Amido-derivatives of Metals and Metalloids. Part VI.[1] Reactions of Titanium(IV), Zirconium(IV), and Hafnium(IV) Amides with Protic Compounds

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The reactions of metal (Ti, Zr, or Hf) dialkylamides with acidic hydrocarbons (such as C_5H_6), hexamethyldisilazane, alcohols, and thiols are reported. In this way, numerous π-organometallic derivatives, such as $CpTi(NMe_2)_3$ and $(\pi\text{-}C_5H_5)_2Zr(NMe_2)_2$, silylamides, alkoxides, and thiolates have been prepared. Noteworthy are (*a*) differences (possibly steric in origin), with regard to the number of groups displaced, between Ti amides and amides of either Zr or Hf, (*b*) the displacement order $NR_2 > SR > Cp \gg OR$, and (*c*) the monomeric nature of all the products. Reactions between decaborane and either $Ti(NMe_2)_4$ or Me_3SnNMe_2 afforded $Ti(NMe_2)_4,2B_{10}H_{14}$ and $Me_3SnNMe_2,B_{10}H_{14}$, which are probably best formulated as $[Ti(NMe_2)_2]^{2+}[B_{10}H_{13},Me_2NH]_2^-$ and $[Me_3Sn]^+[B_{10}H_{13},Me_2NH]^-$, respectively.

WE have made a detailed study of the chemistry of amides of titanium(IV), zirconium(IV), and hafnium(IV) [*e.g.*, of $Ti(NMe_2)_4$], and have published some results.[2,3] Some reactions with acidic hydrocarbons, hexamethyldisilazane, alcohols, thiols, and decaborane, and related experiments are now described. The results are comparable with earlier ones on amides of tin (and one case of iron).[4]

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[1] M. F. Lappert and G. Srivastava, *J. Chem. Soc.* (*A*), 1967, 602.

[2] G. Chandra and M. F. Lappert, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 83.

[3] G. Chandra, T. A. George, and M. F. Lappert, *Chem. Comm.*, 1967, 116.

[4] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1964, 22; *J. Organometallic Chem.*, 1965, **3**, 295.

The first amido-derivatives of titanium and zirconium [$Ti(NR^1{}_2)_4$ and $Zr(NR^2{}_2)_4$; R^1 = Me, Et, Pr^n, Bu^i; or $NR^1{}_2 = NC_5H_{10}$; R^2 = Me or Et] were obtained by Bradley and Thomas, by treating the metal(IV) chloride with the appropriate lithium amide.[5] The compounds reacted with the protic compounds water, butan-1-ol, and triethylsilanol, according to the general equation (1);[6] primary and secondary amines behaved similarly,

$$M(NR_2)_4 + 4HA \longrightarrow MA_4 + 4R_2NH \qquad (1)$$

although in some cases (*e.g.*, 2) incomplete displacement

$$Ti(NMe_2)_4 + 4Et_2NH \longrightarrow Me_2NTi(NEt_2)_3 \qquad (2)$$

was effected.[5,7] Thiols (R^3 in R^3SH = Me, Et, or Pr^i) have recently been observed to behave similarly [the $Ti(SR^3)_4$ products were associated with amine and/or thiol], and some compounds of type $(R_2N)_nTi(SR^3)_{4-n}$ have also been obtained; with the exception of $(Me_2N)_3TiSEt$, none was monomeric.[8] A reaction of the general type shown in equation (1) was used[9] for the synthesis (3) of a compound containing a titanium–metal

$$(Me_2N)Ti(OPr^i)_3 + CpMo(CO)_3H \longrightarrow (Pr^iO)_3Ti\text{–}Mo(CO)_3(\pi\text{-}C_5H_5) \qquad (3)$$

bond. Hafnium amides had not been described, although there is a reference to the *reactions* of $Hf(NMe_2)_4$ with carbon disulphide and metal carbonyls.[10]

Three types of reaction have been examined [equations (4)—(6)]. These have led, *inter alia*, to the preparation of a large number of new compounds (Table 1). Their spectra, together with those of other organic derivatives of titanium, zirconium, and hafnium, will be described in Part XI. It is interesting that most of these compounds, as well as the parent $M(NR_2)_4$, are highly coloured; this may be due to charge transfer of ligand lone-pair electrons into vacant *d* orbitals on the metal. It is clear that amides of titanium, zirconium, and hafnium are useful starting materials for the convenient synthesis of a variety of other derivatives.

