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SILYLMETHYL AND RELATED COMPLEXES
II*. PREPARATION, SPECTRA, AND THERMOLYSIS OF THE TETRANEOPENTYLS OF TITANIUM, ZIRCONIUM, AND HAFNIUM

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SUMMARY

The preparation and characterisation of the Group IVA neopentyls $(Me_3CCH_2)_4M$ (M = Ti, Zr, or Hf) is described. Spectroscopic data (IR, Raman, mass, ^{1}H NMR, and PE) are provided; IR and Raman bands have been assigned by comparison with results on Group IVB analogues (M = Ge or Sn). MC_4 stretching vibrations fall in the range 540–485 cm^{-1}, and bending modes at 240–283 cm^{-1}. Thermal decomposition gives neopentane as the sole detectable product; qualitatively, stability increases in the order $M = Ti < Zr < Hf$ and for R_4M: $R = Me \ll Me_3CCH_2 \approx Me_3SiCH_2$. $(Me_3CCH_2)_4Ti$ is aerobically oxidised in benzene to give $(Me_3CCH_2O)_4Ti$

INTRODUCTION

A number of well-characterised, kinetically-stable, binary alkyls of the Group IVA metals (Ti, Zr, or Hf) have been reported: namely, the tetrabenzyls[2], tetranorbornyls[3], and tetrasilylmethyls[1]. The stability of transition metal alkyls has been discussed[4], and the increased stability of these complexes over the simple alkyls can be attributed to the non-availibility or high activation energy of decomposition pathways: primarily the alkene elimination (involving β-hydrogen atoms) and inter- and intramolecular alkane elimination routes. Secondary interactions of the ligand with the metal centre may also afford some stabilisation, *e.g.*, in the tetrabenzyls[5].

In Part I[1] we reported the tetrasilylmethyls of the Group IVA metals. These compounds belong to the series $(Me_3M'CH_2)_4M$ (M' = C, Si, Ge, or Sn), which serially may provide an insight into relationships between the stability of complexes in a given triad with changes of ligand, in terms of steric (hindrance decreasing in the series $C > Si > Ge > Sn$) and/or electronic effects. In organic compounds, as well as in *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$[6], groups $Me_3M'CH_2$ are inductively electron-releasing and if attached to electron-deficient centres then σ–π effects are important for M' = Si, Ge, or Sn[6,7]. A neighbouring Group IVB metal may stabilise a carbanion or radical, as in $(Me_3Si)_3C^-$ (ref. 8) or $(Me_3Si)_3C^\bullet$ (ref. 9).

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[*] For Part I see ref. 1.

Thermal decomposition of the binary Group IVA alkyls has been studied in detail only for tetramethyltitanium. In non-polar media, decomposition affords less than a stoicheiometric amount of methane (2 to 3 moles per mole of $TiMe_4$) as the major organic product; higher hydrocarbons are produced in small quantities[10,11]. Solutions remain diamagnetic throughout with the production of a black diamagnetic solid containing C, H, and Ti, the nature of which is unknown but which may contain low-valent titanium species[10] or titanium(IV)–carbide linkages[11]. Isotopic labelling has shown that the hydrogen in the methane and the carbon in the solid originate from the tetramethyltitanium and not the solvent[11,12,13]. Decomposition is often autocatalytic, and catalysis by the black solid has been demonstrated[10]. A mechanism involving inter- and intramolecular elimination has been proposed, with negligible contribution from radical pathways[11]. In more polar media, radical pathways may be more significant[14].

This paper describes the preparation and characterisation of the tetraneopentyls of titanium, zirconium and hafnium, of which the titanium[15] and zirconium[15,16] compounds have been briefly mentioned in previous communications. Additionally, a qualitative study has been made of the thermolysis of $(Me_3CCH_2)_4M$ and the oxidation of $(Me_3CCH_2)_4Ti$.

