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Reactions of tetrachlorocyclopentadienyltantalum(V) derivatives with hexamethyldialuminium: Crystal and molecular structure of dichlorodimethylpentamethylcyclopentadienyltantalum(V)

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Abstract

The reaction of $[TaCpCl_4](Cp = \eta^5\text{-}C_5Me_5, \eta^5\text{-}C_5H_4SiMe_3$ or $\eta^5\text{-}C_5H_3(SiMe_3)_2)$ with Al_2Me_6 leads to $[TaCpCl_3Me]$ $(Cp = \eta^5\text{-}C_5Me_5$ (**2a**), $\eta^5\text{-}C_5H_4SiMe_3$ (**2b**), or $\eta^5\text{-}C_5H_3(SiMe_3)_2$ (**2c**)) and $[TaCpCl_2Me_2]$ $(Cp = \eta^5 - C_5Me_5$ (**3a**)). The structure of **3a** has been determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/m$, with $Z = 2$, a 6.770(3), b 13.969(3) and c 8.395(2) Å, β 112.25(3)°; the structure was refined to $R = 0.059$ and $wR = 0.095$ for 1197 independent reflections having $F > 4\sigma(F)$. The Ta atom may be considered as being five-coordinate if the substituted cyclopentadienyl ring occupies a single coordination site, and the geometry at the metal approximates to a square-based pyramid.

Introduction

Aluminium trialkyls are soft alkylating agents [1] and in reaction with transition metal halides [2] monoalkylation usually occurs [3], complete alkylation being rather infrequent [4]. Many of these reactions are not simple and may involve several stages such as adduct formation [5], change of oxidation state of the metal [6], and α-hydrogen elimination [7]. An extensive series of monopentamethyl-cyclopentadienylhalo(alkyl)tantalum complexes have been synthesised, and their behaviour in many different types of reaction has been reported [7,8]. They are usually prepared [8d] by introducing the permethylated cyclopentadienyl ring into halo(alkyl)derivatives $[TaCl_{5-n}R_n]$ [9] obtained from $TaCl_5$ by alkylation with
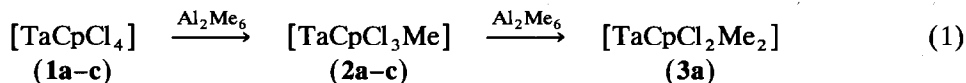

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ZnR_2, which preferentially leads to complexes with $n = 3$ or 2. For this reason the monoalkyl compounds are the least accessible halo(alkyls). In fact, the monomethyl dimeric complex $[\{Ta(\eta^5-C_5Me_5)Cl_3(Me)\}_2]$ [10] has been reported to have been used in CO insertion reactions, but no details of its isolation and characterisation were provided. We are interested in using this compound as a starting material and therefore we first set out to design a convenient method to prepare it.

Here we report the chemical behaviour of $[TaCpCl_4]$ ($Cp = \eta^5-C_5Me_5$, η^5-$C_5H_4SiMe_3$, or $\eta^5-C_5H_3(SiMe_3)_2$) in reactions with Al_2Me_6 and the X-ray crystal structure of one of the alkyls isolated.

Results and Discussion

When toluene suspensions of $[TaCpCl_4]$ ($Cp = \eta^5-C_5Me_5$ (**1a**), $\eta^5-C_5H_4SiMe_3$ (**1b**) or $\eta^5-C_5H_3(SiMe_3)_2$ (**1c**)) are treated at $-40°C$ with Al_2Me_6 in a Ta/Al molar ratio of $1/0.5$ solutions of the monomethyl derivatives **2a–c** are obtained.

$$[TaCpCl_4] \xrightarrow{Al_2Me_6} [TaCpCl_3Me] \xrightarrow{Al_2Me_6} [TaCpCl_2Me_2] \qquad (1)$$
$$\text{(1a–c)} \qquad\qquad\quad \text{(2a–c)} \qquad\qquad\quad \text{(3a)}$$

The reactions with the less soluble **1b** and **1c** are slow but monomethyl derivatives **2** are the unique final products, with no starting materials present after stirring for 8 h at room temperature. The same reaction with the more soluble **1a** proceeds faster and a mixture of **2a** and **3a** in a molar ratio $1/4$ is obtained. If the Ta/Al molar ratio is increased to $1/0.25$, the **2a/3a** ratio increases to $9/1$ and **3a** is the unique final product when an excess of Al_2Me_6 is used. **2a** and **3a** can be separated by extraction with n-hexane in which **3a** is much more soluble.

