Preparation and Molecular Structure of the Unconventional Tantalum Chloride Complex $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$

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Introduction

Only two indenyl metal halides of the group 5 elements are known. The reaction of I_2 with diindenylvanadium(II) yields diindenyliodovanadium(III),[1] and the interaction of $NbCl_4(THF)_2$ with lithium indenide gives $(C_9H_7)_2NbCl_2$ in good yield;[2] no well-characterized indenylmetal halides of tantalum have been reported. The classic route to the preparation of $CpTaCl_4$ or Cp^*TaCl_4 is the interaction of $TaCl_5$ with (trialkylsilyl)- or (trialkylstannyl)cyclopentadienyl reagents.[3−12] The use of these materials as cyclopentadienyl transfer agents pose a distinct advantage over the use of lithium or sodium salts of cyclopentadiene or pentamethylcyclopentadiene, since there is no reduction of the Ta(V) center and the trialkylsilicon chloride or trialkyltin chloride byproducts are easily removed *in vacuo* or washed from the sparingly-soluble tantalum products.

The synthesis and characterization of (trialkylsilyl)- and (trialkylstannyl)cyclopentadienes and -indenes have been the subjects of several studies.[13−18] Even though compounds of the type $Me_3Sn(C_5R_5)$ are dangerously toxic to humans, the butyl analogues $Bu_3Sn(C_5R_5)$, while still requiring caution during handling, have been reported to be toxic to only gram-positive bacteria.[19] Although 1-(trimethylstannyl)indene has been well-studied, 1-(tributylstannyl)indene has only been reported in the patent literature.[20−23]

Recent reports demonstrated that (trialkylsilyl)- or (trialkylstannyl)indene reagents can be used successfully to prepare group 4 monoindenyl trichlorides $(\eta^5\text{-}C_9H_7)MCl_3$ of Ti, Zr, and Hf without the complication of $(\eta^5\text{-}C_9H_7)_2MCl_2$ impurities.[24,25] Although $Me_3SiC_5R_5$ (R = H, Me) can be used to prepare $(\eta^5\text{-}C_5R_5)TaCl_4$ without reduction of Ta(V), 1-(trimethylstannyl)indene *instantly* reduces $TaCl_5$ (or $NbCl_5$) in toluene or methylene chloride, even at low temperatures, to give very soluble, deeply-colored species which are all NMR silent.[26] We wish to report the synthesis, characterization, and molecular structure of the diindenyltantalum(V) salt $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$.

Experimental Section

General Procedures and Materials. All operations were carried out under vacuum or under argon. Solvents were distilled under argon from sodium−benzophenone (pentane) or CaH_2 (dichloromethane) immediately before use. Triethylamine, indene, and tributylstannyl chloride were purchased from Aldrich and distilled before use. Butyllithium (Aldrich) was used as received. Tantalum pentachloride was purchased from Cerac and sublimed immediately before use. 1-(Tri-*n*-butylstannyl)indene was prepared as described elsewhere.[23]

Microanalyses were performed by the University of Illinois Microanalytical Laboratory, Urbana, IL. The IR spectra were recorded on a Nicolet 5ZDX FT-IR spectrometer as Nujol mulls, and ^1H NMR spectra were obtained on a Varian Gemini-200 at 200 MHz.

Preparation of $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$, 1. To a suspension of tantalum pentachloride (14.69 g/0.0410 mol) in dichloromethane (150 mL) was added 1-(tri-*n*-butylstannyl)indene (15.5 mL/0.0410 mol). Upon addition of the (tri-*n*-butylstannyl)indene, a red microcrystalline product, $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$, **1**, precipitated immediately from a pale-red solution. The precipitate was isolated by filtration and subsequently washed with pentane (2 × 100 mL). The product was then dried under full vacuum to give **1** as a red microcrystalline product. Yield: 11.2 g, 62.4%. Mp: 278−282 °C dec. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.72 (m, 4H), 7.53 (m, 4H), 6.97 (d, 4H), 6.64 (t, 2H). IR (cm^{-1}, Nujol, KBr): 722 m, 754 m, 801 m, 851 w, 870 w, 1020 m, 1047 m, 1092 m, 1156 w, 1158 w, 1213 w, 1260 m, 1304 m, 1342 m, 1377 s, 1462 s, 2670 m, 2726 m, 2755 m, 2855 s, 2923 s, 2958 s, 3100 m. Anal. Calcd for $C_{18}H_{14}Cl_8Ta_2$ (found): C, 24.7 (24.6); H, 1.50 (1.60); Cl, 32.7 (32.4).

