Silylmethyl and Related Complexes. Part I. Kinetically Stable Alkyls of Titanium(IV), Zirconium(IV), and Hafnium(IV)

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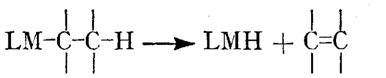
Complexes of the type $Cp_2M(CH_2M'Me_3)_2$ ($Cp = \pi\text{-}C_5H_5$; M = Ti, Zr, or Hf; M' = Si or Ge) have been prepared from $Me_3M'CH_2Li$, or less satisfactorily from the Grignard reagent, and Cp_2MCl_2 in ether. $Cp_2Zr(Cl)CH_2SiMe_3$ was prepared *via* Me_3SiCH_2MgCl in ether–methylene chloride. Isoleptic complexes $(R_nMe_{3-n}SiCH_2)_4M$ (M = Ti, Zr, or Hf; n = 0—2; R = Ph or $PhCH_2$) have been prepared by the reaction of MCl_4 with Me_3SiCH_2Li in ether or hexane, $R_nMe_{3-n}SiCH_2MgCl$ in ether, or $(R_nMe_{3-n}SiCH_2)_2Mg$ in hexane. The complexes are thermally more stable than their methyl analogues; oxidative stabilities of the isoleptic compounds correlate with the degree of steric shielding at the metal centre. Spectroscopic data are provided, and the reactions of the isoleptic compounds with water, iodine, and acetylacetone are described.

WE have drawn attention to a new class of ligands $R_3M'CH_2$– (R = alkyl or aryl; M' = Si, Ge, or Sn) in transition metal chemistry, and we have used these to prepare a number of stable metal alkyls.[1] The trimethylsilylmethyl group is known to be strongly electron releasing when attached to an electron-deficient centre,[2] and we find it has a high *trans*-influence in *trans*-$(PhMe_2P)_2Pt(Cl)CH_2SiMe_3$,[3] but not significantly different from that of other CH_2X groups (except for the neopentyl group).[4] We note that the ligands $R_3M'CH_2$ offer the following features (i)—(iv) [see also ref. 1 and ref. 5 for (i) and (ii)]. (i) It is possible to stabilise high oxidation states. (ii) The β-elimination route to decomposition, which involves migration of a β-hydrogen to the metal with elimination of an unsaturated species [equation (1)], is precluded. (iii) The complexes have considerable solubility in non-polar media. (iv) The steric requirement of the ligand is substantial and hence may lead to a blocking of vacant co-ordination sites. Factors (ii) and (iv) imply that activation energies for decomposition may be expected generally to be greater than for related alkyl complexes.



$$LM{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \longrightarrow LMH + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} \qquad (1)$$

It has been pointed out that the metal–carbon (M–C) bond is not inherently weak, homolytic fission of M–C is often less important than other pathways in decomposition, and the use of π-acceptor ligands is not necessary (see also ref. 1) to enhance stability.[5] Recent reports,[1,3,5-7] drawing attention to a range of stable complexes containing the trimethylsilylmethyl ligand, show that kinetically stable complexes, even the simple binary alkyls [*e.g.*, $(Me_3SiCH_2)_4M$],[1,5,6] are accessible, and that novel geometries can occur.[6] Problems relating to stability of transition metal alkyls have also been discussed elsewhere.[8,9] Data on complexes with Si–C–M bonds have recently been summarised.[9]

This paper reports the preparation and properties of complexes of the Group IVA metals (M = Ti, Zr, and Hf) of the types $Cp_2M(CH_2M'Me_3)_nCl_{2-n}$ ($Cp = \pi\text{-}C_5H_5$; M = Ti, Zr, and Hf; M' = Si and Ge; n = 1 or 2) and

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$(R_nMe_{3-n}SiCH_2)_4M$ (M = Ti, Zr, or Hf; $n = 0$, 1, and 2; R = Ph and $PhCH_2$).

