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Amido-derivatives of Metals and Metalloids. Part X.¹ Reactions of Titanium(ɪv), Zirconium(ɪv), and Hafnium(ɪv) Amides with Unsaturated Substrates, and Some Related Experiments with Amides of Boron, Silicon, Germanium, and Tin(IV)

By G. Chandra, A. D. Jenkins, M. F. Lappert, * and R. C. Srivastava, School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Insertion reactions of amides $LM-(NR_2)_n$ with the dipoles AB to give the adducts $LM(NR_2)_{n-x}(A-B-NR_2)_x$ are described. The amides included the Group IVA [M(NMe2)4 (M = Ti. Zr, or Hf)] and IVB [Me3M·NMe2 (M = Si, Ge, or Sn)] compounds and ρ -C₆H₄O₂B·NEt₂, while the dipoles were PhNCO, PhNCS, MeNCS, p-MeC₆H₄·-N:C:N·C₆H₄Me-p, C₆H₁₁·N:C:N·C₆H₁₁, MeO₂C·C:C·CO₂Me, CO₂, CS₂, CH₂·CH·CN, PhCN, p-MeC₆H₄·CN,

CH2:CCI(CN), C6F5 CN, CCI3 CN, RCH·CH2·S, CH2·CH2·CO·O and MeCH:CH·CHO. The problems discussed are the stoicheiometry of the reaction, the structure of the adducts, and the relative reactivities of the various amides and dipoles.

EARLIER parts of this series have dealt with aspects of the chemistry of some amido-derivatives LM-NR₂ of elements M of Groups III-V and especially of the quadrivalent compounds of tin, titanium, zirconium, and hafnium.

This paper is mainly concerned with insertion reactions [equation (1)] of Group IVA dimethylamides $M(NMe_2)_4$ (M = Ti, Zr, or Hf), of the related compounds $R_3M^1 \cdot NMe_2$ (M¹ = Si, Ge, or Sn) and of o-C₆H₄O₂B·NEt₂, with 1,2-dipoles AB. Results are reported on the following AB systems: PhNCO, PhNCS, MeNCS, p-MeC₆H₄·N:C:N·C₆H₄Me-p, C₆H₁₁·N:C:N·C₆H₁₁, MeO₂C·C:C·CO₂Me, CO₂, CS₂, CH₂:CH·CN, PhCN, p-MeC₆H₄·CN, CH₂:CCl(CN), C₆F₅·CN, CCl₃·CN, RCH·CH₂·S (a 1,3-dipole), CH₂·CH₂·CO·O (a 1,4-dipole), and MeCH:CH·CHO.

$$LM-NR_2 + A=B \rightarrow LM-A-B-NR_2$$
 (1)

These data are complementary to earlier results on amides of boron,²⁻⁴ silicon,³⁻⁵ germanium,⁴ tin(IV),^{3,4,6} and phosphorus(III); ⁶ a few of these have already been briefly noted.7

Since the generality of equation (1) was recognised,⁸ such reactions have been realised for amides of Li, Mg, B, Al, Si, Ge, Sn^{IV}, Pb^{IV}, P^{III}, As^{III}, Sb^{III}, Bi^{III}, S^{IV}, Ti^{IV}, Ti^{III}, Zr^{IV}, Hf^{IV}, V^{IV}, Nb^{IV}, Nb^V, Ta^V, Cr^{III}, and Zn.^{9,10} Unsaturated compounds need not necessarily behave in the sense of equation (1). Thus, (a) if AB also has protic character (e.g., C_5H_6), an amine elimination

¹ Part IX, G. Chandra, T. A. George, and M. F. Lappert, J

Chem. Soc. (C), 1969, 2565.
² R. H. Cragg and M. F. Lappert, Adv. Chem. Ser., 1964, No. 42, 220; Idem and B. P. Tilley, J. Chem. Soc., 1964, 2108; R. Jefferson, M. F. Lappert, B. Prokai, and B. P. Tilley, J. Chem. Sci. (J. 1066), 1564. Soc. (A), 1966, 1584; R. H. Cragg, M. F. Lappert, H. Nöth, P. Schweizer, and B. P. Tilley, *Chem. Ber.*, 1967, **100**, 2377. ³ J. R. Horder and M. F. Lappert, J. Chem. Soc. (A), 1969,

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⁴ T. A. George and M. F. Lappert, J. Organometallic Chem., 1968, **14**, 327.

⁵ R. H. Cragg and M. F. Lappert, J. Chem. Soc. (A), 1966, 82.

⁶ T. A. George, K. Jones, and M. F. Lappert, J. Chem. Soc., 1965, 2157.

⁷ G. Chandra and M. F. Lappert, *Inorg. Nuclear Chem.* Letters, 1965, 1, 83; G. Chandra, T. A. George, and M. F. Lappert, Chem. Comm., 1967, 116.

reaction may occur,¹¹ (b) if AB has good leaving groups (e.g. F, Cl, or OR), a metathetical exchange reaction (with NR_2) is a possibility,¹² (c) if AB has a combination of characteristics (a) and (b), an elimination reaction (e.g.,¹³ dehydrochlorination of CH:C·CH₂Cl) may be favoured, while (d) if the product of equation (1) is capable of reacting with further molecules of AB, then telomerisation (as⁴ with CH₂:CH·CHO-Et₃SnNMe₂) or polymerisation [as ¹⁴ with CH₂:CH·CN-Ti(NMe₂)₄] of AB becomes feasible.

The problems which are involved in the present work are the establishment, in the sense of equation (1), of (i) the stoicheometry of the reaction, (ii) the mode of attachment of the 1,2-dipole to the metal for the case where AB is potentially an ambident nucleophile (e.g., $R\bar{N}-\bar{C}=S$ or $RN=\bar{C}-\bar{S}$, (iii) the possibility of alternative reaction paths (a)—(d), (iv) the relative reactivities of the various amides and dipoles, respectively, (v) the structures of the adducts, and (vi) differences in structures or reaction patterns within recognisable series (e.g., comparison between Ti^{IV} and Zr^{IV}). Reactions (1) are apparently favoured only by those dipoles AB which are susceptible to nucleophilic attack. This suggests a dipolar reaction, with the nucleophilicity of the amide ligand providing the initial driving force, although a cyclic transition-state (I) remains a possibility.

$$A = B$$

⁸ K. Jones and M. F. Lappert, Proc. Chem. Soc., 1962, 358. ⁹ Cf. (for early bibliography) M. F. Lappert and B. Prokai, Adv. Organometallic Chem., 1967, 5, 225.

¹⁰ Cf. (for most recent paper) H. A. Meinema and J. G. Noltes, Inorg. Nuclear Chem. Letters, 1970, 241.

¹¹ K. Jones and M. F. Lappert, Proc. Chem. Soc., 1964, 22;

 ¹² (a) T. A. George and M. F. Lappert, J. Chem. Soc. (A), 1968, 1940.
 ¹² (a) T. A. George and M. F. Lappert, Chem. Comm., 1966, 463; (b) J. Chem. Soc. (A), 1968, 992; (c) P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, ibid., 1969, 2106.

¹³ D. J. Cardin and M. F. Lappert, Chem. Comm., 1967, 1034; A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, unpublished work.

¹⁴ A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, J. Polymer Sci. (B), 1968, 6, 865.

Reactions with Phenyl Isocyanate.—Tetrakisdimethylamido-derivatives of titanium, zirconium, and hafnium, each reacted exothermically at room temperature with an excess of the isocyanate to give the corresponding tetrakisureido-derivative $M(NPh\cdot CO\cdot NMe_2)_4$, (II).

