various methods, but to single out the dative–acceptive component against their backgroud appears to be unattainable.

A convenient object to study the reactivity of the hydride ligand in the metal sandwiches and to elucidate the possibility of an extra binding $M\!: \rightarrow M'$ is tantalocene trihydride $Cp_2TaH_3$, in which the metal atom possesses neither vacant orbitals nor lone pairs. The chemistry of this hardly accessible compound has so far been studied very poorly. The reactions of $Cp_2TaH_3$ with organo-zinc compounds $ZnR_2$, which proceed either with the elimination of HR (R = Cp) to form the σ-bond Ta–Zn [9], or yield an unstable adduct with a 1:1 ratio (R = Et) existing only in solution [10] have been reported. It could be anticipated that stronger Lewis acids would stabilize and allow isolation of the adducts containing the bridging bonds Ta–H–M, and estimation of the role of lone pairs in the intermetallic binding by comparison of the structural parameters

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of these complexes with similar compounds of molybdenocene dihydride. With this in view we have studied the reactions of $Cp_2TaH_3$ with the second group metal halogenides.

## Experimental

Since the starting and final products are highly sensitive to oxidation and moisture, all the operations were performed under argon or in vacuum Solvents were subject to purification along the generally adopted procedure: they were refluxed over a drying agent, $LiAlH_4$ (benzene, THF, $Et_2O$), $CaH_2$ (acetonitrile), LiD ($d_8$-THF, $d_6$-dimethylsulfoxide, *in vacuo*), and distilled directly before use.

$Cp_2TaH_3$ was synthesized by the modified procedure [11]. Anhydrous beryllium and magnesium chlorides of 'chemically pure' grade were used. $ZnI_2$ and $MgI_2$ were obtained by the interaction of the metal with iodine in $Et_2O$, followed by removal of the solvent. Anhydrous $ZnCl_2$ was obtained by the interaction of zinc with dry HCl in $Et_2O$. Anhydrous $CdI_2$ was obtained by the interaction of the aqueous solution of $CdSO_4 \cdot 8/3H_2O$ with KI, followed by recrystallization of the resulting compound from absolute alcohol [12].

The content of halogens in the samples was determined by potentiometric titration with a solution of silver nitrate; the content of zinc and magnesium was determined by complexonometric titration with xylenol orange indicator for zinc and eryiochrom black indicator for magnesium. The content of carbon and hydrogen was determined by elemental microanalysis. The content of tantalum and the Ta:Zn ratio were determined by the X-ray fluorescent method on a 'VRA-20' instrument (W radiation, crystal-analyzer LiF, analytical lines for Ta $L\alpha_1$ 44.4; Zn $K\alpha_1$ 41.74). Samples were burnt down to oxides and pellets for analysis were made using spectrosocpically pure carbon powder ($Ta_2O_5$ + ZnO) and emulsion polystyrene ($Ta_2O_5$ + CdO, $Ta_2O_5$ + MgO). The pellets of artificial mixtures of ZnO ('pure' grade), $Ta_2O_5$ ('chemically pure' grade), CdO ('chemically pure' grade) were used as standards. In some cases the analysis produced underestimated results (Mg, halogens) because of the influence of tantalum which sometimes cannot be avoided.

IR spectra of the samples (suspension in Nujol) in the region 400–4000 $cm^{-1}$ were recorded on an UR-20 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were run on XL-100-12 and WP-200SY instruments with TMS as an internal standard. The temperature of the samples was measured within ±1 °C accuracy.

The complexes of $Cp_2TaH_3$ with the second group metal halogenides were obtained by the standard procedure. To a solution of ~0.3 g (~1 mmol) of $Cp_2TaH_3$ in 30 ml of the solvent were added dropwise 10 ml of 0.1 M solution of $MHal_2$. The mixture was stirred for 15 min. In the case of insoluble complexes the precipitate was filtered off, washed twice on a filter with 5 ml of the solvent, and dried *in vacuo* (method A). In the case of soluble compounds the transparent reaction mixture was evaporated to ~5 ml volume, the precipitated crystals were filtered off, washed twice with 5 ml of the solvent, and dried *in vacuo* (method B).

