Elimination Stabilized Alkyls. Part III.[1] Trimethylsilylmethyl and Neopentyl Alkyls of Transition Metals †

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Trimethylsilylmethyl (R) complexes, $R_2\overline{M\text{–CSiMe}_3\text{–MR}_2\text{–C}}\text{SiMe}_3$ (M = Nb and Ta) and neopentyl (R′) complexes, MR'_4 (M = Ti and Zr), R'_3TaCl_2, and $Mo_2R'_6$ are obtained by the interaction of Grignard or lithium reagents derived from chloromethyltrimethylsilane and neopentyl chloride with the appropriate metal halide. ^{1}H N.m.r. and i.r. spectra are reported.

In recent studies [1,2] on binary transition metal complexes using trimethylsilylmethyl and neopentyl and related alkyls it was proposed that the stability of these compounds was due to their inability to undergo the β-elimination reaction. Our observations were supported by the isolation of other binary alkyl complexes unable to eliminate alkenes, notably the 1-norbornyl and related alkyls of Bower and Tennent,[3] and also by some thermal decomposition studies of Tamura and Kochi on transition metal alkyls prepared *in situ*.[4,5]

In trimethylsilylmethyl and neopentyl complexes with π-bonding ligands [6] and also in the chromium(IV) tetra-alkyls [1,2] it was apparent that in spite of lower thermal stability of the neopentyl compounds they had higher melting points and crystallized more easily. As expected, the titanium and zirconium neopentyls were prepared as crystalline solids; [7] their trimethylsilylmethyl analogues, have recently been isolated as volatile liquids.[8]

Alkyl complexes with niobium and tantalum are rare, the best known examples being the methyls [9] Me_3MCl_2 (M = Nb and Ta). The neopentyl tantalum compound isolated in this work appears to be analogous to these.

The compounds were prepared by conventional procedures and are listed with some of their properties in Table 1.

*Bis-*μ*-(trimethylsilylmethylidyne)tetrakis(trimethylsilylmethyl)-diniobium*(V) *and -ditantalum*(V).—The interaction of niobium or tantalum pentachloride with the Grignard reagent gives distinct colour changes on addition of successive equivalents of ligand. The final stage in the reaction is a dimeric species with a carbene bridge, the crystal structure [10] of which has been determined for the niobium complex. The compounds have a quasi-aromatic ring of which the carbene bridges form part, structure (I).

They are best prepared by addition of metal halide in ether to an excess of Grignard reagent, and after ex-

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† No reprints available.

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

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

[3] B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 1972, **94**, 2512.

[4] M. Tamura and J. K. Kochi, *J. Organometallic Chem.*, 1971, **29**, 111.

[5] M. Tamura and J. K. Kochi, *Bull. Chem. Soc. Japan*, 1971, **44**, 3063.

[6] B. Wozniak, D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3116.

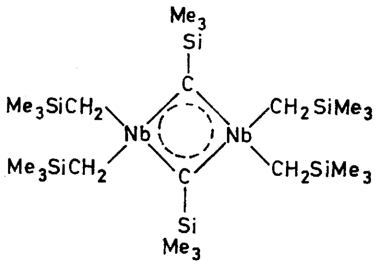
[7] W. Mowat and G. Wilkinson, *J. Organometallic Chem.*, 1972, **38**, C35. The Ti, Zr, and Hf neopentyls have also been prepared by Prof. M. F. Lappert and his co-workers, personal communication.

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

[9] C. L. Juvinall, *J. Amer. Chem. Soc.*, 1964, **86**, 4202.

[10] F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1477.

traction into petroleum the dark red (niobium) or orange (tantalum) crude products may be readily recrystallised. Both compounds have a phase change at 72° when the crystals crack, but are unaffected thereafter up to their melting points of 152 and 170° respectively, when they both decompose.



(I)

Both the niobium and tantalum compounds are air and moisture sensitive, particularly the latter. Exposure to air rapidly causes formation of a white coating of the hydrated oxide, and occasionally they inflame spontaneously. They are readily soluble in ether, petroleum, and benzene, but decompose slowly in chlorinated solvents and rapidly in protic solvents. They do not chromatograph on alumina, silica, or cellulose and fail to sublime *in vacuo*.