Compounds (II) decomposed upon attempted distillation or sublimation. Alcoholysis gave known compounds [equation (2)]. As reaction (2) afforded no dimethylamine, the possibility of (II) being the product of multistep insertions, *i.e.* of structure (III) or (IV), is ruled out. C=O. Details of the ¹H n.m.r. spectra of (II; M = Ti, Zr, or Hf) and (V) are shown in Table 2. The $-NMe_2$ protons absorbed as singlets for (II) and a doublet (Ti-NMe₂ and CNMe₂) for (V), thereby indicating (unless there is fluxional behaviour, which is unprecedented in this class of compound) that all the NMe₂ and TiNMe₂ protons are, for each set, magnetically equivalent. On the basis of the i.r. and ¹H n.m.r. spectra and equation (2), the structures (VI) and (VII) (X = O and Ar = Ph) are suggested; co-ordination numbers of six and eight are quite normal in Group IVA.¹⁵ This suggestion also

:

$$\begin{array}{c} \text{Ti}(\text{NPh} \cdot \text{CO} \cdot \text{NMe}_2)_4 + 4 \text{Pr}^1 \text{OH} \longrightarrow 4 \text{HNPh} \cdot \text{CO} \cdot \text{NMe}_2 + \text{Ti}(\text{OPr}^1)_4 \qquad (2) \\ (II) & & & & & \\ \text{(II)} & & & & & & \\ \text{(Me}_2\text{N})_2 M(\text{NPh} \cdot \text{CO} \cdot \text{NPh} \cdot \text{CO} \cdot \text{NMe}_2)_2 \\ (III) & & & & & & \\ \text{(III)} & & & & & \\ \text{(IIV)} & & & & \\ \end{array}$$

The behaviour of tetrakis(dimethylamido)titanium with phenyl isocyanate in varying stoicheiometric ratios was examined. Reactions in 1:1 and 1:2 molar ratios

is consistent with (i) the failure to observe 1,1- or 1,3-adducts, and (ii) the greater reluctance of zirconium compared with titanium to form a 1,2-adduct, a higher

TABLE	1
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I.r. data on some new compounds ^a

	ν(C=O) δ	(cm1)	v(C=C)	ν (C=N)
Compound	Co-ordinated	Free	(cm1)	(cm1)
(II: $M = Ti$)	1555vs.br		1600vs	· · ·
(II; M = Zr)	1545vs,br		1595s	
(II; M = Hf)	1550vs,br		1595s	
(V)	1573vs		1600vs	
(VIII; $M = Ti, R = Me$)				1550 vs
(VIII; $M = Zr, R = Me$)				1542 vs
(IX; $M = Ti$, $R = p-MeC_6H_4$)				1630s
$(1X; M = Ti, R = C_6 H_{11})$				1637w
$(IX; M = Zr, R = C_6 H_{11})$				1640m
$(IX; M = HI, R = C_6 H_{11})$	1505-	1700	1000	1645m
(\mathbf{X})	10805	1732111	1630m	
(ΔI)	1590vs	1600sh	10405	
$(XII \cdot M - Ti \Delta r - Ph)$	159075	1050511	1586vc	1558278
(XII; M - 7r, Ar - Ph)			1595vs	1573vs
(XII); $M = Hf$, $Ar = Ph$			1608vs	1590vs
(XII: $M = Ti$, $Ar = p$ -MeC _e H _e)			1635s	1571vs
(XII; $M = Zr$, $Ar = p - MeC_eH_e$)			1640sh	1590vs
(XII; $M = Hf$, $Ar = p - MeC_{e}H_{A}$)			1645s	1595vs
(XIII)			$[\nu(C\equiv N), 2$	213 cm. ⁻¹]
(XV)			1640s	1605vs
(XVI)				1665 vs
(XVIII)	1635vs			
$(XIX; M = Ti, R = Me)^{b}$	1645vs			
$(XIX; M = Hf, R = Et)^{b}$	1636vs			

^a vs = Very strong, br = broad, s = strong, m = medium, w = weak, sh = shoulder. ^b May be compared with ν (C=O) in Me₃Si·O·CO·CH₂·CH₂·NEt₂ at 1720 cm.⁻¹ (see ref. 30).

both afforded the 1,2-adduct $(Me_2N)_2Ti(NPh \cdot CO \cdot NMe_2)_2$, (V); while with 3 moles of phenyl isocyanate, the 1,4-adduct, (II), was obtained.

By contrast, the zirconium amide (1 mole) with phenyl isocyanate (2 moles) gave the 1,4-adduct, (II) (M = Zr).

None of the compounds (II) (M = Ti, Zr, or Hf) or (V) showed absorption at *ca.* 2250 cm.⁻¹, characteristic of ν_{as} (N=C=O), but showed ν (C=O) (co-ordinated) at 1545—1573 cm.⁻¹ (see Table 1) with no strong band at *ca.* 1650 cm.⁻¹ which would be assigned to unco-ordinated

¹⁵ Cf. R. J. H. Clark, 'The Chemistry of Titanium and Vanadium,' Elsevier, Amsterdam, 1968.

co-ordination number being more readily accommodated by the larger central-metal ion.



Derivatives of compound (II) dissolved in benzene. A solution of the titanium compound gave, upon evaporation of the solvent, a dark-red spongy solid of the composition $Ti(NPh\cdot CO\cdot NMe_2)_4, C_6H_6$; the benzene was

displaced either by heating the complex at $55-60^{\circ}/0.01$ mm. Hg, or when it was shaken with diethyl ether.

Reaction with Isothiocyanates.—Phenyl isothiocyanate (4 moles) afforded the 1,4-adduct $M(NR \cdot CS \cdot NMe_2)_4$; (VIII; M = Ti, R = Ph), with the titanium amide. The titanium and zirconium amides and methyl isothiocyanate likewise gave (VIII; M = Ti or Zr, R =Me). The i.r. spectrum of compounds (VIII) did not show absorption at ca. 2100 cm.⁻¹, characteristic of v_{as} (N=C=S). The strong band at 1593 cm.⁻¹ in (VIII; M = Ti, R = Ph) is probably the $CC(A_1)$ phenyl ring stretch; it is possible, however, that this masks a C=N

Zr) did not show the parent ion, but the intense base peak at 44 mass units below the molecular ion may be assigned as $[parent - NMe_2]^+$. We consider it likely that compounds (IX) have the chelate structure (VII) (X = NArand Ar = p-tolyl or cyclohexyl); this might account, on steric grounds for their reluctance to react with more of the carbodi-imide.

Reactions with Dimethyl Acetylenedicarboxylate.— Stable σ-organo-derivatives of titanium, (X), and zirconium, (XI), were obtained by the reaction in equimolar quantities of the amide $M(NMe_2)_4$ and dimethyl acetylenedicarboxylate at -78° . At room temperature, how-

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N.m.r. data (ch	emical sinns,	t) on some ne	w compounds -		
Compound	Solvent	Standard	CNMe ₂	\mathbf{Ph}	Me ₃ Sn
(II: $M = Ti$)	CH ₂ Cl ₂	CH ₂ Cl ₂	7.58s	2.90m	
(II; M = Zr)	$C_{B}\overline{D}_{B}$	TMS -	7.82s	3.00m	
(V) b	CH,Cl,	CH ₂ Cl ₂	7.46s	3.15m	
$(VIII; M = Zr, R = Me)^{\circ}$	C _s H _s	C ₆ H ₆	7.29s		
Ti(OCONMe ₂) ₄	CH2Cl2	CH ₂ Cl ₂	7.98s		
(XII; M = Ti, Ar = Ph)	$C_6 \overline{D_6}$	TMS	7·30s	2.72m	
(XII; M = Zr, Ar = Ph)	$C_6 D_6$	TMS	7.51s	2·86m	
(XII; M = Hf, Ar = Ph)	THĚ	TMS	7.67s	3·1m	
(XII): $M = Zr$, $Ar = p - MeC_6H_4$) ^d	$C_6 D_6$	TMS	7.88s	3∙4m	
(XV)	C ₆ H ₆	C_6H_6	7·18s, 7·29m		9∙83s
Me.Śn·SCH. CH. MMe.	$C_{6}H_{6}$	$C_{6}H_{6}$	7.91s		9.67s
(XŬIII) ^f	C_6H_6	C ₆ H ₆	$7{\cdot}24d$		9.80s

 $s = Singlet, m = multiplet, t = triplet. {}^{b} Ti - NMe_2 at \tau 6.85(s). {}^{e} = NMe at \tau 6.47(s). {}^{d} C - Me at \tau 8.42(s). {}^{e} - CH_2 - CH_2 - at \tau 7.47(m). {}^{f} Also - COCH_2 - at \tau = 7.74(t) and - OCH_2 - at \tau = 6.27(t).$

stretch. By analogy with (VIII; M = Zr, R = Me) this is quite likely, since this compound has a strong band at 1542 cm.⁻¹ and the titanium analogue shows similar absorption at 1550 cm.⁻¹, both assigned to a C=N vibration. The C=S stretching frequency in thioamides and thioureas is generally found 16 as an intense band at 1234-1053 cm.⁻¹. The ¹H n.m.r. spectrum of (VIII; M = Zr, R = Me) showed sharp singlets for =NMe and -NMe₂ protons. Alcoholysis (PrⁱOH) of (VIII; M = Ti, R = Ph) gave the known $Ti(OPr^{i})_{4}$ and HNPhC(:S)NMe₂, but no dimethylamine, thereby excluding the possibility that (VIII) has a structure related to (III) or (IV). On the basis of the foregoing evidence, we suggest that compounds (VIII) are chelates with an eight-co-ordinate central metal (VI; X = S and Ar = Ph or Me).