The following compounds were obtained:

$Cp_2TaH_3 \cdot ZnCl_2 \cdot Et_2O$ (**I**) (white, method A, from $Et_2O/C_6H_6$). Found: Zn, 12.7; Cl, 13.8. Calc. for $C_{14}H_{23}OTaZnCl_2$: Zn, 12.5; Cl, 13.5%. The ratio Ta:Zn was found to be 1:1.2.

$Cp_2TaH_3 \cdot ZnCl_2 \cdot THF$ (**II**) (white, method B, from THF). Found: Zn, 11.0; Cl, 14.1. Calc. for $C_{14}H_{21}OTaZnCl_2$: Zn, 12.5; Cl, 13.6%.

$Cp_2TaH_3 \cdot ZnI_2 \cdot Et_2O$ (**III**) (white, method A, from $Et_2O/C_6H_6$). Found: Zn, 8.6; I, 35.4. Calc. for $C_{14}H_{23}OTaZnI_2$: Zn, 9.2; I, 35.9%. The ratio Ta:Zn was found to be 1:1.1.

$Cp_2TaH_3 \cdot ZnI_2 \cdot THF$ (**IV**) (white, method B, from THF). Found: Zn, 8.0; I, 34.9. Calc. for $C_{14}H_{21}OTaZnI_2$: Zn, 9.3; I, 36.0%.

$Cp_2TaH_3 \cdot CdI_2$ (**V**) (yellow, method A, from $CH_3CN$). Found: Ta, 28.8; C, 17.9; H, 1.8. Calc. for $C_{10}H_{13}TaCdI_2$: Ta, 26.6; C, 17.7; H, 1.9%.

$Cp_2TaH_3 \cdot MgI_2$ (**VI**) (white, method A, from $Et_2O/C_6H_6$). Found: Ta, 29.6; C, 21.3; H, 2.7. Calc. for $C_{10}H_{13}TaMgI_2$: Ta, 30.5; C, 20.3; H. 2.2%.

The spectral characteristics of the complexes **I**–**VI** are listed in Table I.

X-ray analysis of a single crystal of $Cp_2TaH_3 \cdot ZnCl_2 \cdot THF$ (crystal size 0.1 × 0.1 × 0.2 mm) packed in a glass capillary was carried out on an automatic 'Syntex $P\bar{1}$' diffractometer (Mo $K\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning). Crystals of **II** are triclinic: $a = 8.960(1)$, $b = 8.100(1)$, $c = 12.469(2)$ Å, $\alpha = 93.62(1)°$, $\beta = 82.22(1)°$, $\gamma = 111.74(1)°$, space group $P\bar{1}$, $Z = 2$. 1996 reflections with $I \geqslant 3\sigma(I)$ were used in the calculations. The structure was solved by the direct method (with allowance for the absorption correction, $\mu_{Mo} = 87.0$ $cm^{-1}$) and refined by the least-squares method with the weight scheme $\omega = 1/\sigma^2(F)$ in the anisotropic (hydrogen atoms in isotropic) approximation to $R = 0.019$ ($R_w = 0.020$). The main interatomic distances and bond angles in the molecule **II** are given in Table II, the atomic coordinates are given in Table III.

## Discussion

The interaction of $Cp_2TaH_3$ with the second group metal halogenides in all cases studied led to the complexes with the 1:1 ratio of Ta to the other metal, whose NMR spectra, although pertaining to

TABLE I. Spectral Characteristics of $Cp_2TaH_3$ and its Bimetallic Complexes

| Compound | NMR | | | IR |
|---|---|---|---|---|
| | $^{13}C$ (ppm) $C_5H_5$ | $^1H$ (ppm) | | Ta–H ($cm^{-1}$) |
| | | $C_5H_5$ | Ta–H | |
| $Cp_2TaH_3$ | 87.0 | 5.2 | −2.25t<br>−3.35d | 1740 |
| | 85.6 | 5.2 | −2.40t[a]<br>−3.35d[a] | |
| $Cp_2TaH_3 \cdot ZnCl_2 \cdot Et_2O$ (I) | 86.0 | 5.3 | −2.65t[a]<br>−3.29d | 1810, 1730, 1670 |
| $Cp_2TaH_3 \cdot ZnCl_2 \cdot THF$ (II) | 92.5 | 5.4 | −2.64d<br>−4.94t<br>−2.82t[a]<br>−3.32d[a] | 1810, 1720, 1650 |
| $Cp_2TaH_3 \cdot ZnI_2 \cdot Et_2O$ (III) | | 5.2 | −2.52t[a]<br>−3.34d[a] | 1805, 1715, 1660 |
| $Cp_2TaH_3 \cdot ZnI_2 \cdot THF$ (IV) | 93.7 | 5.7 | −2.10d<br>−4.50t | 1805, 1720, 1670 |
| $Cp_2TaH_3 \cdot CdI_2$ (V) | | 5.55 | −2.81d[a]<br>−3.36t[a] | 1835, 1670, 1585 |
| $Cp_2TaH_3 \cdot MgI_2$ (VI) | | 5.27 | −2.37t[a]<br>−3.32d[a] | 1810, 1720, 1620 |
| $Cp_2TaH_3 + MgCl_2$ | | 5.15 | −2.25t[b]<br>−3.35d[b] | |