Table 1

Trimethylsilylmethyl and neopentyl complexes of the transition metals

Compound [a]	Colour, form	M.p./°C	N.m.r. spectra [b]		Analytical data [c]	
			CH_3	CH_2	C (%)	H (%)
$(\mu\text{-CSiMe}_3)_2Nb_2R_4$	Red prisms	*ca.* 152 (d)	9·79(μ), 9·54	8·50 [d]	39·4 (40·9)	8·4 (8·8) [e]
$(\mu\text{-CSiMe}_3)_2Ta_2R_4$	Orange prisms	*ca.* 170 (d)	9·80(μ), 9·54	9·00 [d]	30·9 (30·8)	7·0 (7·2)
TiR'_4	Yellow prisms	*ca.* 103 (d)	8·62	7·64 [f]	71·0 (72·3)	12·8 (13·2)
ZrR'_4	Off-white prisms	*ca.* 105 (d)	8·62	8·34 [f]	64·3 (64·0)	12·2 (11·7)
TaR'_3Cl_2	Pale yellow needles	115—117	8·65	7·23 [f]	38·7 (38·7)	7·1 (7·1) [g]
$Mo_2R'_6$	Yellow plates	135—138	8·64	7·09 [f]	58·5 (58·3)	10·6 (10·6)

[a] R = Trimethylsilylmethyl, R′ = neopentyl. [b] τ Values, benzene solution. [c] Calculated values in parentheses. [d] μ-$CH_3 : CH_3 : CH_2 = 9 : 18 : 4$. [e] Si, 24·4 (23·9); Nb, 26·6 (26·4)%. [f] $CH_3 : CH_2 = 9 : 2$. [g] Cl, 15·0 (15·3); Ta, 38·7 (38·9)%.

Other than towards oxygen and moisture, the compounds are surprisingly inert. Dry oxygen reacts with a petroleum solution of either to yield yellow, petroleum-soluble oils containing a mixture of what appear to be alkoxy-species. Dry chlorine and hydrogen chloride both react immediately with either compound and the reaction of chlorine with the niobium compound was followed by n.m.r. The reaction was not particularly clean, but the major organic products were chloromethyltrimethylsilane and trimethylchlorosilane, with several other minor chloroalkylsilane derivatives. Compounds having no effect on either alkyl include nitric oxide, carbon monoxide, tertiary alkyl and aryl phosphines, amines, and alkenes.

The mechanism of the formation of the bridging carbene is unknown. It is assumed that a penta-alkyl complex cannot exist for steric reasons, and since the trisalkylmetaldichloride is known (see below) it must be at the final stages of chlorine elimination that reduction of an α-carbon atom occurs. The presence of the β-silicon atom probably contributes to the stability of the carbene, as the analogous carbon compound, *i.e.*, the neopentyl, cannot be prepared.

The n.m.r. spectrum of each compound shows only three peaks (see Table 1), two $Si{-}Me_3$ peaks and one methylene. There is no n.m.r. evidence for a proton on the bridging carbon, or a metal hydride, and the i.r. spectra and the *X*-ray structural data support this. The compounds have nearly identical i.r. spectra (Table 2) which are consistent with the observed structure. The usual Me_3SiCH_2 vibrations occur,[2] the metal–carbon stretches are at 492, 465, 438, and 400 cm^{-1} two for terminal M–C and two for bridging, and the bands at 374 and 310 cm^{-1} are assigned as ring deformations. The quasi-aromatic structure allows us to consider the niobium as having oxidation state(v), which explains the diamagnetism of the compound without having to invoke metal–metal interaction.

The electronic spectra of the compounds show only rising absorption in the u.v., as is the case of the neopentyl compounds reported here. On addition of successive equivalents of Grignard to the metal halide MCl_5, it was hoped that complexes of the type MR_nCl_{5-n} would be formed. However, it was shown that petroleum extraction at each ‘ end-point ’ yielded a mixture of compounds. All were moisture sensitive but compared to the binary alkyls, relatively stable towards oxygen. The only compound isolable so far appears to be TaR_3Cl_2, which is similar in its properties to the corresponding neopentyl compound.

Tetrakis(*neopentyl*)-*titanium*(IV) *and -zirconium*(IV).— The interaction of neopentyl-lithium with titanium or zirconium tetrachloride in ether yields dark, almost black petroleum solutions from which, after recrystallisation the tetra-alkyls may be obtained. The compounds are air and moisture sensitive and are volatile and may be sublimed *in vacuo* at *ca.* 50°. They are thermally unstable at room temperature over long periods of time (> one week) the zirconium compound being the more stable. They are soluble in petroleum, benzene, and ether, and are unaffected over short periods by chlorinated solvents. Their sensitivity to moisture precludes chromatography.