Unlike halogenoboranes,¹⁷ titanocene dichloride, Ti- $(\pi$ -C₅H₅)₂Cl₂ did not react with phenyl isothiocyanate.

Reactions with Carbodi-imides.-The guanidino-derivatives of titanium, zirconium, and hafnium, of the type $(Me_2N)_2M[NAr \cdot C(NMe_2):NAr]_2$ Ar = p-tolyl or cyclohexyl), (IX), were synthesised by reaction of the appropriate amide $M(NM_2)_4$ (1 mole) with the appropriate carbodi-imide (2-4 moles).

Upon alcoholysis (MeOH), dimethylamine (2 moles) was liberated, and the appropriate methoxide and guanidine were identified. The i.r. spectra of (IX) did not show the -N=C=N asymmetric stretching absorption at 2200-2100 cm.⁻¹; the C=N stretching frequencies are listed in Table 1. The mass spectra of (IX; M = Ti or IX)16 Cf. L. J. Bellamy, 'Advances in Infrared Group Frequencies,' ed. Methuen, London, 1969, ch. 5 and 6.

ever, and in contrast with the behaviour of the Group IVB amides Me₃M·NMe₂ (ref. 4) even a trace of the amide caused the polymerisation or polycondensation of the acetylenedicarboxylic ester (see ref. 18 for related reactions with organic bases). Compounds (X) and (XI)



were stable, reddish brown powders, which dissolved in benzene and carbon tetrachloride but then slowly decomposed. Upon hydrolysis, (X) liberated 2 moles of dimethylamine, while no amine was liberated in the case of (XI). This supports the hypothesis that insertion into the triple bond is accompanied by amination of the ester

 ${\rm Ti}({\rm NMe}_2)_4$ group. Similar aminations (e.g., MeCO₂Et -(MeCO·NMe₂) have been established.¹ Compounds (X) and (XI) were further characterised by their i.r. spectra (Table 1). The presence and position of two C=O stretching vibrations is consistent with the suggested structures. The greater preference of titanium, rather than zirconium, for the lower co-ordination number may again be attributed to their relative radii.

In contrast to the behaviour of the Group IVA metal

M. F. Lappert and B. Prokai, J. Chem. Soc., 1963, 4223.
 O. Diels, Ber., 1942, 75B, 1452; R. M. Acheson and G. A.

Taylor, J. Chem. Soc., 1960, 1691.

amides, some Group IVB compounds $R_3M \cdot NMe_2$ (R = Me and M = Si; $R = Bu^n$ and M = Ge) gave simple products of insertion (rather than also of amination) $R_3M \cdot C(CO_2Me): C(CO_2Me) \cdot NMe_2$ (see also ref. 4).

Reactions with Carbon Dioxide and Disulphide.-Reactions of the amides $M(NR_2)_4$ (M = Ti or Zr) with carbon disulphide have been reported; 19 the products were the dithiocarbamates $M(S \cdot CS \cdot NR_2)_4$, which were formulated as having the central metal in an eight-coordinate environment. Tetrakis(dimethylamido)titanium and carbon dioxide gave the pale-yellow solid tetracarbamate, which was almost insoluble in light petroleum, benzene, and carbon tetrachloride, but soluble in dichloromethane. The i.r. spectrum showed a very strong and broad absorption at 1590 cm.⁻¹, which is assigned to the co-ordinated C=O stretching vibration, and a shoulder at 1690 cm.⁻¹, which may be due to the unco-ordinated C=O stretching mode. The ¹H n.m.r. spectrum in methylene dichloride, however, showed a singlet at τ 7.98 (C-NMe_o).

An attempt to synthesise the tetradithiocarbamate by reacting the tetracarbamate with carbon disulphide failed; the partially substituted product Me₂N·CO·O·Ti-(S·CS·NMe₂)₂ was obtained. This compound was insoluble in common organic solvents, and may be polymeric. The CS₂/CO₂ displacement reaction is interesting and suggests that Ti4+ has some 'b' character,20 like Sn⁴⁺ but in contrast to Si⁴⁺.⁶

Reactions with Nitriles.-Acrylonitrile. Like Et₃Sn-- NMe_2 ,⁴ other compounds $R_3M \cdot NMe_2$ (R = Me and M = Sn; $R = Bu^n$ and M = Ge; but not R = Me and M =Si) furnished 1,1-adducts with acrylonitrile;⁴ Group IVA metal amides, however, $[M(NMe_2)_4 \text{ and } (\pi - C_5H_5)_2M (NMe_2)_2$ initiate its polymerisation even at -78° , to give high molecular weight polyacrylonitrile, probably via multistep molecular insertions, with initiator reactivities decreasing in the two series $M(NMe_2)_4 >$ $(\pi - C_5 H_5)_2 M(NMe_2)_2$, and Hf $\approx Zr > Ti.^{14}$ The 1,1-adduct of the tin amide and acrylonitrile did not react with further acrylonitrile. The difference between the Group IVA and IVB amides does not lie in the different chosen functionalities, since tetrakis(dimethylamino)stannane Sn(NMe₂)₄ afforded only a 1,4-adduct with acrylonitrile.²¹

Benzonitrile and p-Toluonitrile.-The zirconium and hafnium amides $M(NMe_2)_4$ reacted exothermically at room temperature with each nitrile to give the 1,4-adducts $M[N:C(NMe_2)Ar]_4$, (XII), whereas the titanium analogue reacted only at 100° and this gave dark-brown viscous liquids which were not characterised and decomposed upon attempted distillation. Compounds (XII) were yellow hygroscopic solids, which could not be volatilised below their decomposition temperature. Upon alcoholysis (MeOH), the corresponding methoxide and amidine were obtained. The i.r. spectra showed a strong C=N stretching vibration (Table 1) but no absorption between

2000-2500 cm.⁻¹, thus excluding the possibility of the nitrile simply behaving as a ligand. The intense base peak in the mass spectra of compounds (XII) may be assigned to $[N=C(NMe_2)R]^+$, but no parent ion was observed. ¹H N.m.r. spectra (Table 2) showed features consistent with the proposed four-co-ordinate structures (XII). These are among the first Group IVA metal amidino-complexes (see also ref. 22).

Compounds (XII), like their parent amides, polymerised acrylonitrile at room temperature.

a-Chloroacrylonitrile.—The addition of some aminostannanes to certain olefins containing strong electronwithdrawing groups has been shown to take place even under quite mild conditions.⁴ Not surprisingly, therefore, dimethylaminotrimethylstannane was found to react with α -chloroacrylonitrile at room temperature to give a brown liquid, formulated as Me₂N·CH₂·CCl(CN)·-SnMe₃, (XIII), which decomposed upon attempted distillation. The i.r. spectrum of (XIII) showed a strong C=N stretch at 2213 cm.⁻¹ and absence of C=C (at ca. 1605 cm.⁻¹).