X-ray Structure Determination. A long, orange, oval-shaped needle was cleaved to form a smaller fragment, and the fragment was affixed to the end of a glass fiber using silicone grease. The sample was then transferred to the diffractometer where it was cooled to −173° for characterization. Standard inert-atmosphere handling techniques were used. After the crystal was placed on the goniostat, a systematic search of a limited hemisphere or reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, which indicated a triclinic space group. Subsequent solution and refinement of the structure confirmed the centric $P\bar{1}$ space group to be correct.

The diffractometer utilized for the data collection was designed and constructed at the Molecular Structure Center of Indiana University. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal), a graphite monochromator, and a Picker X-ray generator

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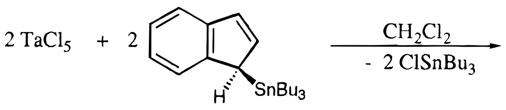
interfaced to a Z80 microprocessor controlled by an IBM PC microcomputer was used. Motors were Slo-Syn stepping motors, and a special top/bottom−left/right slit assembly was used to align the crystal. All computations were performed on IBM-compatible microcomputer systems using DOS or OS/2 operating systems.

Redundant data were collected to $2\theta = 45°$, corrected for Lorentz and polarization terms, and equivalent data were averaged. An absorption correction for the presence of extinction was applied to the data on the basis of Miller indices assigned to cleaned faces. The structure was readily solved by direct methods (SHELXTL-PC) and Fourier techniques. The calculated transmission factors ranged from 0.105 to 0.765. Hydrogen atoms were placed in idealized positions and were included as fixed atom contributors in the least-squares refinement. A final difference Fourier map was featureless with the largest peak being 0.23 e/Å^3.

Results and Discussion

The addition of 1-(tri-*n*-butylstannyl)indene, 1-(Bu_3Sn)C_9H_7, to a room-temperature suspension of $TaCl_5$ in dichloromethane produces $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$, **1**, in good yield as bright red microcrystals which, after being washed with dichloromethane, give satisfactory analyses for C, H, and Cl (eq 1).



$[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$ (1)

1

The ^1H NMR spectrum exhibited by **1** in CD_2Cl_2 appears as a slightly-broadened η^5-indenyl pattern for the two indenyl groups in which there is an AA′BB′ pattern for the six-membered ring protons and a broadened AB_2 pattern for the five-membered ring protons. While this broadening could, in part, be due to one or both of the rings slipping between η^5 and η^3 hapticities or a consequence of the tantalum nuclear quadrupole,[27] it is likely that the sterically-hindered rotation of the indenyl rings is slow on the NMR time scale. Variable-temperature ^1H NMR analysis of **1** was unsuccessful due to the low solubility of the tantalum salt in CD_2Cl_2 (bp 40 °C); **1** is not soluble in nonhalogenated solvents and reacts with Lewis base solvents.

It is interesting that the reaction described in eq 1 results in the diindenyl salt, **1**, while the reaction of $TaCl_5$ with $Me_3Sn(C_5H_5)$ and *n*-$Bu_3Sn(C_5Me_5)$, under similar reaction conditions, results in the neutral species $(\eta^5\text{-}C_5H_5)TaCl_4$ and $(\eta^5\text{-}C_5Me_5)TaCl_4$, respectively.[2,3,28] This could be a result of the relative donor ability of indenyl vs cyclopentadienyl or pentamethylcyclopentadienyl toward early transition metal centers.

A study by Gassman *et al.* has shown that the indenyl group is approximately equal to pentamethylcyclopentadienyl and *better* than cyclopentadienyl as a donor to ruthenium(II) centers.[29] This conclusion was supported by quantitative data such as XPS spectra and electrochemical oxidation potentials of the Ru(II) centers. In addition, we have found that the group 4 indenyl halides $(\eta^5\text{-}C_9H_7)MCl_3$ (M = Zr, Hf) easily coordinate trimethylphosphine and dmpe (1,2-bis(dimethylphosphino)ethane).[30] This is in sharp contrast with the chemical behavior of $(\eta^5\text{-}C_5H_5)MCl_3$ and $(\eta^5\text{-}C_5Me_5)MCl_3$ (M = Zr, Hf), which readily coordinate hard Lewis bases such as ethers and amines but do not easily complex phosphines.[31,32] The indenyl groups in the group 4 indenyl halides $(\eta^5\text{-}C_9H_7)MCl_3$ (M = Zr, Hf) appear to be better electron donors to zirconium and hafnium than cyclopentadienyl or pentamethylcyclopentadienyl groups, and it is likely that this trend is the same with tantalum(V) centers. In the case of tantalum(V), the cyclopentadienyl and pentamethylcyclopentadienyl ligands may not be sufficient electron donors to stabilize species such as $[(\eta^5\text{-}C_5H_5)_2TaCl_2][TaCl_6]$ or $[(\eta^5\text{-}C_5Me_5)_2TaCl_2][TaCl_6]$, respectively, and thus form the neutral species $(\eta^5\text{-}C_5H_5)TaCl_4$ and $(\eta^5\text{-}C_5Me_5)TaCl_4$. In addition, ionization of a chloride ligand may be a direct result of the indenyl ligand *weakening* the Ta−Cl bond. In fact, cationic species such as $[Cp_2TaCl_2^+]$ must be formed by oxidation of neutral Ta(IV) species such as Cp_2TaCl_2.[33,34] In the case of **1**, the indenyl ligands are sufficiently electron donating that the cation of the diindenyl salt is stable.