The n.m.r. spectra (Table 1) of the compounds show only the expected methyl and methylene resonances for TiR'_4 and ZrR'_4. The compounds are moisture sensitive to *such* an extent that a peak at τ 8·86 for neopentane always appears unless the sample is prepared very carefully *in vacuo*.

As with trimethylsilylmethyl,[2] the ligand vibrations dominate the i.r. spectrum, and since they are well characterised alkyl vibrations they are not included in Table 2. For the metal carbon stretches, TiR'_4 and ZrR'_4 both have medium bands at *ca.* 530 and 500 cm^{-1}. This would be in accord with a slightly distorted tetrahedral structure. Crystal structures have been determined for $Ti(benzyl)_4$ [11] and $Zr(benzyl)_4$ [12] and both show that the molecule deviates from a regular tetrahedron but it is possible that this is due to interaction, either steric or electronic, with an α-hydrogen atom of the phenyl ring.

TABLE 2

I.r. spectra of the alkyl compounds/cm^{-1}

$(\mu\text{-}CSiMe_3)_2Nb_2R_4$	$(\mu\text{-}CSiMe_3)_2Ta_2R_4$	TiR'_4	ZrR'_4	TaR'_3Cl_2	$Mo_2R'_6$
690s	690s				
				639s	639w
621m	619m				
615m	610m				615w
		540s	525s	566s	540s
		505s	485s		
495m	492m	*ca.* 495sh			
470m	465m	448w	435w	461m	
430m	400m			410m	
399m					
373m	374s			380m	372m
			ca. 390sh		
		365s	365s	351s	
310m	310m				
		299s	262s	305s	300m
269m	268m				
240w	250w			258s	
230w	230m				

The compounds all seem more reactive than the molybdenum, tantalum, or chromium neopentyls. TiR'_4 and ZrR'_4 react with carbon monoxide at one atmosphere and room temperature giving products having terminal CO stretching frequencies but no acyls, while nitric oxide and pyridine also react. Neither compound will react with ethylene or propylene at room temperature and pressure but solutions of the zirconium alkyl have been reported as effective catalysts for the polymerisation of olefins.[13] The compounds fail to react with hydrogen under normal conditions.

Vanadium Neopentyls.—The reaction of VCl_4 or $VOCl_3$ with the neopentyl Grignard or lithium reagent produced no stable compound. Since $V(CH_2SiMe_3)_4$ is the least stable thermally of the trimethylsilylmethyl complexes (it decomposes at room temperature in a few days) it is not surprising that the tetra-neopentyl analogue is unstable. The tetra-benzyl compound, although characterised in solution, is also not isolatable.[14]

The interaction in petrol at $-60°$ of VCl_4 with four equivalents of neopentyl-lithium yielded an intense green solution which turned brown on warming to room temperature. The e.s.r. spectrum of the green solution showed two $S = \frac{1}{2}$ species, presumably compounds of the form $V(CH_2CMe_3)_nCl_{4-n}$, and a free radical.

The corresponding reaction with $VOCl_3$ at low temperature yields a brown solution with a normal anisotropic $S = \frac{1}{2}$ spectrum, different from either of the species obtained from VCl_4. On warming, the eight-line mobile solution spectrum is obtained but above 170 K a new fifteen line spectrum is observed (Figure 1). This signal has the correct intensity distribution 1, 2, 3, 4, 5, 6, 7, 8, 7, 6, 5, 4, 3, 2, 1, for two equivalent vanadium nuclei ($I = \frac{7}{2}$) interacting with the electronic spin. The *g*-factor is 1·989(3) and the hyperfine splitting is 3·06(1) mT. Similar spectra have been observed for dimeric vanadium tartrates.[15]