Similarly, the Group IVA amides $M(NMe_2)_4$ (M = Ti or Zr) and α -chloroacrylonitrile gave, at low temperatures, yellow 1,4-adducts, which became brown at room temperature. These adducts, which did not liberate dimethylamine upon alcoholysis, are presumably polymeric, as they were involatile and insoluble in common organic solvents. A black mass was obtained when the zirconium adduct was freed from solvent below 0° and warmed to room temperature. The instability of the Group IVA adducts is attributed to the usual weakness associated with Group IVA metal-carbon o-bonds.

Pentafluorobenzonitrile.---Nucleophilic substitution of monosubstituted pentafluorobenzenes (which predominantly give *para*-isomers) is well-known.²³ Cyanopentafluorobenzene and dimethylaminotrimethylstannane, not unexpectedly, therefore, reacted at 0° according to equation (3), which is analogous to the reaction of the same amide and hexafluorobenzene to yield dimethylaminopentafluorobenzene.24 Evidently, substitution [equation (3)] is favoured over the potentially competing nitrile insertion into the Sn-N bond; a related reaction is described in the Experimental section:

$$Me_3Sn \cdot NMe_2 + C_6F_5CN \longrightarrow Me_3SnF + p - C_6F_4(NMe_2) \cdot CN$$
 (3)
(XIV)

 $Me_3Sn \cdot NMe_2 + C_6F_5Br \longrightarrow Me_3SnF + \rho - C_6F_4(NMe_2)Br$

However, compound (XIV) was shown to react with further tin amide to give the 1,1-adduct [equation (4)]. Reaction (4) may proceed because the alternative substitution reaction is unfavoured by blockage of the most reactive (para- to CN) position and by the electron-

¹⁹ D. C. Bradley and M. H. Gitlitz, Chem. Comm., 1965, 289; J. Chem. Soc. (A), 1969, 1152. ²⁰ S. Ahrland, J. Chatt, and N. R. Davies, Quart. Rev., 1958,

^{2, 265.}

J. Lynch, M.Sc. Thesis, University of Sussex, 1966.
 D. C. Bradley and M. C. Ganorkar, *Chem. and Ind.*, 1968, 1521.

 ²³ Cf. J. C. Tatlow, Endeavour, 1963, 22, 89.
 ²⁴ T. A. George and M. F. Lappert, J. Chem. Soc. (A), 1969, 992.

amines²⁹ has been supposed to involve the formation of an intermediate cyclic sulphonium ion, which then opens at the centre carbon atom while capturing a negative

$$\rho - C_6 F_4 (NMe_2) \cdot CN + Me_3 Sn \cdot NMe_2 \longrightarrow Me_3 Sn \cdot N = C(NMe_2) \cdot C_6 F_4 \cdot NMe_2 - p \quad (4)$$

amidine, $HN=C(NMe_2)\cdot C_6F_4\cdot NMe_2-p$, when boiled with water.

The silicon amide Me₃Si·NMe₂ was shown to react with cyanopentafluorobenzene in the sense related to equation (3), but not to (4), no doubt due to the greater reactivity of the Sn-N rather than the Si-N bond.

The reactions of the Group IVA metallocene diamides $[(\pi\text{-}C_5H_5)_2M(NMe_2)_2~(M=Zr~or~Hf)]$ with cyanopentafluorobenzene has been utilized for synthesising the corresponding metallocene difluorides.^{12c} The titanium amide Ti(NMe₂)₄ and cyanopentafluorobenzene afforded (XIV) and a light-brown solid, insoluble in common organic solvents, which did not liberate dimethylamine upon alcoholysis, and which may be $F_x Ti[N=C(NMe_2)$. $C_6F_5]_x$.

Trichloroacetonitrile.—The lack of reaction between the amides Ti(NMe₂)₄ or Me₃Sn·NMe₂ and t-butyl cyanide is probably due to the fact that nitriles are not really effective 1,2-dipoles unless they have strong electronwithdrawing groups.²⁵ Acetonitrile was shown to react with the tin amide as a protic species,²⁶ although surprisingly it behaved ²² as a 1,2-dipole with Group IVA metal amides.

The Sn-N bond (like Sn-O)²⁵ was cleaved [equation (5)] by trichloroacetonitrile.

$$Me_{3}SnNMe_{2} + CCL_{3}CN - Me_{3}Sn \cdot N = C(NMe_{2})CCL_{3}$$
(5)
(XVI)

Compound (XVI) showed a strong C=N stretch at 1665 cm.⁻¹, but no absorption at *ca*. 2250 cm.⁻¹ [ν (C=N)] in its i.r. spectrum. It decomposed with explosive violence when distillation through a small Vigreaux column was attempted (this may be due to Me₃SnCl + carbene formation). Upon hydrolysis, (XVI) afforded trimethyltin hydroxide and trichloroacetamidine HN:C(NMe₂)·CCl₃.

Reactions with Epoxides and Cyclic Sulphides.—Cyclic

monomers of the type $RCH\cdot CH_2 \cdot X$ (X = O or S) may be polymerised by Lewis acids or strong bases.²⁷ Insertion of Sn-N in a formal 1,3-manner has been observed with some epoxides; 28 however, a trace of lithium diethylamide was required as catalyst; a chain process, with LiO·CHR·CH₂·NEt₂ as a propagating species, may be involved. The Group IVA amides Ti(NMe2)4 and $Hf(NEt_2)_4$ did not react with ethylene or propene oxide, and lithium dimethylamide failed to initiate a reaction between the titanium amide and propene oxide at 60°.

The ring cleavage of alkene sulphides by secondary

25 A. G. Davies and P. G. Harrison, J. Chem. Soc. (C), 1967,

ion. The amide Et₃Sn·NMe₂ reacted with propene sulphide [equation (6a)] to give the amide (XVII), the identity of which [and especially to distinguish it from the isomer Et₃Sn·S·CH₂·CHMe·NMe₂] was established by an alternative synthesis [equation (6b)].



Similarly, dimethylaminotrimethylstannane and ethylene sulphide gave the thioethanolamide Me₃Sn·S·CH₂· CH₂·NMe₂; these Sn-S compounds failed to react with boiling ethanol, consistent with the class (b) character of $R_{3}Sn^{+}$. The titanium compound $Ti(NMe_{2})_{4}$ caused the polymerisation of ethylene sulphide.¹⁴

β-Propiolactone.--Possible modes of ring opening in the reactions of β -propiolactone with metal amides are shown in equation (7).

$$R_{3}M \cdot NR^{1}R^{2} + CH_{2} \cdot CH_{2}CO \cdot O - \begin{pmatrix} M=Si,Ge \\ (\alpha) \end{pmatrix} R_{3}M \cdot O \cdot CO \cdot CH_{2}CH_{2} \cdot NR^{1}R^{2} \\ (\alpha) \end{pmatrix} R_{3}MO \cdot CH_{2}CH_{2}CO \cdot NR^{1}R^{2}$$
(7)
$$M=Sn R_{3}MO \cdot CH_{2}CH_{2}CO \cdot NR^{1}R^{2}$$

In practice both types of C-O cleavage: (a) alkyl-Ofission and (b) acyl-O-fission have been observed.³⁰ In the present study, reaction (7b) was confirmed by synthesising the amido-alkoxide Me₃SnO·CH₂·CH₂·CONMe₂, (XVIII), also by an alternative route $(Me_3Sn \cdot NMe_2 +$ HO·CH₂·CH₂·CO·NMe₂). The structure of (XVIII) was also established by its i.r. (see Table 1) and n.m.r. (see Table 2) spectra.

Acyl-O-fission was also observed, with the amides $Ti(NMe_2)_4$ and $Hf(NEt)_4$, to yield the amido-alkoxides $M(O \cdot CH_2 \cdot CH_2 \cdot CO \cdot NR_2)_4$ (M = Ti and R = Me; M = Hf and R = Et). Both products were also independently synthesised (from HO·CH₂·CH₂·CO·NMe₂). Unlike the Group IVB analogues, they were unaffected by methanol, which, with their i.r. spectra, supports the chelate structure (XIX).