[a] Spectra were recorded in $d_6$-DMSO; all the other spectra were recorded in $d_8$-THF; t = triplet; d = doublet. [b] Spectrum is recorded immediately after the preparation of solution.

TABLE II. Atomic Coordinates in $Cp_2TaH_3 \cdot ZnCl_2 \cdot C_4H_8O$

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Ta | 0.6903(1) | 0.6808(1) | 0.2041(1) | 0.035(1) |
| Zn | 0.3424(1) | 0.6105(1) | 0.2167(1) | 0.047(1) |
| Cl1 | 0.2674(2) | 0.7194(2) | 0.0818(1) | 0.068(1) |
| Cl2 | 0.1809(2) | 0.3418(2) | 0.2796(1) | 0.072(1) |
| C1 | 0.7469(9) | 0.5660(9) | 0.3583(5) | 0.066(3) |
| C2 | 0.5942(7) | 0.4558(8) | 0.3360(5) | 0.063(3) |
| C3 | 0.6144(9) | 0.3729(7) | 0.2357(6) | 0.072(3) |
| C4 | 0.7767(9) | 0.4353(8) | 0.1962(5) | 0.066(3) |
| C5 | 0.8580(7) | 0.5572(8) | 0.2719(5) | 0.065(3) |
| C6 | 0.8437(8) | 0.9782(7) | 0.1519(5) | 0.064(3) |
| C7 | 0.7048(7) | 0.9221(7) | 0.0993(5) | 0.054(3) |
| C8 | 0.7105(9) | 0.7874(9) | 0.0255(5) | 0.061(3) |
| C9 | 0.8505(8) | 0.7563(8) | 0.0357(5) | 0.066(3) |
| C10 | 0.9345(8) | 0.8757(8) | 0.1135(6) | 0.063(3) |
| C11 | 0.2233(10) | 0.7131(9) | 0.4539(5) | 0.090(4) |
| C12 | 0.2968(12) | 0.9476(8) | 0.3422(6) | 0.089(4) |
| C13 | 0.2090(17) | 0.8576(13) | 0.5192(8) | 0.131(6) |
| C14 | 0.2618(22) | 1.0102(14) | 0.4486(7) | 0.136(7) |
| O1 | 0.2481(5) | 0.7602(5) | 0.3439(3) | 0.054(2) |
| TaH1 | 0.5195(54) | 0.5523(56) | 0.1410(35) | |
| TaH2 | 0.7183(60) | 0.8248(63) | 0.3216(40) | |
| TaH3 | 0.5310(64) | 0.7303(66) | 0.2660(42) | |

TABLE III. Main Interactomic Distances *d* (Å) and Valence Angles *ω* (°) in $Cp_2TaH_3 \cdot ZnCl_2 \cdot THF$

