Bis[(trimethylsilyl)methyl]- and Bis(neopentyl)-zinc, and Tris[(trimethylsilyl)methyl]aluminium–Diethyl Ether (1/1); Their Use as Alkylating Agents in forming Niobium and Tantalum Alkyls †

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Synthesis of bis[(trimethylsilyl)methyl)]zinc, tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1), and bis(neopentyl)zinc is described. Interaction of the first two compounds with tantalum pentachloride affords $(Me_3SiCH_2)TaCl_4$, $(Me_3SiCH_2)_2TaCl_3$, and $(Me_3SiCH_2)_3TaCl_2$, and with $NbCl_5$, $(Me_3SiCH_2)_3NbCl_2$. Bis(neopentyl)zinc reacts similarly. Adducts of the zinc, niobium, and tantalum alkyls with amines are also described.

NUMEROUS binary transition-metal (trimethylsilyl)methyls [1-3] have been synthesized using as alkylating agents the reagents $(Me_3SiCH_2)Li$, $(Me_3SiCH_2)MgCl$, or $(Me_3SiCH_2)_2Mg$.[4] In the present work, bis[(trimethylsilyl)methyl]zinc, tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1), and bis(neopentyl)zinc have been made and their use as alkylating agents for niobium and tantalum studied.

RESULTS AND DISCUSSION

The Zinc and Aluminium Compounds.—These were prepared by standard Grignard procedures, affording spontaneously flammable liquids by distillation. Bis[(trimethylsilyl)methyl]zinc and tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1) were obtained pure, whereas bis(neopentyl)zinc was contaminated with some hydrocarbon impurity which was not readily separated from the parent compound by distillation alone. This was reflected in the slightly high C and H analytical figures for this compound. Bis[(trimethylsilyl)methyl]zinc was also prepared from (iodomethyl)trimethylsilane and zinc–copper couple. The yields were substantially lower than from the Grignard method. The Raman spectrum of the bis[(trimethylsilyl)methyl]zinc was determined; it confirmed the expected linearity of the zinc–carbon bonds, the Zn–C stretch appearing at 508 cm^{-1} (polarized) while ν(Si–C) was at 609 cm^{-1} (polarized).

Niobium and Tantalum Compounds.—Dimethylzinc has been used as an alkylating agent for $NbCl_5$ and $TaCl_5$ and gives Me_3MCl_2,[5-7] Me_2MCl_3,[6,7] and $MeMCl_4$.[8] Alkylation of niobium and tantalum pentachlorides using (trimethylsilyl)methyl-lithium or -Grignard reagents [3] affords the bridging trimethylsilylmethylidyne complexes $[(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2]$. These may well be formed by hydrogen abstraction from $(Me_3SiCH_2)_3MCl_2$ species by the nucleophilic $(Me_3SiCH_2)Li$ or $(Me_3SiCH_2)MgCl$ to give Me_4Si and an intermediate such as $(Me_3SiCH_2)_2MCl_2(\bar{C}HSiMe_3)Li^+$. This could then react with $(Me_3SiCH_2)_3MCl_2$ to give LiCl and $[(Me_3SiCH_2)_2MCl_2(\mu\text{-}CHSiMe_3)MCl(CH_2SiMe_3)]$; repetition of the process would lead to the trimethylsilylmethylidyne complexes. No $(Me_3SiCH_2)_xMCl_{5-x}$ species were isolated in these reactions, although with neopentyl, which is less prone to stabilize the α-carbanion than is Me_3SiCH_2, the stable $(Me_3CCH_2)_3TaCl_2$ was obtained.[3] With bis[(trimethylsilyl)methyl]zinc, such proton abstraction is unlikely to occur, and indeed no methylidyne-bridged species were detected in the reaction mixtures. Bis[(trimethylsilyl)methyl]zinc reacted with $TaCl_5$ in a 1 : 1 ratio affording mixtures of $(Me_3SiCH_2)_2TaCl_3$ and $(Me_3SiCH_2)_3TaCl_2$. These compounds were readily separated by their differing solubilities in hexane. In addition, $(Me_3SiCH_2)TaCl_4$ was also obtained by reaction of $(Me_3SiCH_2)_2Zn$ with excess of $TaCl_5$, probably by way of distribution reaction (1).