TABLE 1

The Group IVA complexes

Compound	Starting reagent	Yield (%)	Properties
$Cp_2Ti(CH_2SiMe_3)_2$	Me_3SiCH_2Li [a]	60	Orange crystals, decomp. to black solid on heating to 300°
$Cp_2Ti(CH_2GeMe_3)_2$	Me_3GeCH_2Li [a]	70	Orange crystals, m.p. 136—138° (decomp.)
$Cp_2Zr(CH_2SiMe_3)_2$	Me_3SiCH_2Li [a]	70	White crystals, m.p. 96—97°
	Me_3SiCH_2MgCl [a]	5 [b]	
$Cp_2Zr(Cl)CH_2SiMe_3$	Me_3SiCH_2MgCl [c]	38 [b]	Pale yellow crystals, m.p. 118—121°
$Cp_2Hf(CH_2SiMe_3)_2$	Me_3SiCH_2Li [a]	50	White crystals, m.p. 83°
$(Me_3SiCH_2)_4Ti$	Me_3SiCH_2MgCl [a]	65	Pale green-yellow liquid, m.p. 0—1°,[f] b.p. *ca.* 25°, 10^{-3} mmHg
	$(Me_3SiCH_2)_2Mg$ [d]	73	
	Me_3SiCH_2Li [d,e]	69	
$(Me_3SiCH_2)_4Zr$	Me_3SiCH_2MgCl [a]	63	Colourless, pyrophoric liquid, m.p. 10—11°,[f] b.p. *ca.* 25°, 10^{-3} mmHg
	$(Me_3SiCH_2)_2Mg$ [d]	60	
	Me_3SiCH_2Li [a]	89	
$(Me_3SiCH_2)_4Hf$	Me_3SiCH_2Li [a,d]	96	Colourless, pyrophoric liquid, m. p. 8—10°,[f] b.p. *ca.* 50°, 10^{-3} mmHg
$(PhMe_2SiCH_2)_4Ti$	$(PhMe_2SiCH_2)_2Mg$ [d]	50—75	Pale green-yellow liquid, m.p. *ca.* 0°, involatile
$(PhMe_2SiCH_2)_4Zr$	$PhMe_2SiCH_2MgCl$ [a]	66	Off-white crystals, m.p. 12—14°
$(Ph_2MeSiCH_2)_4Ti$	$(Ph_2MeSiCH_2)_2Mg$ [d]	60	Pale yellow liquid
$(PhCH_2Me_2SiCH_2)_4Ti$	$(PhCH_2Me_2SiCH_2)_2Mg$ [d]	66	Pale yellow liquid

[a] In Et_2O. [b] After recrystallisation. [c] In Et_2O–CH_2Cl_2. [d] In hexane. [e] Extensive reduction took place with Et_2O as solvent. [f] The m.p.s of the isoleptic compounds are lower than expected by comparison with other compounds of the type $(Me_3SiCH_2)_4M$ (M = Cr, 40; M = V, 43; M = Pb, 24—25°), ref. 5, and may indicate a relatively large depression from traces of impurities. Microanalytical results were, however, satisfactory (see Experimental section).

TABLE 2

Spectroscopic data on the Group IVA complexes

	Chemical shift (τ) [a]						
Compound	Solvent	Ref.	Cp(s)	MeSi(s)	MCH_2Si (s)	Ph(m)	ν(M–C) cm^{-1} [b]
$Cp_2Ti(CH_2SiMe_3)_2$	$CDCl_3$	CH_2Cl_2	3·89	10·06	9·11		446
	C_6D_6	C_6H_6	4·10	9·90	9·04		
$Cp_2Ti(CH_2GeMe_3)_2$	C_6H_6	Me_4Si	4·13	9·88	8·88		444
$Cp_2Zr(CH_2SiMe_3)_2$	C_6H_6	C_6H_6	4·06	9·82	9·82		426
$Cp_2Zr(Cl)CH_2SiMe_3$	C_6H_6	C_6H_6	4·04	9·78	8·97		402 [c]
$Cp_2Hf(CH_2SiMe_3)_2$	C_6H_6	Me_4Si	4·24	9·89	10·33		
	$CDCl_3$	Me_4Si	3·95	10·02	10·37		
$(Me_3SiCH_2)_4Ti$	Hexane	CH_2Cl_2		9·68	7·63		500
	C_6H_6	C_6H_6		9·65	7·62		
$(Me_3SiCH_2)_4Zr$	Pentane	CH_2Cl_2		9·72	8·82		470
	C_6H_6	C_6H_6		9·72	8·82		
$(Me_3SiCH_2)_4Hf$	C_6H_6	C_6H_6		9·70	9·43		470
$(PhMe_2SiCH_2)_4Ti$	Pentane	CH_2Cl_2		9·51	7·73	2·6	505
$(PhMe_2SiCH_2)_4Zr$	C_6H_6	C_6H_6		9·57	8·85	2·2—2·6	475
$(Ph_2MeSiCH_2)_4Ti$	Pentane	CH_2Cl_2		9·16	7·30	2·35	520
$(PhCH_2Me_2SiCH_2)_4Ti$	Pentane	CH_2Cl_2		9·68	7·77 [d]	2·6—2·9	500

[a] s = Singlet, m = Multiplet; chemical shifts (τ) taken as: $CHCl_3$ 2·73, C_6H_6 2·73, CH_2Cl_2 4·70. All the compounds gave correct integrations. [b] Bands broad, medium. [c] ν(Zr–Cl) at 345 cm^{-1} obscured by Cp band. [d] $SiCH_2Ph$ as shoulder.

Compounds containing the π-Cyclopentadienyl Ligand.—The preparation and properties of these compounds are summarised in Table 1. Compounds of the type $Cp_2M(CH_2M'Me_3)_2$ are best prepared by reaction (2).

$$Cp_2MCl_2 + 2Me_3M'CH_2Li \xrightarrow{Et_2O} Cp_2M(CH_2M'Me_3)_2 + 2LiCl \quad (2)$$

This method is similar to that used in the preparation of the dimethyl compound, Cp_2TiMe_2,[10] although only in the preparation of $Cp_2Ti(CH_2SiMe_3)_2$ could the mixture be satisfactorily worked-up by hydrolysis; considerable decomposition took place in the preparation of the zirconium analogue when the reaction mixture was treated with oxygen-free ice-water. However, the enhanced solubility conferred by the trimethylsilylmethyl ligand enabled the products to be obtained by extraction with hexane. Trimethylgermylmethyllithium[4] showed similar reactivity to the silicon compound.

