

Some dimethyl{ tris(trimethylsilyl)methyl} silanolato derivatives of tantalum(V), chromium(III) and manganese(II) *

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Abstract

The reaction between tantalum(V) chloride and one equivalent of $\text{Me}_2\{(\text{Me}_3\text{Si})_3\text{C}\}\text{SiOLi}$ ((trisilox)Li) gave [(trisilox)TaCl₄] (**2**). With two equivalents of (trisilox)Li, the major product was the trisubstituted species [(trisilox)₃TaCl₂] (**3**); **3** was the only complex formed in the reactions employing three or five equivalents of (trisilox)Li. The compounds [(trisilox)₃Cr] (**4**) or [(trisilox)₂Mn · LiCl] (**5**) were obtained by treatment of chromium(III) chloride or manganese(II) chloride with two equivalents of (trisilox)Li, respectively. Preliminary crystallographic results for **4** show a trigonal-planar arrangement of the ligands about the chromium atom.

Introduction

Transition metal compounds having bulky alkoxy, aryloxy or siloxy groups attached display unusual chemical reactivity in a number of cases, for example $[\text{M}(\text{OC}_6\text{H}_3\text{-2,6-R}_2)_2(\text{CH}_2\text{R}')_3]$ (M = Nb, or Ta; R = CHMe₂ or CMe₃; R' = H, Ph, or SiMe₃) [**1**], $[\text{Ta}\{\text{OSi}(\text{CMe}_3)_3\}_3]$ [**2**], or $[(\text{Me}_3\text{CO})_3\text{W}\equiv\text{W}(\text{OCMe}_3)_3]$ [**3**]. We recently reported on the structure of bis- μ -[dimethyl{ tris(trimethylsilyl)methyl} silanolato]bis(tetrahydrofuran)dilithium ($[\{\text{Me}_2\{(\text{Me}_3\text{Si})_3\text{C}\}\text{SiOLi}(\text{C}_4\text{H}_8)\}]_2$) \equiv $[\{(\text{trisilox})\text{-Li}(\text{thf})\}_2]$ (**1**) [**4**] and now the reactions between (trisilox)Li and some transition metal chlorides are described.

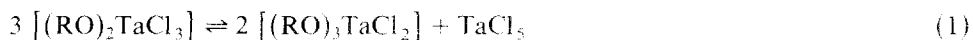
Results and discussion

The amber solid [(Trisilox)TaCl₄] (**2**) was isolated quantitatively from the reaction of tantalum(V) chloride with one equivalent of (trisilox)Li in toluene. The ¹H

* Dedicated to Professor C. Eaborn on the occasion of his 65th birthday (March 15th, 1988). Dr. A.C. Sullivan had the honour and pleasure of doing postdoctoral research with Professor Eaborn 1982–1985.

NMR spectrum of the freshly prepared compound showed two sets of resonances, in intensity ratio 2/1, for the trisilox group. This may suggest the presence of two out of the four possible stereoisomers of **2** based on trigonal bipyramidal and square pyramidal geometries, indicating unusually slow interconversion. When left at room temperature, in solution or in the solid state, the mixture slowly converted to a single isomer (the original major isomer, represented by the higher field set of resonances in the ^1H NMR spectrum). The observation of isomers was not reported for related $[(\text{Cp})\text{TaCl}_4]$ [5], $[\text{MeTaCl}_4]$ [6] or $[(\text{PhO})\text{TaCl}_4]$ [7]. The molecular weight of **2**, as determined by freezing point depression in benzene, was 665 cf. 629 for monomeric **2**. However, when the concentration of the solution was increased by a factor of four, the value 946 (in between the value for the monomer and dimer) was obtained.