$$(Me_3SiCH_2)_2TaCl_3 + TaCl_5 \longrightarrow 2(Me_3SiCH_2)TaCl_4 \quad (1)$$

Similar redistribution reactions are known [7,8] in the Me_2Zn–MCl_5 (M = Nb or Ta) system. When the reaction between $(Me_3SiCH_2)_2Zn$ and an excess of $TaCl_5$ was conducted in an n.m.r. tube, the major initial product formed immediately on adding the zinc alkyl was found to be $(Me_3SiCH_2)_2TaCl_3$, although $(Me_3SiCH_2)_3TaCl_2$ and $(Me_3SiCH_2)TaCl_4$ were also present. After several minutes, only traces of $(Me_3SiCH_2)_3TaCl_2$ remained, and substantial quantities of $(Me_3SiCH_2)_2TaCl_3$ disappeared at the expense of $(Me_3SiCH_2)TaCl_4$

Redistribution reactions occurred quite readily, and $(Me_3SiCH_2)TaCl_4$ was best prepared in excellent yield by reactions (1) or (2). The individual alkyls were readily detected by the characteristic position of the CH_2 resonance. As chlorine atoms were replaced by alkyl groups, there was a shift of the methylene resonance to higher τ values, as was found also for the methyl resonances of Me_nMCl_{5-n} [6,7] (M = Nb or Ta; n = 1—3). Physical properties and n.m.r. data of the compounds are given in the Table. Bis[(trimethylsilyl)methyl]zinc

$$(Me_3SiCH_2)_3TaCl_2 + 2TaCl_5 \longrightarrow 3(Me_3SiCH_2)TaCl_4 \quad (2)$$

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† No reprints available.

[1] W. Mowat, A. J. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[2] W. Mowat, A. J. Shortland, N. J. Hill, and G. Wilkinson, *J.C.S. Dalton*, 1973, 770.

[3] W. Mowat and G. Wilkinson, *J.C.S. Dalton*, 1973, 1120.

[4] M. R. Collier, M. F. Lappert, and R. Pearce, *J.C.S. Dalton*, 1973, 445.

[5] G. L. Juvinall, *J. Amer. Chem. Soc.*, 1964, **86**, 4202.

[6] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1973, 2313.

[7] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1973, 961.

[8] C. Santini-Scampucci and J. G. Riess, *J.C.S. Dalton*, 1973, 2436.

reacted with $NbCl_5$ affording $(Me_3SiCH_2)_3NbCl_2$. This compound exhibited but one sharp singlet at τ 9·84 for the Me_3Si and CH_2 groups, so that redistribution reactions of this species are not so readily studied. The reaction of $(Me_3SiCH_2)_2Zn$ with $TaCl_5$ ceased after introduction of three alkyl groups, even under forcing conditions (80 °C, 10 d, sealed tube). Further alkylation did not occur. During this period $(Me_3SiCH_2)_3TaCl_2$ underwent only superficial decomposition, a brown colouration appearing, and was recovered essentially quantitatively.

Tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1) also alkylated $NbCl_5$ and $TaCl_5$, but the reaction was not clean. Even with an excess of the halide there remained unconsumed alkylaluminium reagent which proved extremely troublesome to remove from the products. Only $(Me_3SiCH_2)_2TaCl_3$ was obtained in any state of purity. Generally, removal of solvent left dark oily material consisting of mixtures of tantalum alkyls. Fractional crystallizations or sublimations were not practicable as purification procedures. The reaction of bis(neopentyl)zinc with $TaCl_5$ also did not afford readily purifiable products, although known[3] tris(neopentyl)-tantalum dichloride was detected in the reaction when $TaCl_5$ was not in excess by comparison of spectra with those of an authentic sample. Oily material was generally formed, which again proved difficult to remove by fractional crystallization or sublimation, and it would appear that the simple Grignard method is preferable for the synthesis of this compound.

