

## SYNTHESIS OF TRIMETHYLBIS(TRIMETHYLSILYLMETHYL)-TANTALUM(V)

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### Summary

The synthesis of  $\text{Me}_3\text{Ta}(\text{CH}_2\text{SiMe}_3)_2$  in 87% yield from  $\text{Me}_3\text{TaCl}_2$  provides another example of a reaction of alkyltantalum halides in which the  $\sigma$ -methyl-metal bond is preserved.  $\text{Me}_3\text{Ta}(\text{CH}_2\text{PPh}_2)_2$  was also obtained, but could not be freed from traces of tetramethylethylene diamine. Similar reactions with phenyllithium or phenylmagnesium bromide, *t*-butyllithium and tetramethylenedilithium led to decomposition products.

### Introduction

We have been interested in establishing the extent to which  $\sigma$ -alkylated niobium(V) and tantalum(V) halides can undergo chemical transformations without breaking of the metal-carbon  $\sigma$  bonds [1,2]. We have now examined the reaction of dichlorotrimethyltantalum with several alkylating agents, with the aim of obtaining mixed alkylated tantalum(V) derivatives. The synthesis of trimethylbis(trimethylsilylmethyl)tantalum represents the most significant result of this study.

Earlier examples of reactions leading to complete replacement of the chlorine atoms of dichlorotrimethyltantalum without loss of the  $\sigma$ -metal-carbon bonds, are provided by the formation of: 1) anionic chelates (e.g.  $\text{Me}_3\text{Ta}(\text{acac})_2$ ) with an accompanying increase in the coordination number and thermal stability [2]; 2) aryl and cyclopentadienyl derivatives (e.g.  $(\eta^5\text{-C}_5\text{H}_5)(\text{C}_6\text{H}_5)\text{TaMe}_3$ ) [3]; 3) carbenoid complexes (e.g.  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaMe}(\text{CH}_2)$ ) involving bulky alkyl and cyclopentadienyl groups [4].

The title compound was obtained by treating  $\text{Me}_3\text{TaCl}_2$  in light petroleum at

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0°C with one equivalent of bis(trimethylsilylmethyl)magnesium,  $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ . This synthesis further illustrates the value of dialkylmagnesium derivatives as mild alkylating agents [5].

Trimethylbis(trimethylsilylmethyl)tantalum(V) is a yellow oily compound which could not be distilled ( $10^{-3}$  mmHg) at temperatures below its decomposition point (25°C). On hydrolysis it gives three molecules of methane per tantalum. The NMR spectrum ( $\text{CH}_2\text{Cl}_2$ , internal T.M.S., -40°C) shows three singlets:  $\delta(\text{Me}(\text{Ta}))$ : 2.00;  $\delta(\text{CH}_2)$ : 1.85 and  $\delta(\text{Me}(\text{Si}))$ : 0.25 ppm. The main peaks observed in the mass spectrum (direct introduction [6],  $10^{-7}$  mmHg, 40 eV, 25°C) are (tentative assignments and abundance): 406, 403 ( $M^+$ ,  $\text{C}_{11}\text{H}_{31}\text{Si}_2\text{Ta}^+$  (10%)); 385, 386 ( $[M - \text{CH}_3]$   $\text{C}_{10}\text{H}_{28}\text{Si}_2\text{Ta}^+$  (3%)); 372, 373 ( $[M - \text{C}_2\text{H}_4]$   $\text{C}_9\text{H}_{29}\text{Si}_2\text{Ta}^+$  (10%)); 370, 371 ( $[M - 2 \text{CH}_3]$   $\text{C}_9\text{H}_{25}\text{Si}_2\text{Ta}^+$  (6%)); 355, 356  $\text{C}_8\text{H}_{22}\text{Si}_2\text{Ta}^+$  (6%); 346, 347 ( $[M - \text{C}_4\text{H}_6]$   $\text{C}_7\text{H}_{25}\text{Si}_2\text{Ta}^+$  (50%)); 310, 311 ( $[M - \text{C}_{14}\text{H}_{12}\text{Si}]$   $\text{C}_7\text{H}_{19}\text{SiTa}^+$  (6%)); 268, 269 ( $[M - 3 \text{CH}_3 - \text{CH}_2\text{SiMe}_3]$   $\text{C}_4\text{H}_{11}\text{SiTa}^+$  (12%)); 175 ( $\text{C}_8\text{H}_{22}\text{Si}_2$  (6%)); 74 ( $\text{C}_3\text{H}_{10}\text{Si}^+$  (100%)).

When  $\text{Me}_3\text{TaCl}_2$  was allowed to react with  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{Li} \cdot (\text{Me}_2\text{N})_2(\text{CH}_2)_2(\text{NMe})_2$  [7] a compound was isolated whose NMR spectrum ( $\delta(\text{Me})$  2.50(s);  $\delta(\text{C}_6\text{H}_5)$  7.1 and  $\delta(\text{CH}_2)$  1.77(d) ppm;  $^2J(\text{PH})$  9 Hz) was that expected for  $\text{Me}_3\text{Ta}[\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ , but which could not be freed from traces of tetramethylethylenediamine. Similar reactions with  $\text{C}_6\text{H}_5\text{Li}$  or  $\text{C}_6\text{H}_5\text{MgBr}$ ,  $t\text{-C}_4\text{H}_9\text{Li}$  and  $\text{Li}(\text{CH}_2)_4\text{Li}$  led only to decomposition when the reaction mixtures were allowed to warm above -50°C.

## Experimental

All reactions and manipulations were carried out under oxygen free, dry argon using Schlenk tube techniques. All solvents were dried and degassed before use. Dichlorotrimethyltantalum was prepared from  $\text{TaCl}_5$  and  $\text{ZnMe}_2$  [8] and bis(trimethylsilylmethyl)magnesium by the published methods [9].

A solution of 0.61 g (2 mmol) of  $\text{Me}_3\text{TaCl}_2$  in 50 ml of light petroleum ether was cooled to -35°C and 4 ml of a 0.6 molar solution of  $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$  in diethyl ether were added. The mixture was kept for 12 h at 0°C. A white precipitate of  $\text{MgCl}_2$  appeared and the solution became yellow. The solution was filtered and the solvents evaporated at -20°C yielding 0.7 g (87%) of an oily yellow compound, highly soluble in pentane, and decomposing at about 25°C.

## References

- 1 C. Santini-Scampucci and J.G. Riess, *J. Chem. Soc. Dalton*, (1973) 2436; (1974) 1433.
- 2 C. Santini-Scampucci and G. Wilkinson, *J. Chem. Soc. Dalton*, (1976) 807.
- 3 S.J. McLain, R.R. Schrock, P.R. Sharp, M.R. Churchill and W.J. Youngs, *J. Amer. Chem. Soc.*, 101 (1979) 263.
- 4 R.R. Schrock, *Accounts Chem. Res.*, 12 (1979) 98.
- 5 C. Santini-Scampucci and J.G. Riess, *J. Chem. Soc. Dalton*, (1976) 195.
- 6 R.C. Copperthwaite and P. Cook, *Chem. Ind.*, 18 (1973) 906.
- 7 L.E. Manzer, *Inorg. Chem.*, 15 (1976) 2567.
- 8 J.L. Juvinal, *J. Amer. Chem. Soc.*, 86 (1964) 4202.
- 9 J. Thomas, *Bull. Soc. Chim. France*, (1973) 1296; R.A. Andersen and G. Wilkinson, *J. Chem. Soc. Dalton* (1977) 809.