RESULTS AND DISCUSSION

The compounds were prepared by the reaction of neopentyllithium with the anhydrous metal chlorides in n-hexane ($TiCl_4$; $-70°$) or n-hexane/ether ($ZrCl_4$ or $HfCl_4$; 0°) (eqn. 1).

$$4\,Me_3CCH_2Li + MCl_4 \rightarrow (Me_3CCH_2)_4M + 4\,LiCl \quad (1)$$

The neopentyls of zirconium and hafnium were obtained in good yields (Table 1); extensive reduction was noted in the reaction with $TiCl_4$ even at $-70°$, and consequently $(Me_3CCH_2)_4Ti$ was isolated in modest yield. Similar reduction occurred in the preparation of tetrakis(trimethylsilylmethyl)titanium via the lithium reagent in ether, although it was less significant if the reaction was carried out in n-hexane[1]. We therefore formulate the order of reducing ability of the lithium reagents as: $Me_3CCH_2Li > Me_3SiCH_2Li$, in accord with the expected carbanion stabilities[17].

The compounds, readily purified by sublimation *in vacuo* (ca. $50°/10^{-3}$ mm), are crystalline solids melting in the range 103–116° (Table 1); *cf.*, $(Me_3CCH_2)_4Ge$ (a new compound), m.p. 109–110°; $(Me_3CCH_2)_4Sn$, 134–135.5° (ref. 18a); $(Me_3CCH_2)_4Pb$, 139–141° (ref. 18b); $(Me_3CCH_2)_4Cr$, 110° (ref. 15b). They are readily soluble in hydrocarbons, although less so than the silylmethyl analogues[1], and may be crystallised from concentrated n-pentane solution at $-70°$. The titanium and zirconium compounds are monomeric in benzene (cryoscopy under argon). They are rapidly decomposed upon exposure to air: qualitatively, stability increases in the order $Hf \approx Zr < Ti$. On exposure to dry air in benzene solution, tetraneopentyltitanium afforded (eqn. 2) the alkoxide in good yield (80% after sublimation), the only other product (by NMR) being a trace of neopentane.

$$(Me_3CCH_2)_4Ti \xrightarrow[C_6H_6]{O_2} (Me_3CCH_2O)_4Ti \quad (2)$$

Solutions of $(Me_3CCH_2)_4Ti$ darkened slowly upon exposure to light; the zirconium and hafnium compounds were unaffected.

Like the tetrabenzyls[16,19] and silylmethyls[16], $(Me_3CCH_2)_4Zr$[16] is active as a catalyst for the polymerisation of α-olefins and dienes; details will be reported elsewhere.

Spectra

The ^1H NMR spectra show two singlets in the ratio 2/9 assigned to the CH_2M and CMe_3 protons, respectively. The upfield shift of the former resonances from Ti to Hf reflects differences in the electronegativity of the metals. Data are included in Table 1.

TABLE 1

GENERAL DATA FOR THE TETRANEOPENTYLS, $(Me_3CCH_2)_4M$

M	*Yield (%)*	*Colour, m.p. (°C)*	*^1H NMR, τ[a] (ppm)*		*Mol. wt.[b] found (calcd.)*
			MCH_2C	*CMe_3*	
Ti	26	Yellow 105–107° (dec)	7.68	8.72	327(332)
Zr	68	Colourless 108–111° (dec)	8.48	8.72	388(376)
Hf	59	Colourless 115–116°	8.98	8.72	

[a] C_6H_6 (2.73 τ). [b] By cryoscopy of ca. 5% w/w solutions in C_6H_6.

A parent ion was not observed in the mass spectrum of the titanium compound; ions with the titanium isotope pattern were observed at the following *m/e* (assignments in parentheses): 261 $[(C_5H_{11})_3{}^{48}Ti^+]$, 205 $[(C_5H_{11})_2{}^{48}TiCH_3^+]$, 189 $[(C_5H_{11})^{48}Ti(C_5H_{10})^+]$, 133 $[(C_5H_{11})^{48}TiCH_2^+]$. Meaningful data were not obtained from the zirconium or hafnium compounds. It may well prove that binary transition metal alkyls, MR_n will not readily give strong parent ions in their mass spectra (see also refs. 3 and 20).

Assignments of bands in the vibrational spectra were made from infrared (IR) and Raman studies, and by comparison with the spectra of similar compounds: the tetrakis(trimethylsilylmethyl) complexes, tetraneopentylgermane and -stannane, and neopentyl chloride. Data are in Tables 2 and 3. Comparisons with neopentyl chloride and the germanium and tin neopentyls facilitated assignments of bands associated primarily with the Me_3CCH_2 group. The main features of interest are, however, the bands associated with metal–carbon stretching and bending modes and here the germanium and tin compounds (presumably tetrahedral) serve as suitable models. Assignments are as follows.

(*i*) Bands in the range 1500 to 1000 cm^{-1} are associated with C–H bending.