TABLE 1

Organometallic amides, alkoxides, and thiolates

Compound	Method [a]	Appearance	B.p. (°/mm.) (sublimation)
$(\pi\text{-}C_5H_5)Ti(NMe_2)_3$	4	Low-melting, red solid	95/0·05
$(\pi\text{-}C_5H_5)_2Ti(NMe_2)_2$	6	Dark-brown, viscous liquid	120—128/0·2
$(\pi\text{-}C_5H_5)Zr(NMe_2)_3$	5	Yellow, slightly viscous liquid	94—96/0·05
$(\pi\text{-}C_5H_5)_2Zr(NMe_2)_2$	4,6	Yellow, shining crystals	(110—120/0·05)
$(\pi\text{-}C_5H_5)_2Hf(NMe_2)_2$	4	Yellow solid	(120—125/0·02)
$(\pi\text{-}C_5H_5)Ti(NEt_2)_3$	4	Reddish-brown, viscous liquid	146/0·2
$(\pi\text{-}C_5H_5)_2Zr(NEt_2)_2$	4	Orange-yellow solid	(120—130/0·03)
$(\pi\text{-}C_5H_5)_2Hf(NEt_2)_2$	4	Yellow crystals	(120—130/0·03)
$Me\text{-}(\pi\text{-}C_5H_4Me)Ti(NM_2)_3$ ...	4	Low-melting, red solid	84/0·02
$[Me\text{-}(\pi\text{-}C_5H_4Me)]_2Zr(NMe_2)_2$	4	Reddish-brown, waxy solid	(125—135/0·1)
$IndZr(NMe_2)_3$.................	4	Orange, viscous liquid	144/0·15
$(Me_2N)_3TiN(SiMe_3)_2$	4	Orange-yellow, low-melting solid	(110—120/0·02)
$(Me_2N)_2Zr[N(SiMe_3)_2]_2$	4	White crystals	(120—140/0·04)
$(\pi\text{-}C_5H_5)Ti(OPr^i)_3$	4,5 [b]	Pale yellow, slightly viscous liquid	59—60/0·015
$(Me_2N)Ti(OPr^i)_3$	6	Yellow liquid	48—50/0·02
$(Et_2N)_2Ti(OBu^t)_2$	5	Orange liquid	76—79/0·03
$(\pi\text{-}C_5H_5)_2Zr(OBu^t)_2$	5	White crystals	(110—120/0·03)
$(\pi\text{-}C_5H_5)_2Hf(OBu^t)_2$	5	White crystals	(110—120/0·03)
$(\pi\text{-}C_5H_5)_2Zr(SBu^t)_2$	1	Yellow, shining crystals	(160—180/0·05)
$(\pi\text{-}C_5H_5)_2Hf(SBu^t)_2$	1	Lemon-yellow crystals	(140—160/0·02)
$Ti(NMe_2)_4,2B_{10}H_{14}$	1	Khaki-brown solid	d.
$Me_3SnNMe_2,B_{10}H_{14}$	1	Orange crystals	(m.p. 49—55°)

[a] Numbers refer to method (see equations). [b] (4) $Me_2NTi(OPr^i)_3$ + excess $\pi\text{-}C_5H_5H$, or (5) $CpTi(NMe_2)_3 + 3Pr^iOH$.

$$\text{Metal amide} + \text{excess of HA} \longrightarrow \text{products} \qquad (4)$$

$$\text{Metal amide} + \text{stoicheiometric quantity of HA} \longrightarrow \text{products} \qquad (5)$$

$$\text{Metal chloride} + n\text{Li}(NMe_2) \longrightarrow \text{Metal amide} + n\text{LiCl} \qquad (6)$$

Interaction of tetrakisamido-compounds and excess of acidic hydrocarbons [reaction (4)] of pK_A = *ca.* 20 afforded organometallic derivatives. The features of interest (Table 1) are (*a*) the synthesis [*e.g.*, equation (7)] of π-cyclopentadienyl and related derivatives of Ti, Zr, and Hf, without recourse to organometallic intermediates, and (*b*) the differences in behaviour between $Ti(NMe_2)_4$ and the Zr and Hf analogues. As for (*b*), a similar

$$M(NMe_2)_4 \xrightarrow[+C_5H_6\ (-Me_2NH)]{M\,=\,Ti,\ Zr,\ or\ Hf} (\pi\text{-}C_5H_5)M(NMe_2)_3$$

$$\xrightarrow[+C_5H_6\ (-Me_2NH)]{M\,=\,Zr\ or\ Hf\ (\textit{not}\ Ti)} (\pi\text{-}C_5H_5)_2M(NMe_2)_2 \qquad (7)$$

distinction [*i.e.*, in $Ti(NMe)_4$, only one NMe_2 group is directly replaceable [equation (4)] by $\pi\text{-}C_5H_5$ or $N(SiMe_3)_2$, whereas two NMe_2 are replaced for $Zr(NMe_2)_4$ and $Hf(NMe_2)_4$] was observed in the reaction between these amides and hexamethyldisilazane. The explanation probably has a steric origin, in the sense of greater hindrance to the formation of a transition state for the titanium compounds. Thus $(\pi\text{-}C_5H_5)_2Ti(NMe_2)_2$ was readily obtained by an alternative procedure [equation (6)], in which steric effects are obviously less significant. The replacement of merely a single NMe_2 group of $Zr(NMe_2)_4$ by the indenyl ligand is consistent with this suggestion. As for (*a*), the only precedent is in the reaction of cyclopentadiene with an iron amide to give ferrocene.[4] Although phenylacetylene did react with $Ti(NMe_2)_4$, releasing dimethylamine, the titanium product was unstable (cf. ref. 11 on lability of σ-organotitanium compounds). On the other hand, the compounds $(\pi\text{-}C_5H_5)_2M(C{\equiv}CPh)_2$ (M = Zr and Hf) have been obtained[12] (and characterised; cf. ref. 13) from interaction of $(\pi\text{-}C_5H_5)_2M(NMe_2)_2$ and phenylacetylene.