The resulting halo(alkyl)aluminium products must be eliminated in order to obtain the complexes **2** and **3** in a pure form, otherwise contaminated pyrophoric solids are obtained. Acceptable yields of pure **2** and **3** can be easily obtained when the aluminium products are first precipitated by addition of PPh_4Cl.

$$Al_2Me_{6-x}Cl_x + PPh_4Cl \rightarrow PPh_4[Al_2Me_{6-x}Cl_{x+1}] \qquad (2)$$
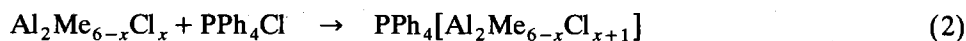
Complexes **2** and **3** are air-sensitive, and complex **2** is soluble in aromatic solvents and chloroform whereas **3** is also soluble in n-hexane. All the products were analytically and spectroscopically characterised. IR absorption bands due to the cyclopentadienyl ring and to the Ta–C and Ta–Cl stretching vibrations are observed between 1020–1250, 415–490 and 370–385 cm^{-1}.

The ^1H NMR spectra of complexes **2**, **3** show the resonances expected for the different substituents. The singlet due to the Me–Ta protons of **3a** is shifted to higher fields in comparison with **2a** as the number of methyl groups increases. A similar shift is also observed for **2a** in relation to **2b** because of better electron-donating properties of the pentamethylcyclopentadienyl ring. However **2c**, containing the bis(trimethylsilyl)cyclopentadienyl ring, surprisingly shows this signal at highest field.

The molecular structure of **3a** is shown in Fig. 1 together with the labelling scheme employed; bond lengths and angles are shown in Tables 1 and 2, respectively. The crystal structure consists of discrete molecules of **3a** with no abnormally short intermolecular contacts.
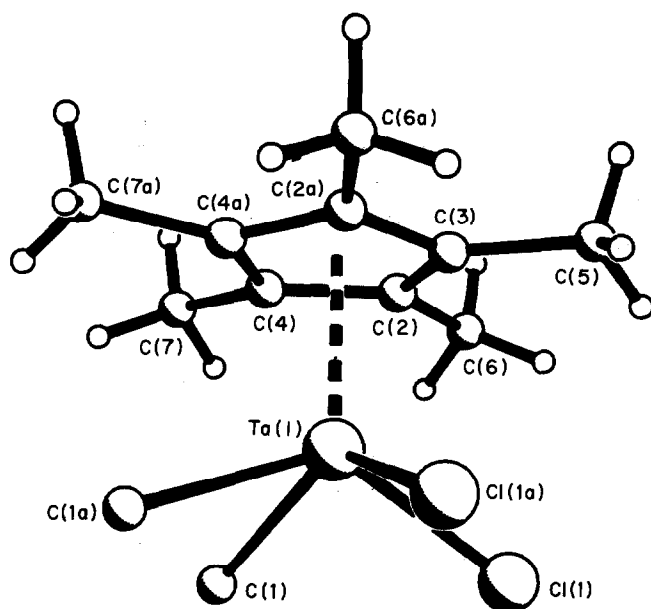
Fig. 1. The molecular structure of complex **3a** showing the atom labelling scheme.

The structure can be described as a monomeric four-legged piano-stool geometry similar to that observed for analogous monocyclopentadienyltantalum derivatives [11]. The tantalum atom is located in the centre of a pseudo-square-based pyramid with the η^5-coordinated ring occupying the apical position. The four basal positions are occupied by two chlorine atoms and two methyl groups. The crystallographic analysis reveals a high degree of disorder between the chlorine and metal-bound methyl groups, that could not be resolved after attempting refinements in space group $P2_1$. The molecule lies on a crystallographic mirror plane which passes through Ta(1), C(3), and C(5).