(*ii*) Absorption in the range 950 to 900 cm^{-1}. A single strong band is found in Me_3CCH_2Cl, whereas there are asymmetric doublets in the other compounds: these are of medium intensity for Ti, Sn, and Ge and are weak in the Zr and Hf compounds. They are assigned to $\nu_{asym.}(Me_3CCH_2)$.

TABLE 2

IR DATA FOR THE TETRANEOPENTYLS, $(Me_3CCH_2)_4M$ (ν_{max} in cm^{-1})

$(Me_3CCH_2)_4Ti$[a]	$(Me_3CCH_2)_4Zr$[a]	$(Me_3CCH_2)_4Hf$[a]	$(Me_3CCH_2)_4Ge$[b]	$(Me_3CCH_2)_4Sn$[b]
1355s	1353s	1355s	1360s	1360s
ca. 1250(sh)	ca. 1250(sh)	ca. 1250(sh)	1231vs	1235vs
1226vs	ca. 1222vs, br	ca. 1222vs, br		1228(sh)
ca. 1068vw	1078w	1085m	1160s	1137m
	1000m	1001m	1127m	1109m
	980(sh)	980(sh)	1016m	1019(sh)
931w	931m	930m		1009m
910w	912m	912w	ca. 935w	ca. 932w
750s	747s	748s	768s	ca. 745(sh)
ca. 730(sh)			755s	727s, br
ca. 540s, br	ca. 530s, br	ca. 536s, br	714m	ca. 695m, br
ca. 507s, br	ca. 488s, br	ca. 491s, br	ca. 638m, br	592m
447w, br	450(sh)	450(sh)	470w	459w
390(sh)	390w	390w	389w	382w
370m	367m	368m		
355(sh)				
300m, br	255s, br	242s, br	295m	260w, br
283(sh)			285(sh)	

[a] As solutions in n-pentane. [b] As solutions in n-hexane

TABLE 3

IR AND RAMAN DATA FOR THE METAL–CARBON STRETCHING REGION OF THE TETRANEOPENTYLS AND TETRASILYLMETHYLS (ν_{max} in cm^{-1})

Compound	*IR*[a]	*Raman*[b]
$(Me_3CCH_2)_4Ti$	540s, br 507s, br	[c]
$(Me_3CCH_2)_4Zr$	530s, br 488s, br	530w, br (dp?) 490s, br (p)
$(Me_3CCH_2)_4Hf$	536s, br 491s, br	535w, br (dp?) 495s, br (p)
$(Me_3CCH_2)_4Ge$	638m	630w (dp) 599s (p)
$(Me_3CCH_2)_4Sn$	592m	590w (dp) 568s (p)
$(Me_3SiCH_2)_4Ti$	500m, br	500vw, br (dp) 425s, br (p)
$(Me_3SiCH_2)_4Zr$	475m, br	470w, br (dp) 420s, br (p)
$(Me_3SiCH_2)_4Hf$	470m, br	470w, br (dp) 425s, br (p)

[a] As solutions in n-pentane (Group IVA compounds) or n-hexane (Ge and Sn compounds). [b] As solutions in cyclohexane. [c] This compound is photosensitive in solution and Raman data were not obtained.

(*iii*) Strong bands centred at 750 cm^{-1} are assigned to $\nu_{\text{sym.}}(\text{Me}_3\text{CCH}_2)$. Other bands in this region in the Ge and Sn compounds may arise from angular motions of the methylene moiety.

(*iv*) Two weak or medium intensity bands occur in $\text{Me}_3\text{CCH}_2\text{Cl}$ and the Ge and Sn compounds in the range 470 to 320 cm^{-1} centred at 460 and 360 cm^{-1}. These are assigned to deformations, $\delta_{\text{asym.}}$ and $\delta_{\text{sym.}}$ of the Me_3CCH_2 group. One band appears in the spectra of the Ti, Zr, and Hf compounds in the region 370 to 367 cm^{-1}; the position of the other band is discussed in (*v*) below.

(*v*) In the metal–carbon stretching region, the Group IVA neopentyls show contrasting features with (*a*) their Group IVB analogues, and (*b*) the Group IVA silylmethyls (see Table 3).