| Bond | *d* | Angle | *ω* |
|---|---|---|---|
| Ta–H(1) | 1.76(5) | Cp(1)–Ta–Cp(2) | 138.9 |
| Ta–H(2) | 1.80(5) | H(1)–Ta–H(3) | 72.4(2,3) |
| Ta–H(3) | 1.70(6) | H(3)–Ta–H(2) | 61.2(2,5) |
| Ta...Zn | 2.939(1) | Ta–H(3)–Zn | 115.3(2,8) |
| Ta–$C_{mean}$ | 2.370 | Ta–H(1)–Zn | 105.7(2,8) |
| Ta–Cp(1) | 2.056 | H(3)–Tn–H(1) | 66.6(2,5) |
| Ta–Cp(2) | 2.052 | H(3)–Zn–Cl(1) | 120.2(1,8) |
| Zn–H(1) | 1.93(5) | H(3)–Zn–Cl(2) | 121.7(1,8) |
| Zn–H(3) | 1.78(5) | H(3)–Zn–O | 83.9 |
| Zn–Cl(1) | 2.234(2) | H(1)–Zn–Cl(1) | 100.7(1,8) |
| Zn–Cl(2) | 2.240(2) | H(1)–Zn–Cl(2) | 99.8 |
| Zn–O | 2.203(2) | H(1)–Zn–O | 150.5 |
| O–C(11) | 1.412(7) | Cl(1)–Zn–Cl(2) | 118.0(1) |
| O–C(12) | 1.417(7) | Cl(1)–Zn–O | 94.3 |
| | | Cl(2)–Zn–O | 95.2 |
| | | C(11)–O–C(12) | 106.5(5) |

all three hydride hydrogens, differ markedly from that of the starting tantalocene trihydride. The $^1H$ NMR spectrum of $Cp_2TaH_3$ is known [13] to be described in the hydride region by the $AB_2$ proton system with the signals for $H_B$ being located in a stronger field (10.69 and 13.02 ppm, respectively). Replacement of the non-polar solvent ($C_6H_6$) by the polar ones (THF, DMSO) causes an upfield shift of the hydride signals (in particular of $H_A$) in $Cp_2TaH_3$ (Table I). The formation of the heterometallic complexes also causes an upfield shift by 1–2.5 ppm of the signal for $H_A$, but simultaneously the remaining signals ($\tau C_5H_5$ and $\tau_{H_B}$) are donwfield shifted (by 0.3–0.5 and 0.6–1.3 ppm, respectively), and the triplet $H_A$ and the doublet $H_B$ exchange their positions (Table I). The signals for the carbon atoms of the Cp ring in the $^{13}C$ NMR spectra are also downfield shifted (Table I). These peculiarities in the spectra indicate unambiguously that the bond in the heterometallic complexes of $Cp_2TaH_3$ with the second group metal halogenides in solution is effected via the ordinary bridge $Ta{-}H_A \rightarrow M$. By special experiments it was shown that the temperature variation (−70–+40 °C) does not change the values of $\tau$(Ta–H) and signal widths. Hence, in this case there is no exchange interactions involving the terminal hydrogen atoms. Similar changes in the $^1H$ NMR spectra have been observed for the complexes of $Cp_2TaH_3$ with $AlEt_3$ (an upfiled shift of $\tau(H_A)$ by 4. ppm), $ZnEt_2$ and $CdEt_2$ [10].

The durability and the composition of the complexes $Cp_2TaH_3 \cdot MX_2$ are determined by the strength of the Lewis acid $MX_2$ and by the basicity of the solvent, playing the role of the competing reagent. Thus, the interaction of $CdI_2$ with $Cp_2TaH_3$ in acetonitrile produces an insoluble (in this solvent) unsolvated complex of composition $Cp_2TaH_3 \cdot CdI_2$ (V). In contrast to the similar complex with $Cp_2ReH$ [14] **V** is soluble in DMSO without decomposition (Table I), and most likely it is unsolvated even in this solvent. With decreasing acidity of $MX_2$ the stability of the heterometallic complexes is reduced. Thus, the complexes $Cp_2TaH_3 \cdot ZnX_2 \cdot L$ crystallize from solutions as the monosolvates, and are stable in THF medium (DN 20.0)†, but in a more donor solvent, DMSO (DN $\sqrt{29.8}$), they decompose into their components. A stronger acid, $ZnCl_2$, causes a greater shift in $\tau(H_A)$ than less strong $ZnI_2$ (Table I). The replacement of the halogen atom in $ZnX_2$ with alkyl groups, resulting in a still larger weakening of acidic properties, leads to the bimetallic compounds existing only in solutions of the non-polar solvent, $C_6H_6$ (DN 0.1), and decomposing on attemps at isolation [10].