The disorder within the structure precludes a detailed discussion of the bond parameters relating to the chlorine atoms and the methyl groups coordinated to the Ta atom. The Ta–Cl and Ta–C(methyl) distances in **3a** differ by only 0.02 Å, reflecting the partial occupancy of both these atom types in each site, and are intermediate in length between the value of 2.268(1) Å found for the Ta–C(methyl) distance in $TaCp_2(CH_2)Me$ [12], and the average Ta–Cl distance of 2.41(1) Å in

Table 1

Bond lengths (Å) for complex **3a**

Ta(1)–Cl(1)	2.387(11)	Ta(1)–C(1)	2.363(18)
Ta(1)–C(2)	2.398(18)	Ta(1)–C(3)	2.345(22)
Ta(1)–C(4)	2.406(13)	Ta(1)–Cl(1A)	2.387(11)
Ta(1)–C(1A)	2.363(18)	Ta(1)–C(2A)	2.398(18)
Ta(1)–C(4A)	2.406(13)	C(2)–C(3)	1.375(19)
C(2)–C(4)	1.411(23)	C(2)–C(6)	1.534(25)
C(3)–C(5)	1.483(33)	C(3)–C(2A)	1.375(19)
C(4)–C(7)	1.494(24)	C(4)–C(4A)	1.408(31)

Table 2

Bond angles (°) for complex **3a**

Cl(1)–Ta(1)–C(1)	81.1(5)	Cl(1)–Ta(1)–C(2)	87.7(4)
C(1)–Ta(1)–C(2)	99.6(6)	Cl(1)–Ta(1)–C(3)	93.5(4)
C(1)–Ta(1)–C(3)	133.3(4)	C(2)–Ta(1)–C(3)	33.7(5)
Cl(1)–Ta(1)–C(4)	114.7(4)	C(1)–Ta(1)–C(4)	83.5(5)
C(2)–Ta(1)–C(4)	34.2(5)	C(3)–Ta(1)–C(4)	56.7(5)
Cl(1)–Ta(1)–Cl(1A)	83.9(5)	C(1)–Ta(1)–Cl(1A)	131.3(4)
C(2)–Ta(1)–Cl(1A)	125.8(5)	C(3)–Ta(1)–Cl(1A)	93.5(4)
C(4)–Ta(1)–Cl(1A)	144.1(5)	Cl(1)–Ta(1)–C(1A)	131.3(4)
C(1)–Ta(1)–C(1A)	75.1(8)	C(2)–Ta(1)–C(1A)	137.5(5)
C(3)–Ta(1)–C(1A)	133.3(4)	C(4)–Ta(1)–C(1A)	104.1(5)
Cl(1A)–Ta(1)–C(1A)	81.1(5)	Cl(1)–Ta(1)–C(2A)	125.8(5)
C(1)–Ta(1)–C(2A)	137.5(5)	C(2)–Ta(1)–C(2A)	55.7(8)
C(3)–Ta(1)–C(2A)	33.7(5)	C(4)–Ta(1)–C(2A)	56.4(5)
Cl(1A)–Ta(1)–C(2A)	87.7(4)	C(1A)–Ta(1)–C(2A)	99.6(6)
Cl(1)–Ta(1)–C(4A)	144.1(5)	C(1)–Ta(1)–C(4A)	104.1(5)
C(2)–Ta(1)–C(4A)	56.4(5)	C(3)–Ta(1)–C(4A)	56.7(5)
C(4)–Ta(1)–C(4A)	34.0(7)	Cl(1A)–Ta(1)–C(4A)	114.7(4)
C(1A)–Ta(1)–C(4A)	83.5(5)	C(2A)–Ta(1)–C(4A)	34.2(5)
Ta(1)–C(2)–C(3)	71.0(11)	Ta(1)–C(2)–C(4)	73.2(10)
C(3)–C(2)–C(4)	108.2(14)	Ta(1)–C(2)–C(6)	122.5(12)
C(3)–C(2)–C(6)	127.5(16)	C(4)–C(2)–C(6)	124.3(16)
Ta(1)–C(3)–C(2)	75.3(12)	Ta(1)–C(3)–C(5)	119.9(15)
C(2)–C(3)–C(5)	125.3(9)	Ta(1)–C(3)–C(2A)	75.3(12)
C(2)–C(3)–C(2A)	109.1(18)	C(5)–C(3)–C(2A)	125.3(9)
Ta(1)–C(4)–C(2)	72.6(8)	Ta(1)–C(4)–C(7)	126.4(14)
C(2)–C(4)–C(7)	130.3(15)	Ta(1)–C(4)–C(4A)	73.0(4)
C(2)–C(4)–C(4A)	107.1(9)	C(7)–C(4)–C(4A)	122.0(10)