Two strong broad bands occur in the IR in the range 550–470 cm^{-1} in the Ti, Zr, and Hf neopentyls. These appear in the Raman spectra also (Zr, Hf), the lower energy band being much stronger and polarised. By contrast, (*a*) the Ge and Sn neopentyls show only one sharp (Ge broader than Sn) band in the IR assigned to $\nu_{\text{asym.}}(\text{MC}_4)$ with a weak depolarised counterpart in the Raman, and a single strong polarised Raman band assigned to $\nu_{\text{sym.}}(\text{MC}_4)$; and (*b*) the Group IVA silylmethyls show *one* medium broad band in the IR assigned to $\nu_{\text{asym.}}(\text{MC}_4)$ with a weak depolarised counterpart in the Raman, and a strong broad polarised band in the Raman assigned to $\nu_{\text{sym.}}$ (MC_4). The corresponding bands in tetramethyltitanium have been assigned[21]: $\nu_{\text{asym.}}$ (TiC_4) at 580 cm^{-1} in the IR and $\nu_{\text{sym.}}$ (TiC_4) at 489 cm^{-1} (p) in the Raman.

On the basis of T_d symmetry, only one MC_4 stretch, the doubly degenerate MC_4 asymmetric stretching mode (ν_3), is to be expected in the IR. A distortion from T_d leads to D_{2d} molecular symmetry, whether or not the MC_4 *skeletal* T_d symmetry is retained: this causes (*i*) the degeneracy of ν_3 to be lifted and (*ii*) the symmetric MC_4 mode (ν_1) to become weakly IR-active. In the Raman, ν_1 is polarised and ν_3 depolarised, for T_d as well as D_{2d} symmetry. Steric crowding, and hence distortion, is likely to be more severe for neopentyl than trimethylsilylmethyl complexes; however, the Sn^{4+} radius, while larger than that of Ti^{4+}, is of similar size to that of Zr^{4+} or Hf^{4+}. Hence, it is not likely that distortion is sensitively controlled by steric effects. A difference between the spectra of neopentyl complexes in the 450–500 cm^{-1} region of Ti, Zr, and Hf with on the one hand their silylmethyl analogues, and on the other $(\text{Me}_3\text{CCH}_2)_4\text{Sn}$, is the possibility of a contribution to the lower energy band by a bending mode ($\delta_{\text{asym.}}$?) of the neopentyl ligand. Thus, we propose that the lower energy band in the IR spectra of the Group IVA neopentyls is made up of contributions from ν_1, $\delta_{\text{asym.}}$(neopentyl), and a second component of $\nu_{\text{asym.}}(\text{MC}_4)$ due to molecular distortion from T_d.

(*vi*) Medium or strong bands appear in the tetraneopentyls at 242 cm^{-1} (Hf), 255 cm^{-1} (Zr), 300 cm^{-1} with 283(sh) cm^{-1} (Ti), 295 cm^{-1} with 285(sh) cm^{-1} (Ge), and 260 cm^{-1} (Sn). These are assigned to a metal–carbon bending mode, the bands moving to lower wavenumber with increasing mass of the central metal.

Photoelectron spectra show a low-energy band in the range 8.3–8.5 eV arising from the metal–carbon orbitals[22].

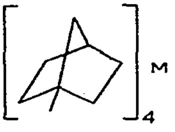
Thermal stability

Qualitative differences in stability were obtained from ^{1}H NMR observations of solutions in benzene when heated in sealed NMR tubes in the absence of light. The solutions darkened rapidly and later deposited a black solid leaving a clear (M = Zr, Hf) or pale yellow (M = Ti) supernatant solution. NMR measurements indicated that the solutions remained diamagnetic throughout, with the formation of neopentane as the sole detectable product. Measurement of the integral of the Me_4C protons relative to the integral $[Me_4C+(Me_3CCH_2)_4M]$ enabled times for ca. 50% decomposition to be obtained: (M, temperature, time) Ti, 60°, 13 h; Zr, 80°, 95 h; Hf, 90°, 900 h; *cf.*[1] data for $(Me_3SiCH_2)_4M$ to give Me_4Si; Ti, 80°, 110 h; Zr, 80°, 65 h; Hf, 90°, 350 h.

A summary of stability trends, from these results and published data, is shown in Table 4.