Treatment of tantalum(V) chloride with two equivalents of (trisilox)Li gave a white solid, which was shown by ^1H NMR spectroscopy to consist mainly of the trisubstituted compound, $[(\text{trisilox})_3\text{TaCl}_2]$ (**3**), and a small amount of another complex (probably the disubstituted species). Formation of the trisubstituted compound suggests a reorganization reaction (eq. 1) involving intermediates with $\mu\text{-OR}$ groups, as found in **1**. No similar tendency was observed for the monosub-



stituted species. The pure compound **3**, obtained from the treatment of tantalum(V) chloride with three equivalents of (trisilox)Li, displayed a single set of resonances for the trisilox group in its ^1H NMR spectrum. If the large trisilox group prevent fluxionality and trigonal bipyramidal structure is adopted by **3**, then an equatorial arrangement of trisilox group is consistent with the ^1H NMR spectrum. The molecular weight of **3**, measured in freezing benzene solution, was 1115 (cf. 1169, calculated for the monomer). The mass spectrum of **3** showed $[M - \text{CH}_3]^+$, as well as fragments representing loss of chloride or trisilox from the monomer. When **3** was treated with two equivalents of MeLi in Et_2O , a mixture was obtained from which no single species could be isolated. A mixture of products was also obtained when $[\text{Ta}(\text{OC}_6\text{H}_3\text{Me}_{2,6})_3\text{Cl}_2]$ was treated with two equivalents of MeLi [8]. Surprisingly, there was no reaction between **3** and benzylmagnesium chloride, even when the latter was present in a large excess and the reaction was held at 60°C for 2 days; other reactions are currently being investigated. An attempt to introduce more than three trisilox groups to tantalum by treatment of tantalum(V) chloride with five equivalents of (trisilox)Li, under conditions similar to those used for the 1/3 reaction, resulted in the isolation of **3** only. Compounds **2** and **3** are thermally very stable, but are readily hydrolyzed in air.

Treatment of chromium(III) chloride with two equivalents of (trisilox)Li gave a pentane soluble pale blue solid. Concentrated thf solutions of this solid deposited long turquoise, extremely air-sensitive, needles of $[(\text{trisilox})_3\text{Cr}]$ (**4**) at room temperature. The isolation of the trisubstituted species **4** probably resulted from reorganization of the expected $[(\text{trisilox})_2\text{CrCl}]$ and, indeed, the initial pale blue solid gave positive chloride tests. Preliminary X-ray crystallographic results confirm a monomeric trigonal planar structure for **4**; the full structure, including modelling of the disordered peripheral silicon and methyl groups, will be reported elsewhere. The magnetic moment, measured by the Evans' method in benzene, was 3.6 BM, slightly less than that expected for three unpaired electrons. The EPR spectrum recorded for

a frozen thf solution of **4** had a sharp signal at $g \sim 3.9$, and a broad signal at $g \sim 1.98$. Similar spectra have been reported for $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_3]$ [9], $[\text{Cr}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ [10] and $[\text{Cr}\{\text{OCH}(\text{CMe}_3)_2\}_4\text{Li} \cdot \text{thf}]$ [11]. Compound **4** appears to be the first example of a trigonal planar chromium(III) alkoxide or siloxide, and the formation and chemistry of this interesting compound are being currently studied.

From the reaction of (trisilox)Li and MnCl_2 (2/1 mol ratio), the pale beige air-sensitive compound $[(\text{trisilox})_2\text{Mn} \cdot \text{LiCl}]$ (**5**) was isolated in reasonable (56%) yield. The compound was too insoluble for molecular weight determination, but the highest peak in the mass spectrum corresponded to $[(\text{trisilox})_2\text{Mn}]^+$. The magnetic moment as determined by Evans' method was 5.9 BM consistent with a high-spin d^5 system. Attempts to establish the crystal structure of **5** were hampered by poor data, probably due to disorder in the trisilox groups.

Experimental

Reactions were carried out in an atmosphere of purified dinitrogen using standard Schlenk techniques. Solvents were distilled from sodium benzophenone and stored under dinitrogen over molecular sieves. TrisiloxLi was prepared as previously described [4] for use in thf; (Trisilox)Li was prepared by addition of one equivalent of MeLi or *n*-BuLi to pentane or toluene solutions of trisiloxH. Spectrometer: NMR: Bruker WP-80 and WM-250 (in CDCl_3 or C_6D_6 ; data in ppm, relative to trichloromethane (δ 7.26 ppm) or benzene (δ 7.19 ppm)). Mass: Kratos MS-902, EI, recorded at 70 eV. EPR: Bruker 200D (X-Band).