Adducts with Amines.—Both the zinc alkyls and the alkyl-niobium and -tantalum halides readily formed adducts with suitable ligands. On addition of the zinc alkyls to a solution of 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy) in benzene or hexane, a bright red colouration appeared immediately. *NNN′N′*-Tetramethylethylenediamine (tmen) formed colourless complexes. These adducts are remarkably stable oxidatively, those with the (trimethylsilyl)methyl radical possessing superior stability to those of neopentyl. The bipy and phen adducts of $(Me_3SiCH_2)_2Zn$ are stable in air for several days. Complexes of tmen possess less oxidative stability. On addition of phen or bipy to the alkyl-niobium or -tantalum halides in hexane or diethyl ether, immediate precipitation of the pale yellow niobium or off-white tantalum complexes occurred. These are only sparingly soluble in non-polar solvents, and were freed from impurities by washing with diethyl ether or hexane. They are rather light sensitive, especially tantalum derivatives with a large number of halogens attached. Indeed, when phen was added to a solution of $(Me_3SiCH_2)TaCl_4$ in the presence of light, a brown tar formed immediately. The niobium and tantalum adducts were too insoluble for n.m.r. study. They are presumably seven-co-ordinate, similar to $(bipy)Ta(Cl)_2Me_3$ whose crystal structure has recently been reported.[9]

EXPERIMENTAL

Analyses (Table) were carried out by the Microchemical Laboratories of Imperial College and A. Bernhardt. N.m.r. spectra were obtained on a Perkin-Elmer R14 spectrometer and Raman spectra on a Cary 81 instrument, using the yellow line (5 682 Å).

Solvents used in the preparations were purified by distillation from sodium diphenylketyl. Niobium and tantalum pentachlorides were freshly prepared just prior to use; inferior results were obtained from samples of the halides that had not been so prepared. Commercial anhydrous zinc(II) chloride was finely powdered, heated under reflux with freshly distilled thionyl chloride, and pumped dry before usage in the preparation of the organozinc reagents. Commercial anhydrous aluminium(III) chloride was freshly sublimed before conversion to the alkylaluminium reagent. Water of crystallization was removed from 1,10-phenanthroline–water (2/1) by azeotropic distillation with benzene using a Dean and Stark apparatus. After all the water had been removed (*ca.* 36 h), the pale pink residue was sublimed affording a pure white product.

Preparation of Compounds.—*Bis[(trimethylsilyl)methyl]-zinc.* (a) To a solution of [(trimethylsilyl)methyl]magnesium chloride (1 mol) in diethyl ether (300 cm^3) at 0 °C was added powdered anhydrous zinc(II) chloride (68 g, 0·5 mol) through a solids vessel over 2 h. The solution was allowed to attain ambient temperature and maintained thus with stirring for 4 d. The majority of the solvent was then removed by distillation until the fractionation temperature reached 50 °C. Then all volatiles were removed by heating the reaction vessel at 100 °C (10^{-4} mmHg) over a period of 2 d, trapping them at -196 °C. These were refractionated and pure product, b.p. 44 °C (1·5 mmHg), was collected as a colourless *liquid*, spontaneously flammable in air (108·0 g, 90%).

(b) *From (iodomethyl)trimethylsilane and zinc–copper couple.* In a round-bottomed flask (250 cm^3) equipped with a reflux condenser and heavy stirrer was placed powdered zinc–copper couple (32·5 g, 0·25 mol). (The couple was prepared by reduction of CuO in the presence of Zn dust with dihydrogen just below the m.p. of the mixture.) To this was added a portion of (iodomethyl)trimethylsilane (20 cm^3; 107 g, 0·5 mol), and the mixture then heated under gentle reflux. After 2 h the remainder of the (iodomethyl)-trimethylsilane was added over a further 1 h. The reaction mixture was allowed to cool at room temperature and then fractionally distilled collecting the *product* (33·5 g, 56%) at 60 °C (5·0 mmHg).

Tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1). To a solution of [(trimethylsilyl)methyl]magnesium chloride (1 mol) in diethyl ether (400 cm^3) at 0 °C, was added powdered anhydrous aluminium(III) chloride (44·5 g, 0·33 mol) through a solids vessel over 3 h. After stirring at ambient temperature for 2 d, the majority of the solvent was removed and the pure white residue digested with oxygen-free benzene (500 cm^3). After filtration, benzene was removed by distillation and the liquid residue fractionated under reduced pressure to afford a colourless *liquid*, spontaneously flammable in air, b.p. 64 °C (2×10^{-2} mmHg) (72·4 g, 60%).

Bis(neopentyl)zinc. To neopentylmagnesium chloride (0·2 mol) in diethyl ether (100 cm^3) was added powdered anhydrous zinc(II) chloride (13·6 g, 0·1 mol) at 0 °C over 2 h through a solids vessel. After stirring for 2 d at room temperature, solvent was removed at 0 °C under reduced pressure, leaving a sticky white residue. This was digested with pentane, filtered, and solvent removed by distillation at atmospheric pressure leaving a yellow liquid. This was

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[9] H. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 1830.

fractionated under reduced pressure, collecting the *product* (17·9 g, 86%), b.p. 58—59 °C (9·7 mmHg).