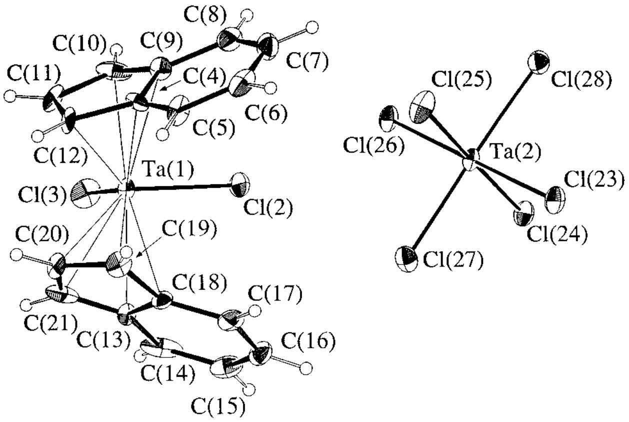


Figure 1. ORTEP drawing of the cation and anion of $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$, **1**.

Table 1. Summary of Crystal Data for $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$ (**1**)

formula	$C_{18}H_{14}Cl_8Ta_2$	*Z* (molecules/unit cell)	2
fw	875.83		
temp (°C)	−173	*V* (Å^3)	1130.02
space group	$P\bar{1}$	calcd density (g/cm^3)	2.574
a (Å)	10.140(1)		
b (Å)	13.499(1)	λ (Å)	0.710 69
c (Å)	8.263(1)	crystal dimens (mm)	0.07 × 0.40 × 0.43
α (deg)	92.03(1)	R^a	0.0456
β (deg)	90.61(1)	$R_w{}^b$	0.0415
γ (deg)	91.24(1)		

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = \Sigma w||F_o| - F_c||/\Sigma w|F_o|$.

Crystallographic Studies. Single crystals of $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$, **1**, were grown by cooling a saturated dichloromethane solution of **1** to −20 °C. The structural analysis shows that crystals of **1** are composed of discrete monomers of $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$, in which the cation and anion are clearly separated; a perspective view of the salt is presented in Figure 1. Molecules of **1** have no crystallographically-imposed symmetry. Crystal data are collected in Table 1, and bond distances and angles for **1** are presented with estimated standard deviations in Tables 2 and 3. Selected bond distances for relevant Cp compounds are given for comparison in Table 4.

Cation. In **1**, the tantalum center of the cation adopts a pseudotetrahedral geometry, with the indenyl groups and the chloride ligands occupying the ligand sites. The two indenyl

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Table 2. Selected Bond Distances (Å) for $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$ **(1)**

	$[(\eta^5\text{-}C_9H_7)_2TaCl_2^+]$		
Ta(1)−Cl(2)	2.297(4)	Ta(1)−C(12)	2.363(18)
Ta(1)−Cl(3)	2.333(5)	Ta(1)−C(13)	2.462(18)
Ta(1)−C(4)	2.542(16)	Ta(1)−C(19)	2.531(17)
Ta(1)−C(9)	2.485(17)	Ta(1)−C(20)	2.385(17)
Ta(1)−C(10)	2.394(18)	Ta(1)−C(21)	2.364(17)
Ta(1)−C(11)	2.351(17)	Ta(1)-ring centroid(1)	2.115(17)
Ta(1)−C(18)	2.531(17)	Ta(1)-ring centroid(2)	2.104(17)
	$[TaCl_6^-]$		
Ta(22)−Cl(23)	2.355(4)	Ta(22)−Cl(26)	2.315(4)
Ta(22)−Cl(24)	2.390(4)	Ta(22)−Cl(27)	2.361(4)
Ta(22)−Cl(25)	2.342(4)	Ta(22)−Cl(28)	2.316(4)

Table 3. Selected Bond Angles (deg) for $[(\eta^5\text{-}C_9H_7)_2TaCl_2][TaCl_6]$ **(1)**