The Grignard reagent was less satisfactory giving $Cp_2Zr(CH_2SiMe_3)_2$ in only 5% yield (*cf.*, 70% using Me_3SiCH_2Li), while with $PhMe_2SiCH_2MgCl$ we were unable to isolate the expected $Cp_2M(CH_2SiMe_2Ph)_2$ (M = Ti or Zr).

The use of ether–tetrahydrofuran (THF) as solvent in preparations involving the lithium reagents gave products that did not contain the Me_3SiCH_2– group. Spectra suggested the composition $(Cp_2MCl)_2O$; there is evidence that the Ti–Cl bond in the compounds Cp_2TiClR (where R is a bulky group, *e.g.*, CH_2Bu^t or CH_2Ph) is relatively easily ionised,[11] and this would be enhanced in the

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more polar THF. It may also be relevant that reaction of Ph_3SnLi with Cp_2TiCl_2 in THF gave a Ti^{III} product, $Cp_2Ti(THF)SnPh_3$.[12]

A number of mono-alkyls of Ti [11,13] and Zr [14] have been prepared by the reaction of a Grignard reagent with the appropriate Cp_2MCl_2 in methylene chloride. We find that reaction of trimethylsilylmethylmagnesium chloride with Cp_2ZrCl_2 in ether–methylene chloride gives a satisfactory yield (38% after recrystallisation) of $Cp_2Zr(Cl)CH_2SiMe_3$. However, the titanium analogue was obtained in poor yield by this method, while reaction of Me_3SiCH_2Li (1 mol) with Cp_2TiCl_2 (1 mol) in ether gave a mixture (1 : 2) of $Cp_2Ti(CH_2SiMe_3)_2$ and $Cp_2Ti(Cl)CH_2SiMe_3$.

The ^1H n.m.r. data are in Table 2. The differences in chemical shift of the methylene protons in the series $Cp_2M(CH_2SiMe_3)_2$ correlate well with differences in electronegativity of the metals, with a progressive upfield shift from Ti to Hf (*cf.*, data on Cp_2MX_2).[15] The vibrational spectra show bands characteristic of the groupings Cp_2M and $CH_2M'Me_3$. Of interest are the bands assigned to ν(M–C) which occur at 425 ± 25 cm^{-1}. In $Cp_2Zr(Cl)CH_2SiMe_3$, an unambiguous assignment of ν(Zr–Cl) could not be made as it is in all probability obscured by a Cp band at 345 cm^{-1}. The compounds $Cp_2M(CH_2SiMe_3)_2$ (M = Ti or Zr) and $Cp_2Zr(Cl)CH_2SiMe_3$ showed weak parent ions in their mass spectra.

The complex $Cp_2Ti(CH_2SiMe_3)_2$ reacted rapidly with an excess of hydrogen chloride in ether to give Cp_2TiCl_2 quantitatively. In an attempt to prepare compounds of the type $Cp_2M(Cl)CH_2SiMe_3$ we carried out a carefully controlled reaction of $Cp_2Zr(CH_2SiMe_3)_2$ with one equivalent of hydrogen chloride at both room temperature and −78°. However, a mixture of starting material and Cp_2ZrCl_2 was obtained in both cases. A similar effect has been found in the related platinum(II) dialkyls, although the compounds $(R_3P)_2Pt(Cl)CH_2SiMe_3$ were accessible by this route; [4] the effect is attributed to the bulk of the trimethylsilylmethyl substituent and its enhancement of solubility, the still soluble and less hindered monochloroalkyl complex reacting preferentially with hydrogen chloride.

The compounds were considerably more thermally stable than the simple alkyls, although decomposition was rapid on exposure to air in solution. The solids were briefly stable upon exposure to air. $Cp_2Ti(CH_2SiMe_3)_2$ was indefinitely stable at *ca.* 20° but decomposed when heated to give a black solid. The Zr and Hf compounds were more stable, melting to colourless liquids and resolidifying unchanged after 1 h at 100°. $Cp_2Zr(Cl)CH_2SiMe_3$ sublimed with little decomposition at *ca.* 90°. Thus, the thermal stabilities lie in the order Hf ~ Zr > Ti, and as a class parallel the aryls [16] (which decompose *via* benzynes) [17] and benzyls,[18] being stable at *ca.* 100°, whereas the methyl [10,19] and ethyl [20] analogues decompose at or near ambient temperature.