TaCpCl$_2$(butadiene) [13]. The Ta–C(C$_5$Me$_5$) distances lie in the range 2.35–2.41 Å, which is slightly shorter than the range of values found in Ta(C$_5$Me$_5$) (CHPh)(CH$_2$Ph)$_2$ (2.40–2.48 Å) [8e] and Ta(C$_5$Me$_5$)(PhCCPh)Cl$_2$ (2.40–2.44 Å) [14]. The C–C distances and angles in the pentamethylcyclopentadienyl ring do not deviate significantly from the expected values.

Experimental

All preparations were carried out under an atmosphere of dry O$_2$-free argon, using Schlenk techniques or in a Vacuum Atmosphers glovebox equipped a HE-63-P Dri-Train. Solvents were reagent grade, distilled from the appropriate drying agents under argon and degassed prior to use. The [TaCpCl$_4$] starting materials were prepared by using reported methods (Cp = η^5-C$_5$Me$_5$ [8c,15], η^5-C$_5$H$_4$SiMe$_3$ [16]) and for Cp = η^5-C$_5$H$_3$(SiMe$_3$)$_2$ the procedure is reported here [17*]. Al$_2$Me$_6$ was purchased from Ethyl Corporation and 4% in *n*-hexane or toluene solutions prepared immediately before use. PPh$_4$Cl was used without purification and obtained from Fluka.

The IR spectra were recorded over the range 4000–200 cm^{-1} on a Perkin–Elmer 883 spectrophotometer using Nujol mulls. The NMR spectra were run on Varian

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* Reference numbers with asterisk indicate a note in the list of references.

FT 80A spectrometer. The C and H analyses were made with a Perkin–Elmer 240B microanalyzer.

Preparation of $[Ta(\eta^5-C_5Me_5)Cl_{4-x}Me_x]$, (x = 1 (2a), 2 (3a))

2a. A 4% solution of Al_2Me_6 in toluene (4.39 ml, 1.10 mmol) was injected dropwise into a stirred suspension of **1a** (2.01 g, 4.39 mmol) in toluene (50 ml). The resultant orange suspension was allowed to warm to ambient temperature, PPh_4Cl (1.67 g, 4.39 mmol) was added and stirred for 12 h. The suspension was then filtered and concentrated to *ca.* 25 ml. *n*-Hexane (20 ml) was added and the mixture cooled to $-40°C$ overnight to give an orange **2a–3a** mixture solid in 9/1 ratio. The monomethyl complex **2a** was isolated as the pure sample, by washing the mixture with n-hexane (3 × 15 ml).

Yield 60% (1.15 g); IR (Nujol mull) 1159m, 1096w, 1023m, 798m, 725m, 671w, 610w, 504m, 467m, 387m, 332m and 295m cm^{-1}. ^{1}H NMR (benzene-d_6) δ: 1.96 (s, 15H, $C_5(CH_3)_5$); 1.45 (s, 3H, CH_3) ppm. Anal. Found C, 30.40; H, 4.28. $C_{11}H_{18}Cl_3Ta$ calc.: C, 30.19; H, 4.15%.