Tris[(trimethylsilyl)methyl]tantalum dichloride. (a) To a solution of tantalum pentachloride (10·1 g, 28·17 mmol) in diethyl ether (150 cm^3) was added bis[(trimethylsilyl)-methyl]zinc (10·1 g, 42·26 mmol) over 1 h at 0 °C. After the addition was complete, the reaction mixture was stirred at ambient temperature for 4 h. Solvent was removed under vacuum, the yellow residue digested with pentane (200 cm^3), and the mixture filtered. Solvent was removed from the filtrate at −20 °C until crystals began to form. After cooling to −80 °C, filtration at this temperature afforded pale yellow crystals of bis[(trimethylsilyl)methyl]tantalum trichloride (1·28 g, 10%). Evaporation of the filtrate to dryness followed by sublimation (60 °C, 10^{-2} mmHg) afforded the *product* (11·12 g, 77%) contaminated with *ca.* 1% of the dialkyl compound.

Physical properties, analyses, and n.m.r. data for the alkyl compounds

Compound	Colour	M.p. (or b.p.), θc/°C	Analyses (%) C	H	Cl	N	Si	Zn(Al)	Ta(Nb)	N.m.r. data (τ) CH$_2$	Me$_3$Si	CMe$_3$
$(Me_3SiCH_2)_2Zn$	Colourless	(44, 1·5 mmHg)	39·9 (40·1)	9·0 (9·2)			23·2 (23·4)			10·69	10·02	
$(Me_3CCH_2)_2Zn$	Colourless	(58—59, 9·7 mmHg)	58·9 (58·0)	11·7 (10·6)						10·03		9·07
$(Me_3SiCH_2)_2Al,OEt_2$	Colourless	(64, 2 × 10^{-2} mmHg)	52·8 (53·0)	11·7 (11·9)			23·3 (23·2)	7·3 (7·5)		10·83 [b]	9·95 [b]	
$(Me_3SiCH_2)_3TaCl_2$	Yellow	64—67	27·8 (28·1)	6·2 (6·4)	13·6 (13·8)		16·1 (16·4)		34·6 (35·3)	8·00	9·83	
$(Me_3SiCH_2)_2TaCl_3$	Pale yellow	68—70	20·7 (20·8)	4·8 (4·8)	23·0 (23·0)		12·0 (12·2)		38·9 (39·2)	7·43	9·84	
$(Me_3SiCH_2)TaCl_4$	Bright yellow	56—59	11·5 (11·7)	2·6 (2·7)	34·4 (34·6)		6·7 (6·8)		43·4 (44·2)	6·39	9·91	
$(Me_3SiCH_2)_3NbCl_2$	Orange	68—70 decomp.	52·8 (53·0)	11·7 (11·9)	16·7 (16·7)		19·5 (19·8)		21·2 (21·9	9·84	9·84	
$(Me_3CCH_2)_3TaCl_2$	Yellow	*c*								7·15		9·00
$(tmen)Zn(CH_2SiMe_3)_2$	White	84—85	46·8 (47·3)	10·5 (10·7)		7·4 (7·9)				10·71	9·87	
$(phen)Zn(CH_2SiMe_3)_2$	Orange	166—167 decomp.	57·4 (57·3)	7·3 (7·2)		6·6 (6·7)				10·70	9·87	
$(bipy)Zn(CH_2SiMe_3)_2$	Red-orange	91—92	54·6 (54·7)	7·7 (7·6)		7·0 (7·1)				10·74	9·88	
$(tmen)Zn(CH_2CMe_3)_2$	White	87—88·5	59·1 (59·4)	11·6 (11·8)		8·5 (8·7)				9·68		8·67
$(phen)Zn(CH_2CMe_3)_2$	Red	154 decomp.	67·9 (68·2)	7·6 (7·8)		7·3 (7·2)				9·59		9·07
$(bipy)Zn(CH_2CMe_3)_2$	Red-orange	121—122	66·1 (66·1)	8·2 (8·3)		7·7 (7·7)				9·41		8·68
$(phen)Ta(CH_2SiMe_3)_3Cl_2$			41·8 (41·6)	6·0 (5·9)	10·4 (10·2)	4·1 (4·0)						
$(phen)Ta(CH_2SiMe_3)_2Cl_3$			37·5 (37·4)	4·8 (4·7)	16·9 (16·6)	4·8 (4·4)						
$(phen)Nb(CH_2SiMe_3)_3Cl_2$			48·1 (47·6)	7·0 (6·8)	11·4 (11·7)	4·8 (4·6)						

