Journal of Organometallic Chemistry, 241 (1983) C21—C23
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS AND CRYSTAL STRUCTURE OF THE COMPOUND $\{[Ta(\eta\text{-}C_5Me_5)Cl_2]_2(\mu\text{-}Cl)_3\}^+_2$ $\{[TaCl_5(\mu\text{-}O)TaCl_3]_2(\mu\text{-}Cl)_2\}^{2-}$

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(Received October 6th, 1982)

Summary

The compound $\{[Ta(\eta\text{-}C_5Me_5)Cl_2]_2(\mu\text{-}Cl)_3\}^+_2$ $\{[TaCl_5(\mu\text{-}O)TaCl_3]_2\text{-}(\mu\text{-}Cl)_2\}^{2-}$ is formed as a by-product of the reaction of $[Sn(Bu^n)_3(C_5Me_5)]$ with tantalum pentachloride. Characterisation by X-ray diffraction shows the cation to consist of two pentamethylcyclopentadienyltantalum dichloride units bridged by three chlorine atoms. The anion has a central $(TaOCl_3)_2(\mu\text{-}Cl_2)$ unit linked through the oxygens to two $TaCl_5$ units. The Ta—O—Ta bridges are linear and unsymmetrical.

In the course of a systematic investigation of pentamethylcyclopentadienyltantalum chemistry, we have synthesised a tantalum compound containing a binuclear organometallic cation and a tetrameric tantalum oxochloride anion.

Refluxing $TaCl_5$ with $[Sn(Bu^n)_3(C_5Me_5)]$ in dichloromethane gives $Ta(\eta\text{-}C_5Me_5)Cl_4$ as the main product [1]; on recrystallization of the reaction product from dichloromethane a small amount of deep red crystals was also found. These were characterised by X-ray crystallography and shown to have the structure given in Fig. 1.

Crystal data: $C_{40}Cl_{32}H_{60}Ta_8$, M = 3156, monoclinic, space group $P2_1/c$, $Z = 2$, a 16.839(3), b 15.225(4), c 17.065(7) Å, β 111.18(3)°, U 4079.4 Å^3, ρ_c 2.57 g cm^{-3}, μ (Mo-K_α) 12.33 mm^{-1}. The structure was solved by Patterson and Fourier techniques and refined by least-squares using 2087 independent observed ($I \geq 3\sigma(I)$) reflections. The C and O atoms were isotropically refined. The remaining non-H atoms were allowed anisotropic thermal parameters. An absorption and an extinction correction were applied. The final R values were R = 0.050, R_w = 0.065. Figure 1 shows the structure of the

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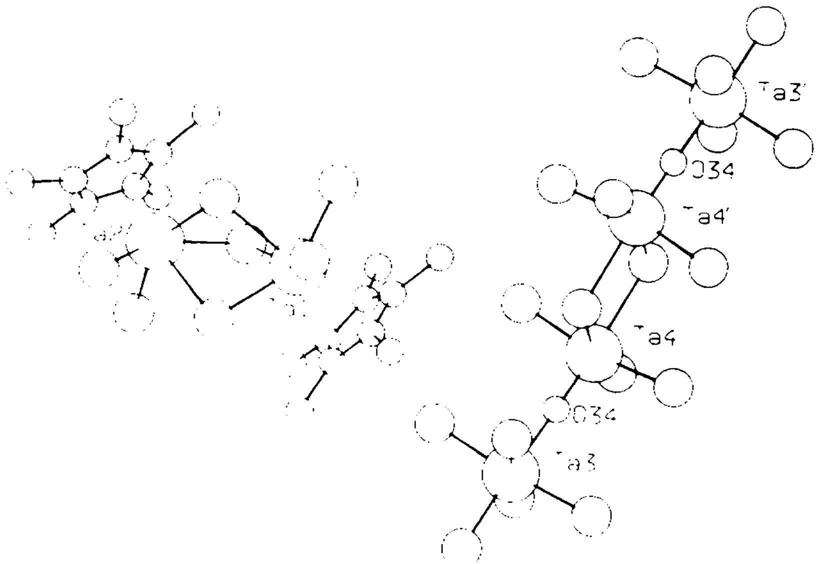

Fig. 1. The structures of the cation $\{[Ta(\eta\text{-}C_5Me_5)Cl_2]_2(\mu\text{-}Cl)_3\}^+$ and the anion $\{[TaCl_5(\mu\text{-}O)TaCl_3]_2\text{-}(\mu\text{-}Cl)_2\}^{2-}$, as they occur in the crystal. Labels for the C and Cl atoms are omitted for clarity.

dimeric monocation and the tetrameric dianion in their relative disposition in the crystal.