TABLE 4

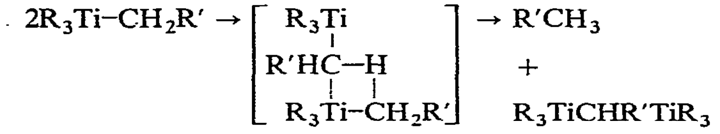
QUALITATIVE THERMAL STABILITIES OF R_4M

Compound	*Stability order*	*Ref.*
$(Me_3CCH_2)_4M$	$Ti < Zr < Hf$	
$(Me_3SiCH_2)_4M$	$Ti \gtrsim Zr < Hf$	
$(PhCH_2)_4M$	$Ti < Zr < Hf$	2
	$Ti > Zr \sim Hf$	3
$(Me_3M'CH_2)_4Ti$	$M' = C < Si$	
$(Me_3M'CH_2)_4Zr$	$C \gtrsim Si$	
$(Me_3M'CH_2)_4Hf$	$C > Si$	

The reasons for the differences in stability are, as yet, unclear. However, the following points are of note.

(*i*) The complexes are considerably more stable than the tetramethyls, and when compared one with another, differences in stability are small compared with the appropriate tetramethyl.

(*ii*) The systems are not directly comparable: the tetrabicycloheptyls contain β-hydrogens but no α-hydrogens, while the reverse is true for the other systems. If intermolecular elimination (eqn. 3) is an important decomposition pathway, then there will be clear mechanistic differences between the bicycloheptyls and the other systems (*cf.* ref. 11).



$$2R_3Ti{-}CH_2R' \rightarrow \left[\begin{array}{l} R_3Ti \\ \quad | \\ R'HC{-}H \\ \quad |\quad | \\ R_3Ti{-}CH_2R' \end{array}\right] \rightarrow \begin{array}{c} R'CH_3 \\ + \\ R_3TiCHR'TiR_3 \end{array} \qquad (3)$$

With the tetrabicycloheptyls, decomposition pathways involving the formation of bridgehead radicals (homolytic fission) or bridgehead double bonds (β-elimination) will clearly be unfavourable and these factors will enhance the stability of compounds of this type. The recent report of 1-adamantylpentacyanocobaltate(III), which is considerably more stable than its tert-butyl analogue, illustrates this point[23]. Additionally, secondary interactions between the aromatic ring and the metal in the tetrabenzyls cannot be neglected.

(*iii*) In the complexes of the late transition metals, relative stabilities $Me_3SiCH_2 > Me_3CCH_2$ have been observed[24]. Here, there is some evidence (^1H NMR) that stabilisation may be afforded by a d_π–d_π interaction between the metal and silicon in the trimethylsilylmethyl complexes, but such arguments are clearly inappropriate for the Group IVA, d^0 systems.

(*iv*) While increased crowding at the transition metal centre may increase stability by blocking vacant co-ordination sites (presumably favouring titanium), there is also the possibility of steric acceleration to decomposition in a unimolecular reaction due to overcrowding at the metal centre. Models show that tetraneopentyltitanium is not unduly crowded, and the recent report of the preparation of the even more crowded tetra-tert-butylchromium shows that this cannot be an important factor[20].

Preliminary experiments show that the decomposition of the zirconium and hafnium compounds is approximately first order in metal alkyl, and experiments are in hand to investigate the mechanism of the decompositions. Important points are the stoicheiometry, the source of the hydrogen in the neopentane, the activation energy, the nature of the black solid, and the possibility of autocatalysis.

EXPERIMENTAL

All reactions and manipulations were carried out under an atmosphere of dry argon. Solvents were dried and degassed and the metal tetrachlorides freshly sublimed/distilled before use. Neopentyllithium was prepared from neopentyl chloride and lithium sand (excess; containing 1% sodium) in n-hexane. Vibrational spectra were measured in n-pentane or n-hexane solution on a Perkin Elmer 257 Grating Spectrometer and Grubb-Parsons DM4 Spectrometer, and the Raman spectra in cyclohexane on a Cary 82 Raman Spectrometer using a Spectra Physics 165 argon ion laser operating at 5145 Å. Mass spectra were recorded on an A.E.I. MS9 Spectrometer. Molecular weights were measured cryoscopically in benzene solution (*ca.* 5% w/w) under argon. Analyses were by Bernhardt, Mülheim, and I.C.I. Ltd., Runcorn, and the University of Sussex Analytical Laboratories.