It has been possible to obtain the bimetallic complex with magnesium halogenides only for $MgI_2$ (**VI**) and only in the medium of the mixed solvent, $Et_2O$ (DN 19.2)/$C_6H_6$, in which **VI** is insoluble. In THF or DMSO this compound decomposes into its components (Table I, eqn. (1))

$$Cp_2TaH_3 + MgI_2 \underset{\text{THF, DMSO}}{\overset{Et_2O}{\rightleftarrows}} Cp_2TaH_3 \cdot MgI_2 \qquad (1)$$

An increase in the degree of covalent binding in beryllium and magnesium chlorides and the respective increase in the $M \leftarrow O$ bond strength in their solvates with oxygen-containing ligands leads to an absolutely unexpected result. The interaction of $BeCl_2$ with $Cp_2TaH_3$ in $Et_2O$ or THF and of $MgCl_2$ in THF does not take place immediately (Table I). However, on standing (for 20–30 min) or on slight heating the solution turns green ($BeCl_2$) or dark blue ($MgCl_2$). The EPR spectrum shows in this case a six-component signal with $g = 1.986$, typical of $Cp_2TaCl_2$ [15]. Next, the elimination of hydrogen takes place accompanied by the solution gradually turning dark brown and by the precipitation of a small amount of brown crystals of $Cp_2TaCl_2$, identified by X-ray analysis*. A small yield for tantalocene dichloride (~5%) suggests that the reaction of its formation is not the main one. The intensity of the signals $\tau(C_5H_5)$ and $\tau$(Ta–H) in the $^1H$ NMR spectrum of $Cp_2TaH_3{-}MgCl$ in $d_8$-THF gradually reduces, and simultaneously there appear and begin to grow the signals at $\tau$ 3.33 and 3.40 ppm, belonging to free cyclopentadiene. At the end of the reaction the spectrum shows only the signals for $C_5H_6$ and the solvent, and no signals associated with the $\pi$-bonded Cp rings and hydride protons are detected. Upon evaporation the solution produces a mixture of at least two substances (coloured and colourless), which, according to the IR data, contain no hydride hydrogens. (The interaction in the system $\{Cp_2TaH_3 + AlCl_3\}$ proceeds in a similar way.) The mechanism of this reaction, which is untypical of other biscyclopentadienyl hydrides [16], is still not clear. It can merely be suggested that one of the reaction steps requires the transfer of the chlorine atoms to the tantalum atom, and the subsequent reduction of Ta(V) to Ta(IV) with the elimination of hydrogen (the step when the colour appears, eqn. (2))

$$Cp_2TaH_3 + MgCl_2 \longrightarrow \{Cp_2TaHCl_2 + MgH_2\} \xrightarrow{-\frac{1}{2}H_2} \{Cp_2TaCl_2 + MgH_2\} \longrightarrow \ldots \qquad (2)$$

The interaction of such a type is essentially accelerated in solvents like DMSO and DMFA. This reaction appears to be stipulated both by a greater strength of the Be–H and Mg–H bonds, as compared to the Zn–H one, and by a greater hydride character of the Ta–H bond, as compared to the Mo–H and Re–H bonds [11, 16]. However, it should be pointed out once again that none of the possible hydride compounds of magnesium, such as $MgH_2 \cdot n$THF, $MgHCl \cdot n$THF, CpMgH·THF, have been identified by us using the $^1H$ NMR and IR technique.

Carrying out the reaction of $Cp_2TaH_3$ with the second group metal halogenides in weakly solvating solvents, such as acetontrile (Cd), diethyl ether (Mg,

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†DN, donor number.

*The results of the X-ray study of $Cp_2TaCl_2$, which has the structure typical of the transition metal biscyclopentadienyl chlorides, will be published later.