Reactions of Aminoboranes.-These are relatively unreactive and did not insert CH₂=CHX (X=CN, CO·OMe), CH_2 =CClY (Y = Cl and CN), and PhCH=

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 A. Tzchach and E. Reiss, J. Organometallic Chem., 1967, 8, 255. ²⁹ B. Hansen, Acta Chem. Scand., 1959, **13**, 151. ²⁹ B. Hansen, Acta Chem. Scand., Tetrahedron
- ³⁰ Y. Ishii, K. Itoh, and S. Sakai, Tetrahedron Letters, 1966, 4941; J. Org. Chem., 1966, 31, 3948.

^{1313.} ²⁶ K. Jones and M. F. Lappert, J. Organometallic Chem., 1965, **3**, 295.

2.

CH-CN. This may be due to the considerable B-N bond strength and their somewhat lower basicity. However,



o-phenylene diethylaminoboronate, when treated with crotonaldehyde at 20° , gave an orange 1,1-adduct

$${}^{o-C_{6}H_{4}O_{2}BNEt_{2}+CH_{3}CH=CH\cdot CHO}$$

$${}^{o-C_{6}H_{4}O_{2}B\cdot O\cdot CH(NMe_{2})\cdot CH\cdot CH_{3}}$$

$$(8)$$

[equation (8)], which showed no i.r. absorption at *ca*. 1680 cm.⁻¹ [the expected region for v(C=O)].

EXPERIMENTAL

General procedure have been described in earlier parts. Known compounds were identified as described and additionally by comparing their i.r. spectra with authentic specimens.

Tetrakis(dimethylamido)-titanium, -zirconium, and -hafnium were prepared as described in Part VI. cyanates.—Two typical experiments are described. Further details are in Table 3.

Phenyl isocyanate (12.75 g., 4.25 mol.) in light petroleum (b.p. 40—60°; 10 ml.) was added dropwise with constant stirring to tetrakis(dimethylamido)titanium (5.65 g., 1 mol.) in the same solvent (20 ml.). The reaction was exothermal. Orange crystals formed. The reaction mixture was set aside (ca. 12 hr.) and was then filtered. The orange tetrakis-(NN-dimethyl-N'-phenylureido)titanium (14.12 g., 80%), m.p. 149°, was washed with light petroleum (3×15 ml.) and was freed from solvent at 20°/0·1 mm. (2 hr.).

A portion (2.51 g., 1 mol.) of this product was heated under reflux (2 hr.) with isopropyl alcohol (3.5 g., >4 mol.) in benzene (20 ml.). Amine was not liberated. The mixture was freed from volatiles under reduced pressure and was then shaken with light petroleum (15 ml.). NN^4 Dimethyl-N'-phenylurea (2.11 g., 89.8%) (Found: C, 65.7; H, 7.3; N, 16.9. Calc. for C₉H₁₂N₂O: C, 65.8; H, 7.4; N, 17.1%) [v(N-H), 3320 cm.⁻¹], was filtered off, washed with light petroleum (3 × 15 ml.), and freed from solvent at 21°/0.01 mm. (2 hr.). The combined filtrate and washings afforded titanium tetrakisisopropoxide (0.72 g., 70.7%), b.p. 45°/0.01 mm.

Similarly, methyl isothiocyanate (0.90 g., 4 mol.) in light petroleum (b.p. 40–60°; 5 ml.) was added to tetrakis-(dimethylamido)zirconium (0.82 g., 1 mol.) in the same solvent (10 ml.) at 20°. A mild exothermic reaction ensued and a white solid formed. The mixture was stirred ($\frac{1}{2}$ hr.) and was then freed from volatiles under reduced pressure.

TABLE 3

Characterisation of insertion products of Group IVA metal amides and some dipoles a

				Reactio	n conditio	ons		P	1 (0/)				1 (0()	· ·
Compound			Temp.	Time	Yield	M.p.		Found	1 (%)			Requi	red (%	.) .
$(Me_2N)_{4-n}M(A-B-NMe_2)_n$		(°C)	(hr.)	(%)	(°Ĉ)	C	н	Ν	м	c	H	Ν	M	
м	n	AB												
Ti	4	PhNCO	20	12	80.0	149	61 ·0	6.3	15.9	6.7	61.7	6.3	16.0	6.8
Zr	4	PhNCO	20	12	95.0	158 - 160			14.9	12.5			15.1	12.5
Hf	4	PhNCO	20	12	60.0	177			13.4	21.4			13.5	21.5
Ti	2	PhNCO	20	12	88.5	123(d)	56.9	7.4	18.0	10.5	57.1	7.4	18.2	10.4
Tið	4	PhNCO	20	12	99.9		64.0	6.6	14.3	$6 \cdot 1$	64.7	6.5	14.4	6.15
Ti۰	4	PhNCS	20	12	99.5		56.65	6.1	14.7	6.3	56.5	5.8	14.7	6.3
Zr	4	MeNCS	20	1	81.4		34.5	7.1	19.7	15.9	34.3	6.5	20.0	16.3
Ti	2	R ¹ N=C=NR ¹	20	12	100	> 150(d)			16.3	6.9			16.7	7.2
Ti	2	$R^2N=C=NR^2$	20	24	63.0	148(d)	64.1	10.8	17.6	$7 \cdot 5$	$64 \cdot 1$	10.8	17.6	7.5
Zr	2	R ² N=C=NR ²	20	12	81.8	227(d)	59.9	10.1	16.3	13.5	60.0	10.0	16.5	13.4
Hf	2	$R^2N=C=NR^2$	20	12	81.1	()			14.3	$23 \cdot 1$			14.6	2.35
Zr	4	PhCN	20	2	89.0	> 120(d)	64.1	6.1	16.3	13.3	63.6	6.5	16.5	13.4
Hf	4	PhCN	20	2	96.0	>100(d)	55.8	6.1	14.8	23.8	56.4	5.8	14.6	23.3
Zr	4	p-MeC.H.CN	20	2	95.0	> 85(d)'	65.5	7.5	15.0	12.9	65.3	7.1	15.2	12.4
Hf	4	p-MeC H CN	20	2	90.0	>85(d)			13.8	22.0			13.6	21.7
Ti ^d	4	CH,=CClČN	-78	2	87.8	>150(d)			18.6	7.7			19.5	$8 \cdot 3$
Zr•	4	CH,=CCICN	-50	2	81.4	>150(d)	37.9	5.4	18.6	14.4	38.9	$5 \cdot 2$	18.2	14.8
		<u> </u>				- ()								
Ti	4	$\dot{C}H_2CH_2\dot{C}(:O)$	0	1	94.7				10.6	9.7			10 ·9	9.3
۹F	$R^1 = p$ -	MeC_6H_4 ; $R^2 = C$	6H11. & Ti	(NPh·CO	·NMe ₂) ₄ ,C	He. Four	nd: S, 1	6.0. 1	Require	d: S,	16.8%	4 Fo	und:	Cl, 21.3
Requ	ired: C	Cl, 24.7%. • Fou	nd: Cl, 21.	5. Requ	ired: Cl,	Ž2·9%.			-					

Molecular weights were determined isopiestically with a Mechrolab vapour pressure osmometer, i.r. spectra with Perkin-Elmer 237 and 337 instruments, ¹H n.m.r. spectra with a Varian A.60 or H.A.100 spectrometer, and mass spectra with an A.E.I. M.S.9 instrument; relevant spectroscopic data on new compounds are shown in Tables I and 2. Titanium products were usually, except the yellow aliphatic nitrile adducts, orange-red to red-brown, and the zirconium and hafnium compounds were yellow or white. The residue was triturated with light petroleum (10 ml.), and then filtered to yield the white, microcrystalline *tetrakis*(NNN'-*trimethylthioisoureido*)*zirconium* (2·4 g., 81·4%). A portion (0·80 g.) of this product was heated under reflux (1 hr.) with water (0·5 ml.) in benzene (5 ml.). Zirconium-(IV) oxide was filtered off and the filtrate and washings afforded NNN'-trimethylthioisourea (0·54 g., 80·0%) (Found: C, 40·9; H, 8·4; N, 23·5. C₄H₁₀N₂S requires C, 40·6; H, 8·5; N, 23·7%) [v(N-H), 3270 cm.⁻¹; v(C=N), 1540 cm.⁻¹], m.p. 80°.

Reactions of Metal Amides with Isocyanates and Isothio-

Reactions of Metal Amides with Carbodi-imides.—Two experiments are described. Further details are in Table 3.