The Isoleptic Compounds $(R_3SiCH_2)_4M$.—The simple alkyls of the Group IVA metals are generally unstable (*e.g.*, Me_4Ti decomposes at or near −70°).[21] As well as the β-elimination reaction for transition metal alkyls, there is evidence that disproportionation (both intra- and inter-molecular) is important in the decomposition of tetramethyltitanium.[22] These two routes are of lower activation energy than simple homolysis of the Ti–C bond. Bulky groups not containing β-hydrogens (or leading to thermodynamically unstable 'olefinic' fragments, *e.g.*, $Me_2Si{=}CH_2$) will clearly render such routes to decomposition less favourable, and hence increase their kinetic stability. The isolation of tetrabenzyls [23] and the recent report of tetrakisbicyclo[2.2.1]hept-1-yls [24] of titanium, zirconium, and hafnium show that stable binary alkyls are accessible and that their stability is kinetic in origin.

The compounds were prepared by three methods, as summarised in Table 1 and equations (3)—(5). The

$$4R_3SiCH_2MgCl + MCl_4 \xrightarrow[Et_2O]{-50\text{ to }0°} (R_3SiCH_2)_4M + 4MgCl_2 \quad (3)$$

$$4Me_3SiCH_2Li + MCl_4 \xrightarrow[Et_2O\text{ or }n\text{-}C_6H_{14}]{0°} (Me_3SiCH_2)_4M + 4LiCl \quad (4)$$

$$2R_3SiCH_2MgCl + 2\text{ dioxan} \xrightarrow{Et_2O} (R_3SiCH_2)_2Mg + MgCl_2(dioxan)_2 \downarrow;\ 2(R_3SiCH_2)_2Mg + MCl_4 \xrightarrow[n\text{-}C_6H_{14}]{0°} (R_3SiCH_2)_4M + 2MgCl_2 \quad (5)$$

reactions proceeded smoothly giving the products in good yield (50 to 90%). Whereas in the preparation of tetrabenzyltitanium from benzylmagnesium chloride some reduction to Ti^{III} took place, with dibenzylmagnesium this was negligible.[23a] We also find that the purest compounds are obtained using the dialkylmagnesium rather than the Grignard reagent; using the

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latter, the Ti product is coloured. Reactions of Me_3SiCH_2Li with $TiCl_4$ in hexane, $ZrCl_4$ in ether, or $HfCl_4$ in *ether–hexane* proceeded smoothly, but extensive reduction took place with $TiCl_4$ in ether. We formulate the following order for the reducing ability of the reagents used: $Me_3SiCH_2Li > Me_3SiCH_2MgCl > (Me_3SiCH_2)_2Mg$ (which parallels their reactivity as alkylating agents), with Ti^{IV} reduced more readily than Zr^{IV} or Hf^{IV}.

The stoicheiometry for the reactions is critical. The purity of the crude product (as judged by analysis for Group IVA metal, magnesium, or lithium, and chloride) indicated a preferred *ca.* 5% excess of MCl_4. Under exact stoicheiometric conditions, the magnesium or lithium content became significant [possibly due to the presence of soluble species, such as $(R_3SiCH_2)_4M{\cdot}Mg(CH_2SiR_3)_2$], whereas with greater than 5% excess, the chloride content increased [possibly due to the presence of soluble stable species such as $(R_3SiCH_2)_3MCl$]. The reactions were reproducible, and at *ca.* 5% excess of MCl_4, magnesium and chloride were less than 5 mol % with respect to the Group IVA metal.

We were unable to isolate the expected product from the reaction between $TiCl_4$ and HMe_2SiCH_2MgCl in ether, obtaining a low yield of an ether-soluble material which decomposed slowly at 0°.

The isoleptic compounds are extremely soluble in hydrocarbons. The trimethylsilylmethyl compounds, which are liquids at room temperature, are miscible in all proportions with n-pentane. On cooling to $-78°$, crystals of the pure compounds are deposited from concentrated pentane solutions. Solubility for the titanium compounds of the type $(Ph_nMe_{3-n}SiCH_2)_4Ti$ decreases in the sequence: $n = 0 > 1 > 2$.

Four compounds, $(Me_3SiCH_2)_4M$ (M = Ti, Zr, or Hf) and $(PhMe_2SiCH_2)_4Zr$, were carefully purified for microanalysis and for an investigation of their thermal stability. The Ti and Hf compounds were purified by distillation (at 10^{-3} mmHg) and the Zr compounds by repeated crystallisation from n-pentane. The pure products were heated at 80° in benzene solution in sealed n.m.r. tubes in the absence of light. The solutions rapidly darkened to a deep brown, eventually depositing a brown-black solid. N.m.r. showed that the solutions remained diamagnetic with the formation of Me_4Si, or appropriately $PhSiMe_3$, as the sole detectable product. Approximate times for 50% decomposition at 80° were: $(Me_3SiCH_2)_4Ti$, 110; $(Me_3SiCH_2)_4Zr$, 65; $(Me_3SiCH_2)_4Hf$, 350 (at 90°); $(PhMe_2SiCH_2)_4Zr$, 500 h. Initial measurements on pure $(Me_3SiCH_2)_4Zr$ showed that the benzene solvent had little effect on the rate of decomposition; measurements after 24 h were not possible in this case due to extensive line broadening presumably associated with the deposition of the brown-black solid. Impure samples were less stable: both $(Me_3SiCH_2)_4Ti$ and $(Me_3SiCH_2)_4Zr$ decomposed significantly on distillation at temperatures below 50°. All the compounds are extremely sensitive to air and moisture, $(Me_3SiCH_2)_4M$ (M = Zr or Hf) being pyrophoric. Qualitatively, stability to air decreased in the sequence: Ti > Zr > Hf; $(Ph_2MeSiCH_2)_4M > (PhMe_2SiCH_2)_4M > (Me_3SiCH_2)_4M$.