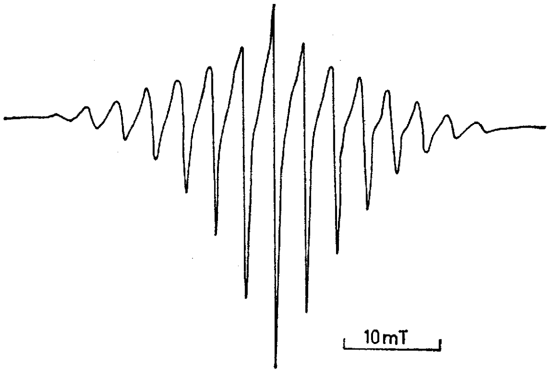


FIGURE 1 E.s.r. spectrum of a vanadium–neopentyl compound with one unpaired electron interacting with two equivalent vanadium nuclei

Tris(neopentyl)dichlorotantalum(V).—As mentioned be-

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[11] I. W. Bassi, G. Allegra, R. Scordimaglia, and G. Chioccola, *J. Amer. Chem. Soc.*, 1971, **93**, 3787.

[12] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *Chem. Comm.*, 1971, 677.

[13] D. G. H. Ballard, 23rd Internat. Congress of Pure and Applied Chem., Butterworths, London, 1971, vol. 6, p. 213.

[14] S. D. Ibekwe and J. Myatt, *J. Organometallic Chem.*, 1971, **31**, C65.

[15] R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, 1967, **6**, 735.

fore, the niobium and tantalum systems are very complex, and no binary neopentyls have been prepared. Addition of $NbCl_5$ or $TaCl_5$ to an excess of Grignard reagent produces a dark brown oil containing many species. However, the reaction of three equivalents of Grignard reagent with $TaCl_5$ does produce, in a relatively clean reaction, the trisalkyldichloro-species, R'_3TaCl_2. The methyl complexes[9] are yellow volatile oils which decompose at room temperature over several hours, but R'_3TaCl_2 is remarkably stable to heat and may be sublimed *in vacuo* with a flame without significant decomposition. It is moisture sensitive but relatively stable towards oxygen. It is soluble in petroleum, ether, benzene, and halogenated solvents but decomposes in protic solvents.

The n.m.r. spectrum shows only the expected resonances for methyl and methylene. The i.r. spectrum in the region below 600 cm^{-1} is complex, as both the metal–carbon and metal–chlorine stretches occur here. An attempt to make the bromide, R'_3TaBr_2, to try to assign the metal halogen stretches, was unsuccessful.

Further work on the niobium and tantalum systems is in progress.

Hexakis(*neopentyl*)*dimolybdenum*(III).—The interaction of neopentyl-lithium with $MoCl_5$ in ether yields the compound $Mo_2R'_6$, in the same way as the trimethylsilylmethyl analogue.[2] The yield of the reaction is lowered considerably if the Grignard reagent is used. The compound is stable in air over short periods, but quite oxygen-sensitive in solution. As with $Mo_2(CH_2SiMe_3)_6$, the terminal oxidation product is the blue oxide. The neopentyl is volatile, sublimes *in vacuo* at 130°, but in poor yield due to thermal decomposition. It is soluble in most organic solvents and is relatively stable to protic solvents and water. Concentrated mineral acids liberate neopentane, with the formation of complex anionic molybdenum halides (*cf.* the trimethylsilylmethyl analogue). $Mo_2R'_6$ reacts rapidly with carbon monoxide and nitric oxide, but apart from this, it is rather inert.

The n.m.r. spectrum is simple, and the i.r. suggests a structure similar to that found for the trimethylsilylmethyl compound.

EXPERIMENTAL

Microanalyses by Beller, Göttingen; Bernhardt, Mülheim; and Imperial College Microanalytical Laboratories. Metal analyses were obtained using a Perkin-Elmer Atomic Absorption instrument model 303, or standard gravimetric methods. The analytical data are collected in Table 1.

Spectroscopic Instruments.—N.m.r. spectra were obtained in benzene using Perkin-Elmer R 14 and 12A n.m.r. spectrometers. I.r. spectra were recorded on a Perkin-Elmer 325 spectrophotometer calibrated with polystyrene over the region 5000—200 cm^{-1}. For the region 4000—450 cm^{-1} samples were run between KBr plates and in the region 500—200 cm^{-1} between polyethylene plates. Electronic spectra were recorded on a Cary 14 spectrophotometer as solutions in petroleum.

Preparations.—All preparations and other operations were carried out in oxygen-free nitrogen, argon (for preparation of lithium reagents), or *in vacuo* unless otherwise stated. Chloromethyltrimethylsilane (Peninsular Chemresearch Inc.) and neopentyl chloride (K and K Laboratories, Inc.) were used as received. Solvents were dried and degassed before use. Petroleum used had b.p. 30—40° except for chromatography when it had b.p. 60—80°. Chromatography was carried out using acid-washed alumina (Spencer Chemicals for Industry, Type H).