Tetrakis(dimethylamido)titanium (1.68 g., 1 mol.) was treated with bis-(p-tolyl)carbodi-imide (3.33 g., 2 mol.) in light petroleum (b.p. 0—40°; 40 ml.). A dark-red solution was obtained. Removal of solvent under reduced pressure afforded bis(dimethylamido)bis-(N-p-tolyl-N'N'-dimethyl-N''p-tolylguanidino)titanium (5.01 g., 100%), as an orange, spongy solid, soluble in methylene chloride.

Tetrakis(dimethylamido)zirconium (3.29 g., 1 mol.) in light petroleum (b.p. 40-60°; 10 ml.) was slowly added, with stirring, to bis(cyclohexyl)carbodi-imide (10.15 g., 4 mol.) in the same solvent (30 ml.). An exothermic reaction ensued and a white solid separated out. The reaction mixture was set aside (ca. 12 hr.) and was then filtered. White, crystalline bis(dimethylamido)bis-(N-cyclohexyl-N'N'dimethyl-N''-cyclohexylguanidino)zirconium (6.84 g., 81.8%), insoluble in ether, methylene chloride, pyridine, or dimethyl sulphoxide, but sparingly soluble in hot benzene and tetrahydrofuran was obtained after washing with light petroleum (4 × 15 ml.) and solvent removal at 20°/0.05 mm. (3 hr.). It was sublimed at 210-30°/0.05 mm. The combined filtrate and washings afforded unchanged bis(cyclohexyl)carbodi-imide (6.60 g.) [v(N=C), 2138 cm.⁻¹].

A portion (2·28 g., 1 mol.) of the adduct was heated under reflux (ca. 2 hr.) with methanol (3·0 g., >2 mol.) in benzene. Dimethylamine (0·29 g., 96·7%) was liberated and white crystals separated. The reaction mixture was freed from volatiles and was again heated under reflux (ca. 1 hr.) with methanol (10 ml.). Zirconium methoxide (0·51 g., 70·8%) was filtered off and washed with methanol (2 × 10 ml.). The combined filtrate and washings afforded N-cyclohexyl-N',N'-dimethyl-N''-cyclohexylguanidine (1·40 g., 83·3%) (Found: C, 71·2; H, 11·5; N, 16·5. Calc. for C₁₅H₂₉N₃: C, 71·5; H, 11·6; N, 16·7%) [v(N-H), 3410 cm.⁻¹, v(C=N), 1642 cm.⁻¹], b.p. 86°/0·1 mm., as a viscous liquid which slowly solidified to white needles.

Reaction of Tetrakis(dimethylamido)titanium with Dimethyl Acetylenedicarboxylate.—Dimethyl acetylenedicarboxylate (2·30 g., 1 mol.) in diethyl ether (8 ml.) was added dropwise to a solution of tetrakis(dimethylamido)titanium (3·63 g., 1 mol.) in the same solvent (20 ml.) at -78° . An exothermic reaction ensued, to give a dark-brown liquor and a reddish brown solid. The mixture was set aside (ca. 12 hr.) at -20° and was then filtered. The solid was washed (3 × 15 ml.) with ether and dried to give the reddish brown 1: 1-complex, MeO·(Me₂N)₂Ti·C(CO·NMe₂)= C(CO₂Me)·NMe₂ (3·0 g., 50·6%) (Found: N, 14·7; NMe₂, 23·0; Ti, 12·7. C₁₄H₃₀N₄O₄Ti requires N, 15·3; NMe₂, 24·1; Ti, 13·1%), m.p. 58° (decomp.), soluble in benzene and carbon tetrachloride.

Reaction of Tetrakis(dimethylamido)zirconium with Dimethyl Acetylenedicarboxylate.—The experiment was performed as described for the titanium analogue. Dimethyl acetylenedicarboxylate (2.37 g., 1 mol.) in diethyl ether (10 ml.) and tetrakis(dimethylamido)zirconium (4.37 g., 1 mol.) in the same solvent (25 ml.) at 5—10° afforded the reddish-brown 1: 2-complex, (MeO)₂Zr[C(CO·NMe₂):C(CO₂-Me)·NMe₂]₂ (1.04 g., 23%) (Found: N, 10.1; Zr, 16.4. $C_{20}H_{36}N_4O_8Zr$ requires N, 10.15; Zr, 16.5%), m.p. >240° (decomp.).

Reaction of Dimethylaminotrimethylsilane with Dimethyl Acetylenedicarboxylate.—Dimethylacetylene dicarboxylate (2.74 g., 1 mol) in diethyl ether (10 ml.) was slowly added to dimethylaminotrimethylsilane (2.26 g., 1 mol.) at 20°. Heat was evolved. The reaction mixture was heated under reflux (1 hr.); solvent was removed at $20^{\circ}/0.05$ mm. to leave yellow (1,2-dicarbmethoxy-2-dimethylaminovinyl)trimethylsilane (4.50 g., 90%) (Found: C, 50.9; H, 8.0; N, 5.55; Si, 10.65%; *M* (mass spec.), 259. C₁₁H₂₁NO₄Si requires C, 50.95; H, 8.15; N, 5.4; Si, 10.85%; *M*, 259.4), b.p. 78-80°/0.02 mm.

Reaction of Dimethylaminotri-n-butylgermane with Dimethyl Acetylenedicarboxylate.—Dimethyl acetylenedicarboxylate (1.44 g., 1 mol.) in diethyl ether (5 ml.) was added to dimethylaminotri-n-butylgermane (2.92 g., 1 mol.) in the same solvent (5 ml.) at 20°. A mild exothermic reaction ensued and the reaction mixture was heated under reflux (2 hr.). Volatiles were removed at 20°/0.05 mm. The yellow residue was (1,2-dicarbmethoxy-2-dimethylaminovinyl)tri-n-butylgermane (3.0 g., 66.05%) (Found: C, 56.0; H, 9.2; N, 3.15. $C_{20}H_{39}GeNO_4$ requires C, 55.8; H, 9.15; N, 3.25%), b.p. 126—127°/0.03 mm.

Reaction between Tetrakis(dimethylamido)titanium and Carbon Dioxide.—Carbon dioxide was bubbled (ca. 3 hr.) through a benzene or light petroleum (20 ml.) solution of the amide (3.57 g.). Heat was evolved and the colour gradually darkened, whereafter a solid began to separate. The precipitate was filtered off, washed with benzenelight petroleum (3×15 ml.), and freed from solvent (ca. 3 hr. at 20°/0.05 mm.). The light-yellow tetrakis-(NN-dimethylcarbamato)titanium (4.33 g., 68%) (Found: N, 13.8; NMe₂, 43.8; Ti, 12.0. C₁₂H₂₄N₄O₈Ti requires N, 14.0; NMe₂, 44.0; Ti, 12.0%), m.p. 235° (decomp.), was sparingly soluble in light petroleum, benzene, and carbon tetrachloride, but soluble in dichloromethane. The combined filtrate and washings afforded a light-yellow powder (1.40 g.) (Found: N, 14.6; Ti, 11.7%).

Reaction between Tetrakis-(NN-dimethylcarbamato)titanium and Carbon Disulphide.—Carbon disulphide (2.02 g., 4.2 mol.) was added to a solution of the titanium compound (2.52 g., 1 mol.) in dichloromethane (20 ml.). The reaction mixture was gently heated under reflux ($\frac{1}{2}$ hr.) and set aside (4 hr.); orange-red crystals of NN-dimethylcarbamatotris-(N'N'-dimethyldithiocarbamato)titanium (2.33 g., 75%) (Found: C, 28.3; H, 4.4; N, 11.1; S, 37.5; Ti, 9.8. C₁₂H₂₄N₄O₂S₆Ti requires C, 29.0; H, 4.85; N, 11.3; S, 38.7; Ti, 9.6%), m.p. >250° (decomp.), were filtered off, washed, and freed from solvent.

Reactions of Metal Amides with Benzonitrile, p-Toluonitrile, and α -Chloroacrylonitrile.—Four typical experiments are described. Further details are in Table 3.