[a] Calculated values are given in parentheses. [b] CH$_2$ of co-ordinated Et$_2$O at τ 6·45 (quartet), CH$_3$ at τ 9·16 (triplet). [c] Lit.,[3] 115—117 °C.

(b) *From bis[(trimethylsilyl)methyl]tantalum trichloride and bis[(trimethylsilyl)methyl]zinc.* To a solution of bis[(trimethylsilyl)methyl]tantalum trichloride (9·23 g, 20 mmol) in pentane (50 cm^3) was added bis[(trimethylsilyl)methyl]-zinc (2·39 g, 10 mmol) at room temperature. After stirring for 1 h the mixture was filtered and solvent removed from the filtrate. The dry residue was sublimed (60 °C, 10^{-2} mmHg) to afford yellow *crystals* of the product (10·10 g, 98%), m.p. 65—68 °C.

Bis[(trimethylsilyl)methyl]tantalum trichloride. To a solution of tantalum pentachloride (17·93 g, 60 mmol) in diethyl ether (350 cm^3) was added bis[(trimethylsilyl)methyl]zinc (11·95 g, 50 mmol) at 10 °C over 1·5 h. On addition of the first few drops of the zinc reagent, the essentially colourless solution of tantalum pentachloride became pronouncedly yellow. After the addition, the mixture was stirred for 3 h and solvent removed under reduced pressure. The resulting yellow residue was extracted with pentane (150 cm^3) and filtered from the white precipitate of zinc chloride. Solvent was removed from the filtrate at *ca.* 0 °C under reduced pressure until crystals began to form, and the mixture was then cooled to −80 °C, precipitating a further crop. Filtration at −80 °C afforded pale yellow *crystals* of the product (17·05 g, 74%), which was further purified by sublimation (60 °C, 10^{-2} mmHg) onto a water-cooled probe, m.p. 68·5—70·5 °C. The darker yellow filtrate from the pentane concentrates contained substantial amounts of tris[(trimethylsilyl)methyl]tantalum dichloride (1·88 g, 11%) which was obtained by removal of solvent followed by sublimation (60 °C, 10^{-2} mmHg).

[(Trimethylsilyl)methyl]tantalum tetrachloride. (a) A mixture of tantalum pentachloride (17·4 g, 48·54 mmol) and bis-[(trimethylsilyl)methyl]zinc (2·39 g, 10 mmol) was stirred at room temperature in diethyl ether (50 cm^3) for 4 d. Diethyl ether was removed and the resulting yellow residue digested with hot hexane. The mixture was filtered hot and solvent removed from the filtrate until yellow crystals began to form. Cooling to −40 °C caused further precipitation. The *product* was obtained by filtration at this temperature (5·31 g, 65%). The mother liquor contained further *product*, slightly contaminated with bis[(trimethylsilyl)methyl]-tantalum trichloride.

(b) *By redistribution.* A mixture of tris[(trimethylsilyl)-methyl]tantalum dichloride (5·13 g, 10 mmol) and tantalum pentachloride (14·34 g, 40 mmol) was stirred in benzene

(70 cm^3). After several days the majority of the tantalum pentachloride had dissolved. After filtration, benzene was removed under reduced pressure and the yellow residue remaining sublimed (60 °C, 10^{-3} mmHg) to afford bright yellow *crystals* of the product (11·98 g, 97%), m.p. 56—59 °C.