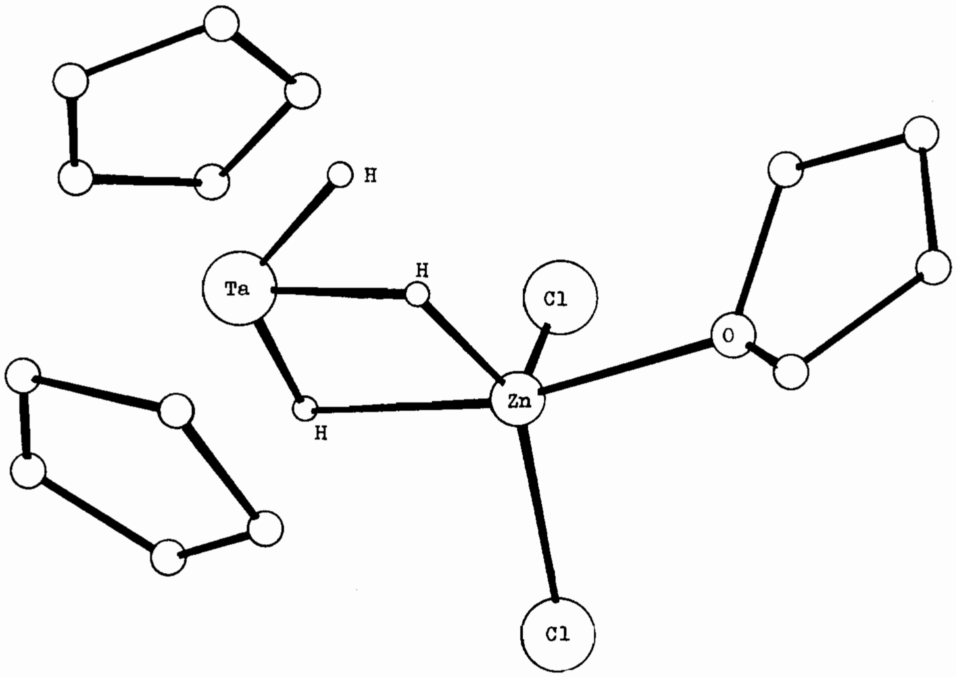
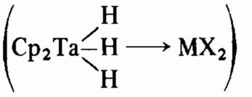


Fig. 1. The molecular structure of $(\eta^5\text{-}C_5H_5)_2TaH(\mu_2\text{-}H)_2ZnCl_2\cdot C_4H_8O$.

Zn), THF (Zn), it has been possible to isolate a series of complexes in the crystal state. Analysis of their IR spectra allowed us to make the following conclusions. Firstly, the spectra of all the complexes are similar and contain in the region of bond vibrations of the M–H bond a singlet of weak intensity at 1800–1835 $cm^{-1}$ and an asymmetric doublet at 1585–1730 $cm^{-1}$. Secondly, the observed spectra differ markedly from those anticipated for the compounds containing an ordinary hydrogen bridge



$$\left(Cp_2Ta\begin{array}{l}\diagup H\\ -H \longrightarrow MX_2\\ \diagdown H\end{array}\right)$$

and two terminal hydrogen atoms, but are consistent fairly well with the other type of binding suggested, namely, via the double hydrogen bridge with one terminal hydrogen pertained. This suggestion has been confirmed by the X-ray study of the complex $Cp_2TaH_3\cdot ZnCl_2\cdot THF$ (Tables II and III, Fig. 1).

The geometry of the $Cp_2TaH_3$ moiety in **II** is practically identical to that in the starting molecule, in which the tantalum atom is connected with two $\eta^5\text{-}C_5H_5$ groups and three hydride atoms of hydrogen located in the bisector plane of the wedgelike sandwich $Cp_2Ta$ [17]. So, the angle CpTaCp (140°), $d(Ta–C) = 2.07$ Å and $d(Ta–H) = 1.77$ Å, found in $Cp_2TaH_3$ [17], is practically identical to the similar parameters in **II**. The cyclopentadienyl rings both in **II** and in $Cp_2TaH_3$ are planar to within 0.01 Å. The only noticeable distinction is observed in the HTaH bond angles: for the bridge hydrogens in **II** these are 72° (in $Cp_2MoH_2\cdot ZnBr_2\cdot DMFA$ 64° [8]), and the $H^bTaH^t$ angle is 61°, whereas in $Cp_2TaH_3$ both angles are equal to 63° [17]. The Zn–H bond length (1.8–1.9 Å) in **II** is somewhat greater than in the other complexes involving the Zn–H–M bond: $Cp_2MoH_2\cdot ZnBr_2\cdot DMFA$ (1.6–1.8 Å) [8], $Cp_2Nb(CO)HZn(BH_4)$ (1.75 Å) [18] $(PMePh_2)_4V_2[(\mu_2\text{-}H)_2ZnBH_4]$ (1.6–1.7 Å) [19], and this suggests that the bond in the obtained compound is less strong.