A mixture of tetrakis(dimethylamido)titanium (2.43 g., 1 mol.) and benzonitrile (4.47 g., 4 mol.) was stirred (ca. 3 hr.) at 100° to give a reddish brown, viscous liquid (6.80 g.), believed to be tetrakis-(NN-dimethylbenzamidino)titanium. A sample (4.60 g., 1 mol.) of this product was treated with methanol (1.5 g., >4 mol.) in diethyl ether at 20°. An exothermic reaction ensued with the separation of a white solid. The reaction mixture was heated under reflux $(\frac{1}{2}$ hr.). Dimethylamine was not liberated. Tetramethyl titanate (1.21 g., 97.36%) was filtered off, washed with diethyl ether $(2 \times 10 \text{ ml.})$, and freed from solvent. The combined filtrate and washings afforded colourless NN-dimethylbenzamidine (2·13 g., 49·72%) (Found: C, 73·2; H, 8·35; N, 19·1. Calc. for $C_9H_{12}N_2$: C, 72·85; H, 8·15; N, 18·9%), b.p. 49-50°/0.02 mm. Tetrakis-(NN-dimethyl-p-methylbenzamidino)titanium (90.0%) was similarly prepared and characterised.

p-Toluonitrile (1.93 g., 4 mol.) in diethyl ether (5 ml.)

was slowly added to tetrakis(dimethylamido)zirconium (1.10 g., 1 mol.) at 20°. Heat was evolved and the reaction mixture was stirred (ca. 2 hr.). Diethyl ether was replaced by light petroleum (b.p. 40-60°, 15 ml.). The yellow tetrakis-(NN-dimethyl-p-toluamidino)zirconium (2·28 g., 95.0%) was filtered off, washed with light petroleum (2 \times 5 ml.), and freed from solvent. A sample (0.5 g.) of this product in diethyl ether (15 ml.) was heated under reflux (1 hr.) with methanol (0.5 ml.). Dimethylamine was not evolved. Light petroleum (20 ml.) was added, and the white tetramethyl zirconate (0.14 g., 92.4%) (Found: Zr, 42.0. Calc. for $C_4H_{12}O_4Zr$: Zr, 42.4%) was filtered off, washed with light petroleum $(2 \times 5 \text{ ml.})$, and freed from solvent. The combined filtrate and washings afforded colourless NN-dimethyl-p-toluamidine (0.42 g., 95.5%).

Dimethylaminotrimethylstannane (3·39 g., 1 mol.) in benzene (5 ml.) was slowly added to α -chcloroacrylonitrile (1·43 g., 1 mol.) in benzene (5 ml.) at 20°. An exothermic reaction ensued; the reaction mixture was stirred for 1 hr. Evaporation of volatiles under reduced pressure left the dark-brown, viscous (1-chloro-1-cyano-2-NN-dimethylaminoethyl)trimethylstannane (4·70 g., 97·5%) (Found: N, 9·57%; M, 283. C₈H₁₇ClN₂Sn requires N, 9·48%; M, 295·4).

 α -Chloroacrylonitrile (0.67 g., 4 mol.) in light petroleum (b.p. 40—60°; 5 ml.) was slowly added at -50° to a solution of tetrakis(dimethylamido)zirconium (0.51 g., 1 mol.) in the same solvent (15 ml.). A yellow solid slowly separated out and became dark-brown as it warmed to 20°. The solid (0.96 g., 81.4%), believed to be tetrakis-(1-chloro-1-cyano-2-NN-dimethylaminoethyl)zirconium, was filtered off, washed with light petroleum (2 \times 5 ml.), and dried at 20°/ 0.005 mm.

Reaction of Dimethylaminotrimethylstannane with Pentafluorobenzonitrile .--- Dimethylaminotrimethylstannane (1.86 g., 1 mol.) in light petroleum (b.p. 40-60°; 5 ml.) was slowly added to pentafluorobenzonitrile (1.73 g., 1 mol.) in the same solvent (10 ml.) at 0°. An exothermic reaction ensued and a white solid separated out. The reaction mixture was stirred (2 hr.) at 20° and was then filtered. The solid trimethyltin fluoride (1.60 g., 97.85%) (Found: C, 19.9; H, 4.9. Calc. for C₃H₉FSn: C, 19.7; H, 4.95%), was washed with light petroleum (3 \times 5 ml.) and then dried. The combined filtrate and washings afforded the colourless 4-NN-dimethylamino-2,3,5,6-tetrafluorobenzonitrile (1.6 g., 82.1%) (Found: C, 49.4; H, 2.5; N, 12.7. Calc. for $C_9H_6F_4N_2$: C, 49.5; H, 2.7; N, 12.8%), [v(C=N), 2237 cm.⁻¹; triplet at τ 7.57 (NMe₂), J (F-H) = 2.85 c./sec.], b.p. 50°/0.005 mm., which solidified at room temperature. A portion (1.04 g.) of this product was heated under reflux (ca. 2 hr.) with dimethylaminotrimethylstannane (1.01 g., 1 mol.) in light petroleum (b.p. 40-60°; 5 ml.). Trimethyltin fluoride (0.12 g.) was filtered off and the filtrate was concentrated to afford the colourless (NN-dimethyl-4-N'N'-dimethylamino-2,3,5,6-tetrafluorobenzamidino) trimethylstannane (1.91 g.).

A portion (1.6 g.) of this adduct was heated under reflux (0.5 hr.) with water (0.5 ml.) in light petroleum (10 ml.). Trimethyltin hydroxide (0.55 g., 80.9%) was filtered off, washed with light petroleum $(2 \times 5 \text{ ml.})$, and dried. The combined filtrate and washings afforded the colourless NN-dimethyl-N'N'-dimethylamino-2,3,5,6-tetrafluorobenz-

amidine (0.65 g., 65.8%) (Found: C, 49.9; H, 5.1; N, 16.0%; M, 252. C₁₁H₁₃F₄N₃ requires C, 50.2; H, 5.0; N, 15.95%; M, 263.3) [v(N-H), 3320 cm.⁻¹; v(C=N), 1600 cm.⁻¹], b.p. 69°/0.01 mm. The i.r. spectrum suggests the

presence of a trace of impurity, possibly of disubstituted product.

Reactions with Pentafluorobenzonitrile and Bromopentafluorobenzene.—The nitrile (1.62 g., 4 mol.) was slowly added to tetrakis(dimethylamido)titanium (0.47 g., 1 mol.) in diethyl ether (2 ml.) at 20°. The dark-brown mixture was heated under reflux (1 hr.), after which light petroleum (10 ml.) was added. A yellow-brown solid (0.7 g.) (Found: C, 31.5; H, 4.05; N, 10.85; F, 19.85; Ti, 11.8%), was filtered off, washed with light petroleum (2 \times 5 ml.), and dried at 20°/0.005 mm. The combined filtrate and washings were concentrated, and the resultant solid was recrystallised from cold, light petroleum (10 ml.) to afford colourless needles of 4-NN-dimethylamino-2,3,5,6-tetrafluorobenzonitrile (0.92 g., 50.3%), m.p. 45—47°.

Dimethylaminotrimethylsilane (1·1 g., 1 mol.) was slowly added to pentafluorobenzonitrile (1·8 g., 1 mol.). An exothermic reaction ensued. The reaction mixture was stirred at 20°/10 mm. and trimethylfluorosilane (0·75 g., $87\cdot2\%$) was trapped at -198° . The residue was recrystallised from cold, light petroleum to give colourless 4-dimethylamino-2,3,5,6-tetrafluorobenzonitrile (1·8 g., $88\cdot7\%$) (authentic i.r. spectrum).

A mixture of bromopentafluorobenzene (4·17 g., 1 mol.) and dimethylaminotrimethylstannane (3·51 g., 1 mol.) was stirred at 20° (2 hr.) and then in refluxing light petroleum (10 ml.) (2 hr.). Trimethyltin fluoride (2·8 g., 90·6%) was filtered off and washed with light petroleum (3 × 5 ml.). The combined filtrate and washings afforded colourless 1-bromo-4-NN-dimethylamino-2,3,5,6-tetrafluorobenzene (3·71 g., 80·8%) (Found: C, 35·5; H, 2·3; Br, 29·0; F, 27·7; N, 5·0%; M, 278·6. C₈H₆BrFN requires C, 35·3; H, 2·2; Br, 29·4; F, 27·9; N, 5·1%; M, 272·1) [τ , triplet at 7·3 (NMe₂), J (F-H) = 2·25 c./sec.], b.p. 36-38°/0·001 mm.