Tris[(*trimethylsilyl*)*methyl*]*niobium dichloride*. (a) To a solution of niobium pentachloride (8·2 g, 30·31 mmol) in diethyl ether (150 cm^3) was added bis[(trimethylsilyl)methyl]zinc (10·87 g, 45·47 mmol) at −10 °C over 1 h. After stirring for 4 h at ambient temperature in the absence of light, solvent was removed under reduced pressure leaving a dry flaky brown-orange residue. To this was added pentane (150 cm^3) and the resultant orange-red solution was filtered from zinc(II) chloride. Solvent was removed from the filtrate under reduced pressure until crystallization commenced. The solution was then cooled to −80 °C until complete precipitation had occurred, and filtered at this temperature to afford orange-red *crystals* of the product (6·77 g, 53%), m.p. 68—70 °C. A further crop of less pure product (4·33 g, 34%), m.p. 66—71 °C, was obtained by evaporation of this filtrate to small volume, followed by further cooling and filtration.

(b) *From tris*[(*trimethylsilyl*)*methyl*]*aluminium–diethyl ether* (1/1). To a solution of niobium pentachloride (4·41 g, 20 mmol) in diethyl ether (50 cm^3) was added tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1) (7·24 g, 20 mmol) over 2 h, producing an orange solution. After work-up in the usual manner, the residue was sublimed (40 °C, 10^{-3} mmHg). Initially, oily material sublimed and was discarded; continued sublimation afforded more oily material that slowly solidified to the product (4·73 g, 56%). The n.m.r. spectrum revealed that the product was contaminated with *ca.* 5% of the organoaluminium compound. As this sublimation is a somewhat slow process, quite extensive decomposition of the rather unstable product occurred, a black insoluble residue remaining in the sublimation vessel.

Lewis-base adducts of bis[(*trimethylsilyl*)*methyl*]*zinc*. Adducts of bis[(trimethylsilyl)methyl]zinc with 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), and *NNN′N′*-tetramethylethylenediamine (tmen) were prepared as follows. To a solution of the organozinc compound (2·39 g, 10 mmol) in benzene (15 cm^3), was added phen, bipy (10 mmol), or tmen (20 mmol). With phen and bipy the solutions immediately became bright red; with tmen there was no colour change. After stirring for 1 h at ambient temperature, solvent was removed under reduced pressure and the residues sublimed to afford the *products* (phen and bipy adducts, 100%; tmen adduct, 80%).

Lewis-base adducts of bis(*neopentyl*)*zinc*. These were prepared in similar fashion to the adducts of bis[(trimethylsilyl)methyl]zinc. Sublimation (120 °C, 10^{-3} mmHg) afforded red phen and bipy adducts (100%), or at 80 °C (10^{-3} mmHg) the white tmen adduct (91%).

phen Adducts of $(Me_3SiCH_2)_3TaCl_2$, $(Me_3SiCH_2)_2TaCl_3$, *and* $(Me_3SiCH_2)_3NbCl_2$. These were prepared as follows. To a solution of the alkylmetal halide (10 mmol) in hexane was added phen (1·80 g, 10 mmol) dissolved in benzene (20 cm^3) in the absence of light. Immediate precipitation of the adduct occurred. The off-white tantalum or pale yellow niobium complexes were filtered off, washed with hexane–benzene (10 : 1), and dried in the absence of light. Yields were in the region of 90%.

Reaction of Tris[(*trimethylsilyl*)*methyl*]*aluminium–Diethyl Ether* (1/1) *with Tantalum Pentachloride*.—To a solution of tantalum pentachloride (3·59 g, 10 mmol) in diethyl ether (150 cm^3) was added tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1) (3·62 g,10 mmol). An immediate yellow colouration was observed on addition of the first few drops of the organoaluminium compound. After stirring for 2 h, the reaction mixture was freed from solvent under reduced pressure, a sticky yellow-brown residue remaining. Hexane (50 cm^3) was added to this, and the mixture filtered. Evaporation of solvent from the filtrate until the volume was *ca.* 15 cm^3, followed by cooling to −80 °C and filtration, precipitated crude bis[(trimethylsilyl)methyl]tantalum trichloride (0·43 g, 9%), which was further purified by sublimation (60 °C, 10^{-2} mmHg). Evaporation of filtrate left only a yellow oil, shown by n.m.r. spectroscopy to be an approximately 1 : 10 : 3 mixture of bis[(trimethylsilyl)methyl]tantalum trichloride, tris[(trimethylsilyl)methyl]tantalum dichloride, and tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1). Similar reactions, using tantalum pentachloride: organoaluminium compound 2 : 1, still left unreacted tris[(trimethylsilyl)methyl]aluminium–diethyl ether (1/1), together with quantities of [(trimethylsilyl)methyl]tantalum tetrachloride.

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