Melting points were recorded in capillaries sealed under dinitrogen, and are uncorrected. Microanalyses were obtained from University College, London.

*Preparation of $[(\text{trisilox})\text{TaCl}_4]$ (**2**)*

To a slurry of tantalum(V) chloride (0.75 g, 2.09 mmol) in toluene (10 cm^3) at -78°C , (trisilox)Li (2.09 mmol) in toluene (20 cm^3) was added dropwise. The reaction mixture was stirred for 1 h at -78°C , and then for 24 h at room temperature. The amber toluene solution was filtered, and the filtrate evaporated to yield analytically pure **2** (1.25 g, 95%), (Found: C, 23.43; H, 5.56; Cl, 22.42. $\text{C}_{12}\text{H}_{33}\text{Cl}_4\text{OSi}_4\text{Ta}$ calcd.: C, 22.9; H, 5.3; Cl, 22.6%). Molecular weight in freezing benzene (0.028 g of **2** in 4 cm^3) was 665 (calcd.: 629) but for 0.224 g of **1** in 4 cm^3 was 946. M.p. 220–225 $^\circ\text{C}$. NMR: $\delta(\text{H})$ (CDCl_3) two isomers are indicated in a 2/1 ratio. For the major isomer: δ 0.34 (s, 27H, Me_3Si), 0.73 ppm (s, 6H, Me_2Si). For the minor isomer: δ 0.39 (s, 27H, Me_3Si), 0.82 ppm (s, 6H, Me_2Si).

After the solid had been standing at room temperature for several months, only the major isomer was observed in the ^1H NMR spectrum.

Treatment of tantalum(V) chloride with two equivalents of (trisilox)Li

A mixture of (trisilox)Li (2.03 g, 6.5 mmol) and tantalum(V) chloride (1.16 g, 3.25 mmol) was dissolved in toluene (30 cm^3) at -78°C . The reaction mixture was stirred for several hours at low temperature, and then at room temperature for 24 h. The solvent was removed by evaporation and pentane (60 cm^3) added. The pentane-soluble material was removed by filtration and the insoluble residue (the bulk of the product) was extracted with hot heptane (50 cm^3). The pentane and

heptane extracts were evaporated to dryness to give white solids. The heptane extract was shown by ^1H NMR spectroscopy to be identical to $[(\text{trisilox})_3\text{TaCl}_2]$ (**3**). NMR $\delta(\text{H})$ (CDCl_3) pentane extract: peaks due to **3**, and also δ 0.34 (s, Me_3Si , 27H), 0.67 ppm (s, Me_2Si , 6H).

*Preparation of $[(\text{trisilox})_3\text{TaCl}_2]$ (**3**)*

3 was prepared in a manner similar to that for **2**; except using (trisilox)Li (2.5 g, 7.99 mmol) and tantalum(V) chloride (0.95 g, 2.66 mmol) in toluene (80 cm^3). The toluene was removed by evaporation, and the residue was extracted with pentane ($3 \times 50 \text{ cm}^3$). Evaporation of the pentane from the extracts gave the product **3** as a white solid (2.21 g, 71%), m.p. $> 320^\circ\text{C}$ (Found: C, 36.37; H, 8.59; Cl, 6.53. $\text{C}_{36}\text{H}_{99}\text{Cl}_2\text{O}_3\text{Si}_{12}\text{Ta}$ calcd.: C, 36.98; H, 8.55; Cl, 6.5%). NMR: $\delta(\text{H})$ (CDCl_3): 0.32 (s, 27H, Me_3Si), 0.64 ppm (s, 6H, Me_2Si); $\delta(\text{H})$ (C_6D_6): 0.43 (s, 27H, Me_3Si), 0.86 ppm (s, 6H, Me_2Si). The molecular weight in benzene was 1115 (calcd. 1169). The mass spectrum had peaks at m/z 1151 (9) ($[\text{M} - \text{CH}_3]^+$), 1096 (12.5) ($[(\text{trisilox})_3\text{Ta}]^+$); 826 (9) ($[(\text{trisilox})_2\text{TaCl}]^+$); 556 (73) ($[(\text{trisilox})\text{TaCl}_2]^+$).