Tetraneopentylgermane and tetraneopentylstannane

Tin(IV) chloride (1.56 g, 6 mmole) was added to a solution of neopentyllithium (26 mmole) in n-hexane (100 ml). The mixture was heated to 120° with removal of the hexane by distillation. The resulting white slurry was heated at this temperature for 2 h. After hydrolysis and extraction with ether, tetraneopentyltin was obtained by sublimation (ca. $80°/10^{-3}$ mm) and crystallisation from n-hexane; m.p. 134–135°, lit.[18a] 134–135.5°.

Similarly, reaction of germanium(IV) chloride (1.3 g, 6 mmole) and neopentyllithium (26 mmole) gave a low-melting sublimate that contained two products (GLC). Preparative GLC (SE 52) afforded: (*a*) chlorotrineopentylgermane, m.p. 67–68°; IR: ν 370 cm^{-1} (Ge–Cl); ^1H NMR (CCl_4): 8.68 (CH_2), 8.92 (CMe_3) τ (Found: C, 55.6; H, 9.8. $C_{15}H_{33}ClGe$ calcd.: C, 56.05; H, 10.35%.); and (*b*) tetraneopentylgermane, m.p. 109–110°; ^1H NMR (CCl_4): 8.83 (CH_2), 8.93 (CMe_3) τ (Found: C, 67.2; H, 12.3. $C_{20}H_{44}Ge$ calcd.: C, 67.3; H, 12.4%.)

Tetraneopentyltitanium

Neopentyllithium (54 mmole) in n-hexane (200 ml) was added dropwise to a solution of titanium(IV) chloride (2.56 g, 13.5 mmole) in n-hexane (50 ml) at ca. −70° The reaction mixture became black during the addition and was stirred at room temperature for 6 h. Filtration through celite gave a black filtrate (the first few drops were yellow) which was evaporated to a black solid. Crystallisation from n-hexane (5 ml) at −70° gave a yellow-black solid which was sublimed, ca. 40°/10^{-3} mm, to give pale-yellow crystals of tetraneopentyltitanium (1.16 g, 26%). (Found: C, 72.0; H, 13.1; Ti, 14.5. $C_{20}H_{44}Ti$ calcd.: C, 72.3; H, 13.3; Ti, 14.4%.) The compound is photosensitive in solution and light was excluded where appropriate during the preparation.

Tetraneopentylzirconium

Zirconium(IV) chloride (2.03 g, 8.70 mmole) was added during 4 h to a solution of neopentyllithium (24.8 mmole) in n-hexane (220ml) and ether (50 ml) at ca. 0°. After further stirring at room temperature for 4 h, the reaction mixture was filtered and the pale-yellow filtrate evaporated to a brown solid [3.14 g, 96% as $(Me_3CCH_2)_4Zr$]. Sublimation, ca. 50°/10^{-2} mm, afforded colourless crystals of tetraneopentylzirconium (2.20 g, 68%). (Found: C, 63.1; H, 11.5; Zr, 24.1. $C_{20}H_{44}Zr$ calcd.: C, 63.9; H, 11.8; Zr, 24.3%.)

Tetraneopentylhafnium

Hafnium(IV) chloride (2.90 g, 9.05 mmole) was added during 3 h to a solution of neopentyllithium (24.8 mmole) in n-hexane (220 ml) and ether (50 ml) at ca. 0°. stirring at room temperature overnight, the reaction mixture was filtered and the pale-yellow filtrate evaporated to a brown solid [3.98 g, 95% as $(Me_3CCH_2)_4Hf$]. Crystallisation from n-pentane (10 ml) at −70° gave a white solid which was separated by decantation, washed with a small quantity of n-pentane at ca. −70°, and sublimed, ca. 50°/10^{-3} mm, to give colourless crystals of tetraneopentylhafnium (2.45 g, 59%). (Found: C, 51.6; H, 9.46. $C_{20}H_{44}Hf$ calcd.: C, 51.9; H, 9.58%.)

Oxidation of $(Me_3CCH_2)_4Ti$

Tetraneopentyltitanium (0.390 g, 1.17 mmole) in benzene (20 ml) was allowed to react with air through a calcium chloride guard tube over 12 h. The colourless solution was evaporated to a white solid which on sublimation (50°/10^{-3} mm) yielded colourless crystals of tetraneopentoxytitanium (0.373 g, 80%), m.p. 64–65°, lit.[25] 64°. ^1H NMR (C_6H_6): 5.83 (CH_2), 8.88 (CMe_3) τ.

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