	$[(\eta^5\text{-}C_9H_7)_2TaCl_2^+]$		
Cl(2)−Ta(1)−Cl(3)	97.70(18)		
ring centroid(1)−Ta(1)−ring centroid(2)	132.36(2)		
	$[TaCl_6^-]$		
Cl(24)−Ta(22)−Cl(28)	88.62(16)	Cl(26)−Ta(22)−Cl(27)	91.15(17)
Cl(23)−Ta(22)−Cl(24)	89.38(15)	Cl(23)−Ta(22)−Cl(28)	90.94(16)
Cl(25)−Ta(22)−Cl(26)	90.25(16)	Cl(26)−Ta(22)−Cl(28)	92.45(17)
Cl(23)−Ta(22)−Cl(25)	179.08(15)	Cl(24)−Ta(22)−Cl(25)	90.57(15)
Cl(25)−Ta(22)−Cl(27)	89.27(15)	Cl(27)−Ta(22)−Cl(28)	176.33(16)
Cl(23)−Ta(22)−Cl(26)	89.78(16)	Cl(24)−Ta(22)−Cl(26)	178.66(16)
Cl(25)−Ta(22)−Cl(28)	89.97(16)	Cl(24)−Ta(22)−Cl(27)	87.80(15)
Cl(23)−Ta(22)−Cl(27)	89.81(16)		

Table 4. Selected Bond Distances and Angles for **1**-Relevant Cp Complexes

	$[(\eta^5\text{-}C_9H_7)_2\text{-}TaCl_2]$[a]	$(MeCp)_2\text{-}TaCl_2$[36]	$[Cp_2Nb\text{-}Cl_2^+]$[35]	$[Cp_2\text{-}VCl_2{}^+]$[37]
M(1)−Cl(1)	2.297(4)	2.445(4)	2.343(1)	2.293(3)
M(1)−Cl(2)	2.333(5)	2.439(4)		2.298(3)
M(1)-centroid(1)	2.115	2.11		1.986(5)
M(1)-centroid(2)	2.104	2.02		1.965(5)
Cl(1)-M−Cl(2)	97.70(18)	84.5	97.6(1)	96.3(1)

[a] This work.

groups are slightly rotated with respect to each other, and each indenyl ligand coordinates to the tantalum center in an η^5 fashion. The bridgehead carbons in **1** (C(4), C(9), C(18), and C(13); average Ta−C distance = 2.505(17) Å) form longer Ta−C bonds than do the allyl-like carbons (C(10), C(11), C(12), C(19), C(20), and C(21); average Ta−C distance = 2.398(17) Å). This bonding pattern is consistent with the HOMO of the indenyl anion, which has small contributions from the p_z orbitals on the bridgehead carbons, and these differences in the metal−carbon bond distances are normal for an η^5-indenyl ligand.[35] The overall geometry of **1** is similar to that of $[Cp_2NbCl_2^+]$,[36] $(MeCp)_2TaCl_2$,[37] and $[Cp_2VCl_2^+]$.[38] In **1**, the average Ta(V)−C bond lengths of 2.441(17) Å are somewhat longer than the average Nb(V)−C bond lengths of 2.401(1) Å in $[Cp_2NbCl_2^+]$, and they are longer than the average Ta(IV)−C bond distances of 2.384(4) Å in $(MeCp)_2TaCl_2$ due to the lengthened distances to the bridgehead carbons in **1**. The Ta−centroid distances of 2.115(17) and 2.104(17) Å are similar to those of 2.11 and 2.02 Å in $(MeCp)_2TaCl_2$. The Ta−Cl distances of 2.297(4) Å and 2.333(4) Å in **1** are significantly shorter than the Ta(IV)−Cl distances of 2.445(4) and 2.439(4) Å in $(MeCp)_2TaCl_2$ and are similar to the V−Cl distances of 2.293(3) Å and 2.298(3) Å in $[Cp_2VCl_2^+]$.[38] The Ta(V)−Cl distances in the cation of **1** are consistent with the Ta(V)−Cl distances in the anion of **1**.

Anion. In **1**, the $[TaCl_6^-]$ anion adopts a fairly rigid octahedral geometry, with the chloride ligands forming *cis* angles that range from 87.80(15) to 92.45(17)° and *trans* angles ranging from 176.33(16) to 179(15)°. The Ta−Cl distances range from 2.315(4) to 2.390(4) Å, and they average 2.347(4) Å. These bond distances and angles are nearly identical to those found in the $[TaCl_6^-]$ anions in $[C_9H_8N_3][TaCl_6^-]$ and $[Ta(S_2CN(CH_3)_2)_4][TaCl_6^-]\cdot{}^1/_2CH_2Cl_2$; the anion in **1** is otherwise unremarkable.[39,40]

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Supporting Information Available: Tables of positional parameters and anisotropic parameters and a description of the preparation of 1-(tributylstannyl)indene (7 pages). Ordering information is given on any current masthead page.

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