3a. Into a suspension of **1a** (1.50 g, 3.27 mmol) in toluene (50 ml) at $-40°C$, 6.55 ml of Al_2Me_6 solution in toluene (3.27 mmol) was slowly injected. The mixture was allowed to warm to ambient temperature, PPh_4Cl (1.24 g, 3.27 mmol) added and stirred for 12 h. The reddish suspension obtained was filtered, concentrated to *ca.* 10 ml, and *n*-hexane (15 ml) added and the mixture cooled to $-40°C$ overnight to give yellow-green crystals of **3a**.

Yield 80% (1.09 g); IR (Nujol mull) 1197w, 1069w, 1025m, 961w, 795m, 724m, 680w, 504m, 467m, 381, 332m and 295m cm^{-1}. ^{1}H NMR (benzene-d_6) δ: 1.80 (s, 15H, $C_5(CH_3)_5$); 1.08 (s, 6H, 2CH_3) ppm. Anal. Found, C, 34.21; H, 5.28. $C_{12}H_{21}Cl_2Ta$ calc.: C, 34.54; H, 5.08%.

Preparation of $[TaCpCl_3Me]$ $(Cp = \eta^5-C_5H_4(SiMe_3)$ (2b), $\eta^5-C_5H_3(SiMe_3)_2$ (2c))

A solution of 4% Al_2Me_6 (0.24 ml, 2.50 mmol) in *n*-hexane was slowly added to a stirred suspension of $[TaCpCl_4]$ (2.50 mmol) in toluene (60 ml) at $-60°C$. The resultant suspension was allowed to warm to ambient temperature and stirred for *ca.* 8 h at that temperature and then PPh_4Cl (0.95 g, 2.50 mmol) was added. The red-brown suspension obtained was filtered, concentrated to *ca.* 15 ml, *n*-hexane (20 ml) added, and the mixture cooled to $-40°C$ overnight to give brown-yellow solids of **2b–2c**.

2b: Yield 70% (0.77 g); IR (Nujol mull) 1463s, 1377s, 1250s, 850m, 725m, 525w, 445w and 370s cm^{-1}.

^{1}H NMR (benzene-d_6) δ: 6.10 (m, 2H); 5.80 (m, 2H), ($C_5H_4SiMe_3$); 1.65 (s, 3H, CH_3); 0.12 (s, 9H, $SiMe_3$) ppm.

Anal. Found; C, 24.41; H, 3.58 $C_9H_{16}Cl_3SiTa$ calc.: C, 24.58; H, 3.67%.

2c: Yield 80% (1.00 g); IR (Nujol mull) 1441s, 1375s, 1253s, 837s, 800m, 710w, 635w, 414w, 372m and 275m cm^{-1}.

^{1}H NMR (benzene-d_6) δ: 5.8 (m, 3H, $C_5H_3(SiMe_3)_2$); 1.10 (s, 3H, CH_3); 0.18 (s, 18H, $SiMe_3$) ppm.

Anal. Found: C, 28.10; H, 4.58. $C_{12}H_{24}Cl_3Si_2Ta$ calc.: C, 28.16; H, 4.73%.

X-Ray structural analysis of $[Ta(\eta^5-C_5Me_5)Cl_2Me_2]$ (3a)

Crystal data: $C_{12}H_{21}Cl_2Ta$, mol. wt. 417.1, monoclinic, *a* 6.770(3), *b* 13.969(3), *c* 8.395(2) Å, β 112.25(3)°, *V* 734.8(4) Å^3, D_c 1.885 g cm^{-3}, *F*(000) 400, *Z* = 2.

Space group $P2_1/m$. Graphite monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 77.33 cm^{-1}. Intensity data was recorded on a yellow block-shaped crystal with dimensions $0.35 \times 0.40 \times 0.50$ mm.