*Preparation of $[(\text{trisilox})_3\text{Cr}]$ (**4**)*

To a slurry of chromium(III) chloride (0.4 g, 2.53 mmol) in thf (10 cm^3) was added a solution of (trisilox)Li (5.05 mmol) in thf (20 cm^3) at -78°C . The mixture was stirred for 1 h at low temperature, and at room temperature 24 h. The solvent was removed by evaporation from the royal-blue solution, and the green solid residue was extracted with pentane (80 cm^3). The pentane extracts were evaporated to dryness to give a pale blue solid. Crystallization from concentrated thf solutions afforded long turquoise needles of **4** (0.5 g, 20% based on CrCl_3 used); m.p. 215°C (dec.). $259\text{--}265^\circ\text{C}$ completely melts. μ_{eff} 3.6 BM EPR: (frozen thf) $g = 3.9$, $g_{\parallel} = 2.1$.

*Preparation of $[(\text{trisilox})_2\text{Mn} \cdot \text{LiCl}]$ (**5**)*

To a slurry of manganese(II) chloride (0.52 g, 3.99 mmol) in thf (20 cm^3) was added dropwise a solution of (trisilox)Li (7.98 mmol) in thf (20 cm^3) at -78°C . On warming to room temperature, an orange solution was obtained. After stirring for 1 h, the solution was evaporated to dryness and the residue extracted with heptane (30 cm^3). The heptane extracts were concentrated to 60 cm^3 and white microcrystalline **5** precipitated during 48 h at room temperature (1.58 g, 56%); m.p. $230\text{--}233^\circ\text{C}$. The presence of chloride was confirmed by a sodium fusion test, and lithium by a flame test. (Found: C, 42.3; H, 9.2. $\text{C}_{24}\text{H}_{66}\text{ClLiMnO}_2\text{Si}_8$ calcd.: C, 40.7; H, 9.4%). The mass spectrum showed peaks at m/z 665 (17.4) $[(\text{trisilox})_2\text{Mn}]^+$, 682 (33) $[(\text{Trisilox})_2\text{Mn} - \text{Me}_3\text{Si}]^+$, 434 (11) $[(\text{Trisilox})_2\text{Mn} - \text{Me}_3\text{Si}]\text{Cl}^-$, 360 (69) $[(\text{Trisilox})\text{Mn}]^+$. μ_{eff} 5.9 BM.

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References

- 1 L.R. Chamberlain, I. Rothwell, K. Foltz and J.C. Huffman, *J. Chem. Soc., Dalton Trans.*, (1987) 155.
- 2 R.E. Lapointe, P.T. Wolczanski and J.F. Mitchell, *J. Am. Chem. Soc.*, 108 (1986) 6382.
- 3 M.L. Listemann and R.R. Schrock, *Organometallics*, 4 (1985) 74; M. Chisholm, D.M. Hoffman and J.C. Huffman, *J. Am. Chem. Soc.*, 106 (1984) 6815.
- 4 P.B. Hitchcock, N.H. Buttrus and A.C. Sullivan, *J. Organomet. Chem.*, 303 (1986) 321.
- 5 W.A. Herrmann, W. Kalcher, H. Biersack, I. Bernal and M. Creswick, *Chem. Ber.*, 114 (1981) 3558.
- 6 C. Santini-Scampuccii and J.G. Riess, *J. Chem. Soc., Dalton Trans.*, (1973) 2436.
- 7 M. Schonherr, D. Hass and K. Banfeld, *Z. Chem.*, 15 (1975) 66.
- 8 L.R. Chamberlain, I. Rothwell, and J.C. Huffman, *Inorg. Chem.*, 23 (1984) 2575.
- 9 D.C. Bradley, R.G. Copperthwaite, S.A. Cotton, K.D. Sales and J.F. Gibson, *J. Chem. Soc., Dalton Trans.*, (1973) 191.
- 10 G.K. Barker, M.F. Lappert and J.A.K. Howard, *J. Chem. Soc., Dalton Trans.*, (1978) 734.
- 11 M. Bochmann, G. Wilkinson, G.B. Young, M.B. Hursthouse and K.M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 1863.
- 12 C. Eaborn and K.D. Safa, *J. Organomet. Chem.*, 239 (1982) 1190.