The zinc atom in **II** has an unusual coordination number, which is equal to 5. However, the same coordination number was observed formerly for $Cp_2MoH_2\cdot ZnBr_2\cdot DMFA$ [8]. The coordination polyhedron of this atom is a highly distorted trigonal bipyramid (the H(1)ZnO angle between the axial ligands is 150°). An essential elongation of the Zn–O bond lengths (2.203 Å) should be pointed out, which seems to be related to its axial position in the bipyramid.

The interatomic distance Ta...Zn in **II** (2.931 Å) is greater than the sum of covalent radii of Ta* and Zn (1.58 Å [20] + 1.25 Å = 2.83 Å) and is essentially greater than the length of the σ-bond Ta–Zn in $Cp_2Ta(H)(CpZn)_2$ (2.59 Å) [9]. At the same time, in $Cp_2MoH_2\cdot ZnBr_2\cdot DMFA$ the interatomic distance Mo...Zn (2.793 Å [8]) is even less than the sum of covalent radii of Mo* and Zn (1.53 Å [20] + 1.25 Å

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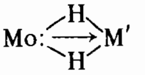
*The covalent radii for the Ta and Mo atoms have been calculated from the M–C bond lengths in the cyclopentadienyl complexes [20].

[21] = 2.78 Å). Since the replacement of halogen atoms or Lewis bases in the analogous heterometallic complexes produces little effect on the interatomic distance M–M′ (in $Cp_2MoH_2{\cdot}FeI_2{\cdot}THF$ it is equal to 2.85 Å [6], in $(Cp_2MoH_2FeBr_2)_2$ 2.82 Å [22], in $Cp_2MoH_2FeI_2{\cdot}NCH_3C$ 2.54 Å [7]), it can be concluded that the short interatomic distances M–Mo in the $d^2$-complexes on the basis of molybdenocene dihydride are due to the additional interaction between the lone pair of d-electrons of Mo and the vacant orbitals of the atom M′, *i.e.* these compounds involve the mixed bond



$\mathrm{Mo}{:}\overset{H}{\underset{H}{\longrightarrow}}\mathrm{M'}$

(It is worth noting that the possibility of an additional binding in $Cp_2MoH_2{\cdot}ZnBr_2{\cdot}DMFA$ has been considered previously [8].)

It is of interest to compare the basicity of the biscyclopentadienyl hydrides $Cp_2MH_n$ as ligands in the complexes of the second group metals depending on the type of metal-binding in the complex, by comparing them with n-donor Lewis acids. Thus, the stability of the complexes $Cp_2MH_n{\cdot}ZnX_2$ in DMSO medium increases in the series Ta < Re < Mo =W: while the complexes of $ZnX_2$ with $Cp_2TaH_3$ in DMSO undergo decomposition, the complexes with $Cp_2ReH$ are stable for several hours [14], whereas the complexes with $Cp_2MoH_2$ and $Cp_2WH_2$ may be recrystallized from DMSO solutions and isolated as the solvates $Cp_2MH_2{\cdot}ZnX_2{\cdot}DMSO$ [23, 24]. In THF medium the complexes with $ZnX_2$ are stable for all the metals, however, their solvation for each metal is determined by the strength of the Lewis acid. For $Cp_2TaH_3$ there were isolated the solvates $Cp_2TaH_3{\cdot}ZnX_2{\cdot}THF$ with X = Cl, I, while for $Cp_2ReH$ the solvates were obtained for X = Br, I (the complex with $ZnCl_2$ crystallizes unsolvated) [14], and for $Cp_2MoH_2$ and $Cp_2WH_2$ the solvate was obtained only for $ZnI_2$ [23, 24]; this shows that the donor ability of $Cp_2MH_n$ increases in this series. In this case for the most weak base, $Cp_2TaH_3$, in THF solution there occurs the rupture of one of two bridging bonds Ta–H–Zn. A similar character of changes in the durability of complexes is also observed for $BeCl_2$ and $MgX_2$ [14, 23, 24], the nature of the interaction between them and $Cp_2TaH_3$ in the donor solvents changing fundamentally.

Thus, in the considered series of complexes $Cp_2MH_n{\cdot}M'X_2$ the hydride ligands (in $Cp_2TaH_3$) are the most weak donors, being essentially inferior in basicity to the lone pair localized on the metal atom (in $Cp_2ReH$). However, the combination of the hydride ligands with the lone pair affords the most donor ligand, $Cp_2Mo(W)H_2$, and, hence, the most strong complexes with Lewis acids.

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