Data were collected on a Siemens R3mV diffractometer using graphite-mono-chromated Mo-K_α radiation. Accurate cell parameters were determined from the angular measurement of 25 reflections in the range $20 < 2\theta < 25°$. 1526 Reflections were collected in the range $5.0 < 2\theta < 50.0°$ ($+h$, $-k$, $\pm l$) using a 96-step $\omega/2\theta$ scan a scan speed in the range $3.0–19.53°$ min^{-1}, with a total scan range of $1.4°$ plus the K_α separation. Three standard reflections showed no significant variation in intensity. A semi-empirical absorption correction was applied based on an ellipsoid model (max., min. transmission factors 0.283, 0.163). A total of 1526 reflections were measured, of these 1351 were unique and 1197 were observed with $F > 4\sigma(F)$.

The Ta atom position was derived from a Patterson synthesis and the remaining non-hydrogen atoms were located by subsequent Fourier difference techniques. The structure was refined by full-matrix least-squares with the Ta, the Cl, the methyl carbon and cyclopentadienyl carbon atoms (except C(3)) assigned anisotropic thermal parameters. The unique chlorine atom and the unique methyl carbon displayed severe positional disorder with Ta–atom distances intermediate between the values expected for Ta–Cl and Ta–C; the site denoted Cl(1) was refined with the scattering factor for Cl and occupancy fixed at 0.5, and the site denoted C(1) was refined with the scattering factor for C and an occupancy fixed at 1.5. Methyl-H atoms were placed in idealised positions and allowed to ride on the relevant C atom (C–H 0.96 Å; C–C–H 109.5°). All the hydrogen atoms were assigned a common isotropic thermal parameter. The weighting scheme $w^{-1} = \sigma^2(F) + 0.003\,F^2$ was introduced and refinement continued until the average Δ/σ shift was reduced to 0.013. The final residuals were $R = 0.059$, $wR = 0.095$. A final electron-density difference map showed ripples in the region of the Ta atom and of the disordered chlorine and methyl ligands. Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3. All calculations were performed on a MicroVAX II computer using the SHELXTL-PLUS package [18]. Tables of hydrogen atom positions, anisotropic thermal parameters, and structure factors are available from the authors.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for **3a**

Atom	x	y	z	U_{eq}[a]
Ta(1)	877(1)	2500	2147(1)	50(1)
Cl(1)	3062(14)	3642(9)	4161(14)	94(4)
C(1)	1610(21)	3531(11)	206(22)	96(7)
C(2)	−2165(25)	3302(12)	2324(20)	62(6)
C(3)	−1735(28)	2500	3349(21)	36(4)
C(4)	−2746(21)	3004(11)	600(19)	53(5)
C(5)	−1088(44)	2500	5246(35)	141(23)
C(6)	−2091(32)	4350(13)	2892(33)	86(10)
C(7)	−3552(37)	3571(16)	−1030(24)	85(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Acknowledgements

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17 [Ta(η^5-C$_5$H$_3$(SiMe$_3$)$_2$)Cl$_4$] was prepared as described [13] from TaCl$_5$ (5.6 g, 15.6 mmol) and the appropriate reagent Sn[C$_5$H$_3$(SiMe$_3$)$_2$]^{n}Bu$_3$ or C$_5$H$_3$(SiMe$_3$)$_3$ (15.6 mmol) in toluene. Yield 90% (9.34 g); IR (Nujol mull): 3090m, 3064m, 1410m, 1255s, 1251s, 1088m, 911m, 841s,br, 785s, 695w, 635m, 450w, 350m, and 310s,br cm^{-1}. ^{1}H NMR (chloroform-d_1) δ: 6.80–7.10 (m, 3H, C$_5$H$_3$(SiMe$_3$)$_2$); 0.38 (s, 18H, (SiMe$_3$)$_2$) ppm. ^{13}C NMR (chloroform-d_1) δ: 141.94 (s, C^{1,3}); 128.52 (s, C^2); 131.22 (s, C^{4,5}); −0.45 (s, SiMe$_3$) ppm. Anal. Found: C, 24.54; H, 3.85. C$_{11}$H$_{21}$Cl$_4$Si$_2$Ta calc.: C, 24.82; H, 3.98%.

18 SHELXTL-PLUS, Release 4.0, Siemens Analytical X-ray Instruments, Inc., Siemens Part No. 269-004200, 1990.