Trimethylsilylmagnesium chloride was prepared in diethyl ether as *ca.* 1M solution.[16] Neopentylmagnesium chloride was prepared by the literature method[17] and neopentyl-lithium was prepared in the same way as trimethylsilylmethyl-lithium.[18]

Bis-μ-(*trimethylsilylmethylidyne*)*tetrakis*(*trimethylsilylmethyl*)*diniobium*(V).—To a solution of trimethylsilylmethylmagnesium chloride (550 mmol) in diethyl ether (500 ml), was added $NbCl_5$ (27 g, 100 mmol) in diethyl ether (250 ml) at room temperature over 3 h. The dark red-brown solution was filtered and the solvent stripped. The residue was extracted with petroleum and the extracts filtered. After concentration *in vacuo* to 50 ml, cooling to −35 °C for several hours, and collection at that temperature the *compound* was recrystallised from petroleum (25 ml) at −40 °C giving red-brown prisms (6 g, 20%).

Bis-μ-(*trimethylsilylmethylidyne*)*tetrakis*(*trimethylsilylmethyl*)*ditantalum*(V).—As for the niobium compound but using $TaCl_5$ (35 g). The orange-red petroleum extract left an orange oil which was dissolved in diethyl ether (150 ml) and allowed to stand at −35°. Light orange prisms of the *compound* slowly formed and were collected at this temperature, washed with chilled ether, and dried *in vacuo*. At this stage the compound could be readily recrystallised from petroleum (7 g, 15%).

Tetrakis(*neopentyl*)*titanium*(IV).—To a solution of neopentyl-lithium (80 mmol) in diethyl ether (100 ml) was added a solution of the etherate of $TiCl_4$ (20 mmol) in diethyl ether (100 ml) at room temperature over 30 min and the mixture stirred for 15 min. The solution was filtered and the solvent stripped, and the resulting dark yellow oil extracted with petroleum. This solution was concentrated *in vacuo* to *ca.* 40 ml and then further concentrated by blowing off solvent (to initiate crystallisation) until a substantial amount of dark crystalline material was formed. The solution was cooled to −20° and the crude product collected (*ca.* 60—80% yield). It was washed several times with chilled petroleum and recrystallised at −20° to give yellow crystals of the *compound* (2 g, 30%). The compound is best purified by vacuum sublimation at *ca.* 50°.

Tetrakis(*neopentyl*)*zirconium*(IV).—As for the titanium tetra-alkyl, using $ZrCl_4$ (25 mmol) to give, from the dark petroleum solution, the crude solid in *ca.* 70% yield. Off-white crystals of the *compound* were obtained by recrystallisation at −25° (3·0 g, 33%).

Tris(*neopentyl*)*dichlorotantalum*(V).—To a solution of tantalum pentachloride (3·7 g, 10 mmol) in diethyl ether (100 ml) was added a solution of neopentylmagnesium

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[17] H. Zimmer, I. Hechenbleinker, O. A. Homberg, and M. Danzik, *J. Org. Chem.*, 1964, **29**, 2632.

[18] H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 1970, **92**, 4664.

chloride (30 mmol) in diethyl ether (40 ml). After filtering and stripping the solvent, the yellow oil was extracted with petroleum, concentrated to 50 ml and cooled to $-30°$. The pale yellow *crystals* were filtered at this temperature and washed with chilled petroleum (3 g, 75%). The solid could be readily purified further by sublimation *in vacuo* at 200 °C.

Hexakis(neopentyl)dimolybdenum(III).—To a solution of neopentyl-lithium (30 mmol) in diethyl ether (80 ml) was added $MoCl_5$ (2 g, 6 mmol) in diethyl ether (50 ml) at room temperature over 15 min and the mixture stirred for 30 min. After filtering and stripping the solvent, the brown, sticky residue was extracted with petroleum. This solution was concentrated to about 5 ml and, after destroying the excess of lithium reagent with a few drops of degassed methanol, was transferred to an alumina column and eluted with petroleum. The yellow fraction, on slow concentration in vacuum, gave crystals of the *compound* (0·3 g, 15%).

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