Details of i.r. and n.m.r. spectra are in Table 2. The MeSi and MCH_2Si protons appear as singlets as expected, the upfield shift of the methylene protons for the zirconium compounds being consistent with electronegativity differences. The vibrational spectra are as expected for compounds containing the R_3SiCH_2 ligands with broad, medium intensity bands assigned to $\nu_{asym}(MC_4)$ at *ca.* 500 (M = Ti) and *ca.* 470 cm^{-1} (M = Zr or Hf). No ions containing zirconium were detected in the mass spectrum of $(Me_3SiCH_2)_4Zr$ (admitted *via* a break-seal), but an ion assigned to $[(Me_3SiCH_2)_3Ti]^+$ was present in the spectrum of $(Me_3SiCH_2)_4Ti$.

The purified products gave satisfactory microanalytical results (see Experimental section). We have also adopted the criteria (i)—(v) outlined below, to characterise the series of compounds. This is particularly relevant to those compounds where final purification for microanalysis was not attempted. The data are in Table 3.

TABLE 3

Molecular weight (*M*), iodinolysis, and hydrolysis data on the isoleptic complexes

Compound	*M* [a] Found (required)	$M : I_2$ [b]	$M : R_3SiMe$ [c]
$(Me_3SiCH_2)_4Ti$	399 (396)	1 : 3·94	
$(Me_3SiCH_2)_4Zr$	466 (439)	1 : 3·81	
$(PhMe_2SiCH_2)_4Ti$	613 (644)	1 : 4·25	1 : 4·14
$(PhMe_2SiCH_2)_4Zr$	664 (687)	1 : 4·20	1 : 4·08
$(Ph_2MeSiCH_2)_4Ti$		1 : 4·7	1 : 4·04
$(PhCH_2Me_2SiCH_2)_4Ti$		1 : 4·20	1 : 3·95

[a] Determined by cryoscopy in C_6H_6 of a *ca.* 10% w/w solution. [b] Ratio of metal to I_2 consumed determined from reaction $MR_4 + I_2$ (excess). [c] Ratio of metal to methylsilane evolved on hydrolysis.

(i) Analysis for Group IVA metal, magnesium, or lithium, and chloride was carried out subsequent to hydrolysis. Crude products contained less than 5 mol % of magnesium and chloride with respect to Group IVA metal. After purification, magnesium and chloride were present in negligible amounts. (ii) Molecular weights, measured in benzene (*ca.* 10% w/w), by cryoscopy under argon, showed the compounds to be monomeric in the solvent. (iii) Hydrolysis with 3M nitric acid gave *ca.* 4 mol of the appropriate methylsilane ($MeSiR_3$) per mol of Group IVA metal. (iv) Iodinolysis showed that *ca.* 4 mol of iodine per mol of Group IVA metal were consumed upon reaction of the isoleptic complex with an excess of iodine in hydrocarbon solution at 0°. With compounds containing Ph–Si bonds, values greater than 4 were obtained, but this was probably due to competing iodinolysis of the Ph–Si bond. (v) The colour of products afforded a good guide of purity, using criteria (i)—(iv). As expected for d^0 complexes, the isoleptic compounds are colourless or pale yellow.

These isoleptic compounds are considerably more stable than Me_4Ti, and of similar stability to the tetrabenzyls and bicyclo[2.2.1]hept-1-yls, which may be rationalised on the basis of the bonding and steric requirement of the ligands. Thus, crystal structures of the tetrabenzyls[25] show an interaction between the benzene nucleus and the metal, with angles at the α-C approximating to 90°, while the high steric requirement of the bicycloheptyl group more effectively shields the metal from incoming reagents.[24] The increasing air stabilities in the orders Hf < Zr < Ti and $(Me_3SiClH_2)_4M <$ $(PhMe_2SiCH_2)_4M < (Ph_2MeSiCH_2)_4M$ correlate well with the expected degree of steric shielding at the metal centre, increased crowding hindering the attack of reagents (oxygen or water) at the metal centre. Thermal stabilities also follow the order $(Me_3SiCH_2)_4Hf >$ $(Me_3SiCH_2)_4Zr < (Me_3SiCH_2)_4Ti$ and $(Me_3SiCH_2)_4Zr <$ $(PhMe_2SiCH_2)_4Zr$. The mechanism of the thermal decompositions is under investigation. Since the neopentyl group has a higher steric requirement than the trimethylsilylmethyl group it is to be expected that the tetraneopentyls will be the more stable. We have prepared *inter alia* the neopentyls of Ti and Zr [26,27] and find that $(Me_3CCH_2)_4Zr$ is somewhat more stable, decomposing slowly in benzene solution at 80° with 50% decomposition after *ca.* 95 h [*cf.* $(Me_3SiCH_2)_4Zr$, *ca.* 65 h]. The preparation of these and other isoleptic neopentyls has been recently reported;[28] our results will be presented in Part II.