The cation has two terminal chlorines on each Ta atom at an average Ta—Cl distance of 2.325(9) Å. Three bridging chlorines and one pentamethylcyclopentadienyl ring complete the coordination sphere of each metal atom. One of the bridging chlorines is symmetrically placed at 2.558(8) Å from each tantalum, while each of the other two is nearer to one metal atom (average short distance 2.468(8) Å) than to the other metal atom (average long distance 2.682(8) Å). The Ta(1)—Ta(2) distance is 3.708(2) Å.

The crystallographically independent part of the anion consists of a $TaCl_5$ unit bonded through an oxo,bridge to a $TaCl_4$ unit. The tetramer as a whole is arranged around the (0,0,½) and (0,½,0) inversion centres, with a μ-dichloro bridge and a Ta(4)—Ta(4)′ distance of 4.048(3) Å. The oxygen bridge is essentially linear (Ta(3)—O(34)—Ta(4) 178.4(15)°) and unsymmetrical [2], the value of the Ta(4)=O(34) distance (1.76(2) Å) indicating a double bond interaction and suggesting that the negative charge is mainly concentrated on the central tantalum unit. The other Ta—O (dative) bond has a metal—oxygen separation of 2.03(2) Å.

The chlorine atoms *trans* to the pentamethylcyclopentadienyl rings in the cation, and the ones *trans* to the Ta(4)=O(34) and Ta(4′)=O(34′) double bonds in the anion show the longest metal—chlorine bond distances (2.690(8), 2.674(10), 2.672(9) and 2.672(9) Å for Ta(1), Ta(2), Ta(4) and Ta(4′), respectively), as a consequence of the *trans* influence of the carbon rings and the oxo groups. Accordingly the chlorines *trans* to the Ta(3)—O(34) and Ta(3′)—O(34′) dative bonds are expected to have relatively strong interaction with the metal atoms, and in fact their respective separation from Ta(3) and Ta(3′) are the shortest of all Ta—Cl distances in this compound, 2.30(1) Å.

Both in the cation and in the anion the geometry round each tantalum(V) atom is that of a distorted octahedron (if the carbon rings are considered as point ligands); the distortion is greater in the case of the cation as expected from the greater bridge multiplicity.

The source of the oxygen necessary for the formation of the anion has not been ascertained but several possibilities suggest themselves: tantalum oxyhalide impurities in the tantalum pentachloride, water held on the walls of the Schlenk tube reaction vessel, or inadvertent admission of dioxygen.

The detailed structures of the halides $Ta(\eta\text{-}C_5H_5)X_4$ and $Ta(\eta\text{-}C_5Me_5)X_4$ are unknown, but they appear not to be monomeric [3]. In the light of the structure of the cations described above, a similar cationic formulation with halide as the counter ion should be considered as a possibility, e.g. $\{[Ta(\eta\text{-}C_5Me_5)Cl_2]_2(\mu\text{-}Cl)_3\}^+ Cl^-$. Similar structural features may be present in the other cyclopentadienyl metal tetrahalides $M(\eta\text{-}C_5R_5)X_4$ with M = Nb or Mo, R = H or Me and X = halogen.

Acknowledgements. We thank the S.E.R.C. for financial support (J.C.G. and C.P.O.) and the Ministerio de Educacion y Ciencia of Spain for the award of a research grant (J.M.M.).

References

1 S.J. MacLain, C.D. Wood and R.R. Schrock, J. Am. Chem. Soc., 101 (1979) 4558.
2 C.K. Prout and J.-C. Daran, Acta Cryst. B, 35 (1979) 2882.
3 M.J. Bunker, A. De Cian, M.L.H. Green, J.J.E. Moreau and N. Singanporia, J. Chem. Soc. Dalton, (1980) 2155.