Reactions with Acrylonitrile.—A mixture of acrylonitrile (0.5 g., 1.2 mol.) and dimethylaminotri-n-butylgermane (2.28 g., 1 mol.) was stirred for 4 hr. at 110°. Distillation gave the colourless (1-cyano-2-dimethylaminoethyl)tri-n-butylgermane (1.68 g., $62\cdot2\%$) (Found: C, $60\cdot1$; H, $10\cdot75$; N, 8.05. C₁₇H₃₆GeN₂ requires C, 59.85; H, $10\cdot65$; N, $8\cdot2\%$) [ν (C=N), 2203 cm.⁻¹; no ν (C=C) at 1610 cm.⁻¹), b.p. 110—116°/0.02—0.03 mm.

Similarly, the nitrile (0.79 g.), and dimethylaminotrimethylstannane (3.1 g., 1 mol.) afforded colourless (1-cyano-2-dimethylaminoethyl)trimethylstannane (Found: C, 36.4; H, 7.3; N, 10.4. $C_8H_{18}N_2Sn$ requires C, 36.8; H, 7.0; N, 10.7%), b.p. 69°/0.003 mm.

Reactions of Dimethylaminotrialkylstannanes with Alkene Sulphides.—Ethylene sulphide (1.00 g., 1 mol.) was added to dimethylaminotrimethylstannane (3.45 g., 1 mol.) in light petroleum (5 ml.). The mixture was heated under reflux (ca. 1 hr.) and was then freed from volatiles at 20°/20 mm., to afford the colourless (1-NN-dimethyl-2-thioethoxy)trimethylstannane (3.5 g., 78.7%) (Found: C, 31.95; H, 7.05; N, 5.15; S, 12.2%; M, 272.9. C₇H₁₉NSSn requires C, 31.35; H, 7.15; N, 5.2; S, 11.95%; M, 268), b.p. 62°/0.9 mm.

A mixture of propene sulphide (0.90 g., 1.2 mol.) and dimethylaminotriethylstannane (2.5 g., 1 mol.) was stirred (ca. 3 hr.) at 100°. Distillation gave the colourless (1-NNdimethylamino-2-thiopropoxy)triethylstannane (2.4 g., 74.1%) (Found: C, 40.7; H, 8.6; N, 4.1. $C_{11}H_{27}NSSn$ requires C, 40.8; H, 8.4; N, 4.3%), b.p. 78-80°/0.04 mm. A portion (0.5 g.) of this product was recovered quantitatively after ca. 2 hr. in refluxing ethanol. The triethylstannane (0.71 g., 1.1 mol.) was slowly added to 1-dimethylaminopropane-2-thiol (0.31 g., 1 mol.) at 20°. Dimethylamine was liberated. The reaction mixture was freed from volatiles under reduced pressure to afford the colourless (1-NN-dimethylamino-2-thiopropoxy)triethylstannane (0.82 g., 97.2%) (authentic i.r. spectrum).

Reactions with β -Propiolactone.—Dimethylaminotrimethylstannane (0.95 g., 1.1 mol.) was slowly added to the lactone (0.30 g., 1 mol.) at 20°. An exothermic reaction ensued. Removal of volatiles at 20°/0.1 mm. afforded viscous NN-dimethyl- β -trimethylstannoxypropionamide (1.15 g., 92.0%) (authentic i.r. spectrum).

Dimethylamine was evolved upon adding the dimethylaminotrimethylstannane (1.35 g., 1.13 mol.) to NN-dimethyl-hydracrylamide (0.75 g., 1 mol.) at 20°. The residue was freed from volatiles and then distilled to afford the colourless NN-dimethyl- β -trimethylstannoxypropionamide (1.27 g., 70.9%) (Found: C, 34.5; H, 6.7; N, 5.2. C₈H₁₉NO₂Sn requires C, 34.3; H, 6.8; N, 5.0%), b.p. 80-81°/0.002 mm.

The lactone (1.90 g., 4 mol.) in tetrahydrofuran (5 ml.) was slowly added to tetrakis(dimethylamido)titanium (1.48 g., 1 mol.) in the same solvent (5 ml.) at 0°. Volatiles were removed under reduced pressure and the residue was triturated with light petroleum (10 ml.). The pale-yellow, solid *tetrakis*-(NN-*dimethylamidopropoxy)titanium* (3.20 g., 94.7%) (Found: N, 10.6; Ti, 9.7. $C_{20}H_{40}N_4O_8Ti$ requires N, 10.9; Ti, 9.3%) was filtered off, washed with light petroleum (5 ml.) and tetrahydrofuran (5 ml.), and dried. The compound decomposed when heated at *ca*. 200°/0.001 mm.

Similarly, tetrakis(diethylamido)hafnium (0.63 g., 1 mol.) in tetrahydrofuran (5 ml.) and the lactone (0.40 g., 4 mol.) in the same solvent (5 ml.) gave a very viscous liquid (1.0 g., 97.1%) which was not crystallised. The product, believed to be tetrakis-(NN-diethylpropoxy)hafnium [v(C=O), 1636 $cm.^{-1}$], did not react (1 hr.) with refluxing methanol (4 ml.).

Reaction of o-Phenylene Diethylaminoboronate with Crotonaldehyde.—The aldehyde (1·33 g., 1 mol.) in light petroleum (b.p. 40—60°; 10 ml.) was slowly added to the boronate (3·61 g., 1 mol.) in the same solvent (20 ml.) at 20°. After an induction period, an exothermic reaction yielded the orange o-phenylene (1-dimethylamino-2-butenyl)boronate (4·70 g., 95·15%) (Found: C, 64·3; H, 7·6; B, 4·4; N, 5·5. C₁₄H₂₀BNO₃ requires C, 64·4; H, 7·7; B, 4·15; N, 5·35%), m.p. 90° (decomp.), which was filtered off, washed with light petroleum (2 × 15 ml.), and dried at 20°/0·02 mm.

Some Unsuccessful Reactions.—In the following systems the reagents did not appear to react under the stated conditions; essentially quantitative recovery of starting materials was achieved in the following systems: (a) $(\pi - C_5 H_5)_2 \text{TiCl}_2$ with 2PhNCS, reflux in light petroleum (b.p. $0-40^{\circ}$); (b) B(NMe₂)₃ with 3CH₂:CH•CN or 3CH₂:CCl₂, reflux (1 hr.) in light petroleum (b.p. $40-60^{\circ}$); (c) $o-C_6H_4O_2BNEt_2$ with CH2:CHCN or CH2:CH•CO2Me, reflux (2 hr.) in light petroleum (b.p. 40—60°); (d) $Bu_2^nB\cdot NMe_2$ with $CH_2\cdot C(Cl)CN$, PhCH=CH₂, or PhCH:CH•CN, reflux (1 hr.) in light petroleum (b.p. 40-60°) or diethyl ether; (e) $Ti(NMe_2)_4$ or Me₃Sn·NMe₂ with Bu^tCN, stirred at 100° for 5 hr. and 1 hr., respectively; (f) Ti(NMe₂)₄ with PhCH:C(CN)Ph, reflux (1 hr.) in diethyl ether; (g) Ti(NPh•CO•NMe₂)₄ or $(\pi$ -C₅H₅)₂-Hf(SBu^t)₂ with CH₂:CH·CN, reflux (1 hr.) in benzene or light petroleum (b.p. $40-60^{\circ}$), respectively; (h) Me₃Sn·CH(CN)·CH₂NMe₂ with CH₂·CH·CN, reflux (1 hr.) in light petroleum (b.p. 40-60°); (i) Et_3SnH with C_6F_5CN heated (2 hr.) at 100° ; and (j) Ti(NMe₂)₄ with (Me₃Si)₂O, heated (2 hr.) at 100°.

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