TABLE 4

^1H n.m.r. data for $(Me_3SiCH_2)_nZr(acac)_{4-n}$ (n = 2 or 3) [a]

		Chemical shift (τ) [b]			
Compound	Solvent	MeSi	$ZrCH_2Si$	Me(acac)	H(acac)
$(Me_3SiCH_2)_2Zr(acac)_2$	C_6H_6	9·77	9·12	8·15	4·47
	Hexane	10·07	*c*	7·95	4·16
$(Me_3SiCH_2)_3Zr(acac)$	C_6H_6	9·78	8·75	8·15	4·46
	Hexane	9·97	8·88	7·80	3·99

[a] Benzene as reference (τ 2·73). [b] Singlet resonances. [c] Obscured by solvent peaks.

Like the tetrabenzyls,[29] the silylmethyl compounds [27] and $(Me_3CCH_2)_4Zr$ [27] are active in the polymerisation of olefins and dienes; this too will be reported in detail elsewhere.

The isoleptic compounds are stable over a period of hours in the presence of halogenated solvents (CCl_4, $CHCl_3$, and CH_2Cl_2) but react readily with reagents containing an acidic hydrogen (*e.g.*, the halogen acids, alcohols, or acetylacetone). The reaction between $(Me_3SiCH_2)_4Zr$ and acetylacetone (acacH) has been examined, using mol ratios of 1 : 2 or 1 : 1 acacH. The reactions proceeded smoothly at *ca.* −70°, and from the ^1H n.m.r. spectra of the crude products we find that $(Me_3SiCH_2)_2Zr(acac)_2$ is the sole product of the former reaction, but that at 1 : 1 stoicheiometry a mixture of $(Me_3SiCH_2)_2Zr(acac)_2$, $(Me_3SiCH_2)_3Zr(acac)$, and $(Me_3SiCH_2)_4Zr$ in ratios of 1 : 7 : 0·3, respectively, is produced. Similar product ratios were obtained on reaction at −20°. The ^1H n.m.r. data are in Table 4. That a mixture of products is obtained in the 1 : 1 reaction is not altogether unexpected as it is known that compounds of the type $X_3Ti(acac)$ readily disproportionate, equation (7).[30]

$$2X_3Ti(acac) \rightleftharpoons X_4Ti + X_2Ti(acac)_2 \qquad (7)$$

EXPERIMENTAL

All reactions and manipulations were carried out under an atmosphere of purified argon or nitrogen. Solvents were dried and degassed before use. Titanium and zirconium tetrachlorides were freshly distilled or sublimed before use. Lithiomethyltrimethyl-silane and -germane were prepared from chloromethyltrimethylsilane (germane) and lithium 'shot' (*ca.* four-fold excess) in ether or hexane and stored at −20°. The Grignard and derived organomagnesium reagents were freshly prepared for each reaction. Vibrational spectra were determined as Nujol mulls or in pentane or hexane solution. Analyses were by Bernhardt, Mülheim, I.C.I. Ltd., Runcorn, and the University of Sussex Analytical Laboratories.

Compounds of the Type $Cp_2M(CH_2M'Me_3)_2$.—*Bis*(π-*cyclopentadienyl*)*bis*(*trimethylsilylmethyl*)*titanium*(IV), $Cp_2Ti(CH_2SiMe_3)_2$. Lithiomethyltrimethylsilane (7·6 mmol) in ether (10 ml) was added over 1 h to a suspension of titanocene dichloride (0·867 g, 3·43 mmol) in ether (20 ml) at *ca.* 12°. The resulting yellow solution was stirred for 20 min and cooled to 0°. Oxygen-free ice-water was added and the mixture stirred for 1 min before transfer to a separating funnel. The blue aqueous layer was separated and chloride ion determined gravimetrically as silver chloride (0·9908 g, 100%). The green organic layer was dried over molecular sieve (Type 4A) at −20° for 3 h and the resulting orange solution filtered. Removal of the solvent gave golden crystals of *the product* (0·74 g, 60%) (Found: C, 61·1; H, 9·55. $C_{18}H_{32}Si_2Ti$ requires C, 61·3; H, 9·15%). When heated slowly to 300° the compound darkened to a black solid.

Bis(π-*cyclopentadienyl*)*bis*(*trimethylgermylmethyl*)*titanium*(IV), $Cp_2Ti(CH_2GeMe_3)_2$.—Lithiomethyltrimethylgermane (8·5 mmol) in ether (16 ml) was added over 15 min to a suspension of titanocene dichloride (1·00 g, 4·02 mmol) in ether (25 ml) at 0°. The mixture was warmed to room temperature and the volatiles removed. The green residue was extracted with hexane (50 ml) and filtered. Concentration of the green filtrate to *ca.* 15 ml and cooling to

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−20° afforded orange crystals of *the product* (1·23 g, 70%), m.p. 136—138° (decomp.) (Found: C, 49·8; H, 7·8. $C_{18}H_{32}Ge_2Ti$ requires C, 49·0; H, 7·3%).

Bis(π-*cyclopentadienyl*)*bis*(*trimethylsilylmethyl*)*zirconium*-(IV), $Cp_2Zr(CH_2SiMe_3)_2$.—Lithiomethyltrimethylsilane (36 mmol) in ether (30 ml) was added over 20 min to a suspension of zirconocene dichloride (5·00 g, 17·1 mmol) in ether (50 ml) at 0°. The mixture was stirred at room temperature for ½ h and the volatiles were then removed. The residue was extracted with hexane (50 ml), filtered, and the filtrate cooled to −20° to give white needles of *the product* (4·73 g, 70%). An analytical sample was obtained by sublimation at 80°, 10^{-4} mmHg, m.p. 96—97° (to a colourless liquid) (Found: C, 54·8; H, 8·0; Si, 14·3. $C_{18}H_{32}Si_2Zr$ requires C, 54·6; H, 8·15; Si, 14·2%).

A preparation from zirconocene dichloride (4·94 g, 16·9 mmol) and trimethylsilylmethylmagnesium chloride (50 mmol) in ether (50 ml) gave the compound (0·30 g, 5%), m.p. 84—86°, after recrystallisation from hexane.

Bis(π-*cyclopentadienyl*)*bis*(*trimethylsilylmethyl*)*hafnium*-(IV), $Cp_2Hf(CH_2SiMe_3)_2$.—Lithiomethyltrimethylsilane (7·2 mmol) in ether (6 ml) was added over 15 min to a suspension of hafnocene dichloride (1·02 g, 2·69 mmol) in ether (20 ml) at 0°. The mixture was allowed to warm over 1 h and then the volatiles were removed. Extraction of the residue with hexane (40 ml) and concentration of the filtrate to *ca.* 10 ml followed by cooling to −20° gave *the product* as white needles (0·65 g, 50%), m.p. 83° (Found: C, 44·9; H, 7·0. $C_{18}H_{32}HfSi_2$ requires C, 44·75; H, 6·7%).

Chlorobis(π-*cyclopentadienyl*)*trimethylsilylmethylzirconium*-(IV), $Cp_2Zr(Cl)CH_2SiMe_3$.—Trimethylsilylmethylmagnesium chloride (31·8 mmol) in ether (35 ml) was added over 2 h to zirconocene dichloride (9·27 g, 31·8 mmol) in methylene chloride (75 ml) at 0°. The reaction mixture was stirred at room temperature for 3 h and filtered to give a pale yellow filtrate. Volatiles were removed to afford a pale yellow solid which was dissolved in methylene chloride (50 ml) and cooled to −78° to give pale yellow needles. These were recrystallised from hexane–toluene (1 : 1) to give *the product* (4·1 g, 38%), m.p. 118—121° (Found: C, 49·0; H, 6·1; Cl, 10·6. $C_{14}H_{21}ClSiZr$ requires C, 48·9; H, 6·15; Cl, 10·3%).

Reaction of $Cp_2Ti(CH_2SiMe_3)_2$ *with an Excess of Hydrogen Chloride.*—Hydrogen chloride (*ca.* 9 mmol) in ether (2 ml) was added to $Cp_2Ti(CH_2SiMe_3)_2$ (0·0803 g). An exothermic reaction took place with deposition of a red solid which was identified as titanocene dichloride (0·0589 g, 96%).

Reaction of $Cp_2Zr(CH_2SiMe_3)_2$ *with Hydrogen Chloride.*—Hydrogen chloride (4·4 mmol) in ether (10 ml) was added over 15 min to a solution of $Cp_2Zr(CH_2SiMe_3)_2$ (1·76 g, 4·46 mmol) in ether (5 ml). A white solid was deposited. Volatiles were removed and the residual white powder extracted with hexane (2 × 40 ml). Filtration gave zirconocene dichloride as the white residue (0·580 g, 1·99 mmol), and evaporation of the filtrate gave unreacted starting material (0·977 g, 2·47 mmol). Similar results were obtained when the reaction was repeated at *ca.* −78°.

Compounds of the Type $(R_3SiCH_2)_4M$.—The methods of preparation and properties of these compounds are summarised in Table 1 and equations (3)—(5), with typical preparations shown in (a)—(e).

(a) *Tetrakis*(*trimethylsilylmethyl*)*titanium*(IV), $(Me_3SiCH_2)_4Ti$. Titanium tetrachloride (29·4 g, 155 mmol) was added dropwise over 3·5 h at *ca.* −20° to a solution of trimethylsilylmethylmagnesium chloride, prepared from chloromethyltrimethylsilane (75·8 g, 620 mmol) and magnesium turnings (16 g, 0·66 mol) in ether (600 ml). The resulting slurry was stirred at 0° for 1·5 h and filtered to give a brown filtrate. The filtrate was evaporated to give the crude product as a brown liquid (40·1 g, 65%). Distillation to a liquid nitrogen cooled probe, at 25—30°, 10^{-3} mmHg, gave *tetrakis*(*trimethylsilylmethyl*)*titanium*(IV), m.p. 0—1° to a pale green-yellow liquid (Found: C, 48·6; H, 11·3; Si, 28·0; Ti, 12·3. $C_{16}H_{44}Si_4Ti$ requires C, 48·4; H, 11·15; Si, 28·3; Ti, 12·1%).

(b) *Tetrakis*(*trimethylsilylmethyl*)*zirconium*(IV), $(Me_3SiCH_2)_4Zr$. To a solution of lithiomethyltrimethylsilane (78·8 mmol) in ether (106 ml) at 0° was added zirconium tetrachloride (4·81 g, 20·7 mmol) in portions over 1·5 h. The resulting slurry was stirred at 0° for 2 h and filtered to give a pale yellow filtrate. Evaporation of the filtrate gave the crude product (7·64 g, 89%) as an orange liquid. Repeated crystallisation from pentane afforded *tetrakis*(*trimethylsilylmethyl*)*zirconium*(IV) as white crystals, m.p. 10—11° to a colourless liquid (Found: C, 43·6; H, 9·85; Si, 25·3; Zr, 20·7. $C_{16}H_{44}Si_4Zr$ requires C, 43·7; H, 10·1; Si, 25·5; Zr, 20·7%).

(c) *Tetrakis*(*trimethylsilylmethyl*)*hafnium*(IV), $(Me_3SiCH_2)_4Hf$. This *compound* was prepared from $HfCl_4$ in ether–hexane, using the procedure of (b), and purified by distillation (*ca.* 50°, 10^{-3} mmHg) (Found: C, 36·2; H, 8·3; Si, 21·1. $C_{16}H_{44}HfSi_4$ requires C, 36·4; H, 8·4; Si, 21·3%)

(d) *Tetrakis*(*dimethylphenylsilylmethyl*)*zirconium*(IV), $(PhMe_2SiCH_2)_4Zr$. Zirconium tetrachloride (8·42 g, 36·2 mmol) was added at 0° to a solution of dimethylphenylsilylmethylmagnesium chloride in ether [prepared from chloromethyldimethylphenylsilane (26·7 g, 145 mmol) and magnesium turnings (3·8 g, 157 mmol) in ether (200 ml)]. The slurry was stirred overnight at 0° and then at room temperature for 4 h. Filtration gave a pale orange filtrate that was evaporated to give the crude product as an orange liquid (16·4 g, 66%). Repeated crystallisation from pentane gave *tetrakis*(*dimethylphenylsilylmethyl*)*zirconium*(IV) as off-white crystals, m.p. 12—14° to a faintly yellow liquid (Found: C, 62·6; H, 7·7; Si, 16·0; Zr, 12·9. $C_{36}H_{52}Si_4Zr$ requires C, 62·8; H, 7·6; Si, 16·3; Zr, 13·25%).

(e) *Tetrakis*(*dimethylphenylsilylmethyl*)*titanium*(IV), $(PhMe_2SiCH_2)_4Ti$. Freshly distilled 1,4-dioxan (1 mol) was added to an ethereal solution of dimethylphenylsilylmethylmagnesium chloride (1 mol) and the resulting slurry stirred for 1 h. Filtration afforded a colourless ethereal solution of the dialkylmagnesium reagent which was estimated by a total-base titration. Then a portion of this solution was evaporated to give the dialkylmagnesium reagent (45·0 mmol) as a white solid that was slurried in hexane (80 ml). To this slurry at 0° a solution of titanium tetrachloride (4·35 g, 23 mmol) in hexane (30 ml) was added over 30 min. The mixture was stirred at 0° overnight and filtered to give a pale yellow filtrate, which on evaporation afforded the crude *product* as pale yellow-green liquid (7·21 g, 50%), m.p. *ca.* 0°.

Reactions of Isoleptic Complexes with Iodine.—A solution containing a known quantity of Group IVA metal (or metal tetra-alkyl) was added to iodine at *ca.* −70°, the reaction

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mixture warmed to 0°, and stirred at 0° for *ca.* 3 h. Excess of iodine was determined by titration of the hydrolysed mixture with sodium thiosulphate solution.

Hydrolysis of Isoleptic Compounds.—A solution containing a known quantity of Group IVA metal (or metal tetra-alkyl) was hydrolysed in 3M nitric acid and to the organic layer was added toluene (1·00 ml). The amount of methylsilane produced was determined by n.m.r. from the ratio of the integrated MeSi and PhMe resonances.

We thank the S.R.C. for the award of a studentship (to M. R. C.) and the Corporate Laboratory and Dr. D. G. H. Ballard of I.C.I. Ltd., for their support.

[2/1981 *Received, 21st August*, 1972]