The displacement of amido- by cyclopentadienyl groups (see Table 1) is surprising in the light of the observation that the reverse reaction is found when

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[5] D. C. Bradley and I. M. Thomas, *Proc. Chem. Soc.*, 1959, 225; *J. Chem. Soc.*, 1960, 3857.

[6] I. M. Thomas, *Canad. J. Chem.*, 1961, **39**, 1386.

[7] R. K. Bartlett, *J. Inorg. Nuclear Chem.*, 1966, **28**. 2448.

[8] D. C. Bradley and P. A. Hammersley, *J. Chem. Soc.* (*A*), 1967, 1894.

[9] D. J. Cardin and M. F. Lappert, *Chem. Comm.*, 1966, 506.

[10] D. C. Bradley and M. H. Gitlitz, *Chem. Comm.*, 1965, 289; D. C. Bradley, J. Charalambous, and S. Jain, *Chem. and Ind.*, 1965, 1730.

[11] Cf., R. Feld and P. L. Cowe, 'The Organic Chemistry of Titanium,' Butterworths, London, 1965.

[12] A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, unpublished observations.

[13] H. Köpf and M. Schmidt, *J. Organometallic Chem.*, 1967, **10**, 383.

treating titanocene dichloride[14] or trichloro-(π-cyclopentadienyl)titanium[15] with excess of ammonia or primary amine under mild conditions.

The replacement of amido- by alkoxy- or alkanethio-groups is not unexpected. New features (see Table 1), however, are (*a*) that cyclopentadienyl groups can also be displaced by treatment with alcohols [*e.g.*, see equation (8)]; (*b*) that relative displacement orders are $NR_2 > SR > Cp \gg OR$ [*e.g.*, see equations (8)—(10)]; (*c*) that the carbamato-group, when attached to titanium, is less easily displaced [see equation (10)] than the amido-group (this contrasts with the silicon situation);[16] (*d*) that some of the alkoxy metal amides may be unstable with respect to disproportionation [*e.g.*, see equation (11)]; and (*e*) that all the compounds shown in Table 1 are monomeric in benzene, and show parent unimolecular ions in their mass spectra and no peak at higher *m*/*e*. A difference from tin amides [see equation (12)][4] is the resistance of the amido-group to being displaced by a phosphido-ligand.

$$(\pi\text{-}C_5H_5)Ti(NMe_2)_3 + 4Pr^iOH \longrightarrow Ti(OPr^i)_4 + 3Me_2NH + \pi\text{-}C_5H_5H \qquad (8)$$

$$(\pi\text{-}C_5H_5)_2Zr(NMe_2)_2 + 2Bu^tSH \longrightarrow (\pi\text{-}C_5H_5)_2Zr(SBu^t)_2 + 2Me_2NH \qquad (9)$$

$$Me_2NTi(OPr^i)_3 \xrightarrow{C_6H_6} (\pi\text{-}C_5H_5)Ti(OPr^i)_3 \not\xleftarrow{C_6H_6} (Pr^iO)_3TiNPhC(\text{:}O)OPr^i \qquad (10)$$

$$Ti(NMe_2)_4 + 3Bu^tOH \xrightarrow{-3Me_2NH} [Me_2NTi(OBu^t)_3] \longrightarrow \tfrac{1}{4}Ti(NMe_2)_4 + \tfrac{3}{4}Ti(OBu^t)_4 \qquad (11)$$

$$\geq M\text{-}NMe_2 + Ph_2PH \xrightarrow[\text{but } \textit{not}\ M = Ti \text{ or } Zr]{M = Sn} \geq M\text{-}PPh_2 + Me_2NH \qquad (12)$$

The bridge-hydrogen atoms of decaborane are acidic.[17] Further, decaborane is known to participate in metallations when treated with Grignard reagents[18] or Group II metal alkyls.[19] Tetrakis(dimethylamido)titanium and dimethylaminotrimethylstannane (we thank Dr. T. A. George for this result) afforded $Ti(NMe_2)_4,2B_{10}H_{14}$ and $Me_3SnNMe_2,B_{10}H_{14}$ respectively, irrespective of the stoicheiometry or order of mixing. The titanium compound is a dark brown, amorphous, pyrophoric solid, insoluble in hydrocarbon or chlorocarbon solvents. In very dilute solution in nitrobenzene its conductivity was *ca.* 10 μmho cm.$^{-2}$, suggestive of an ionic structure; possibilities are $[Ti(NMe_2)_2]^{2+}[B_{10}H_{13},Me_2NH]_2^-$ or $[Ti(NMe_2)_2(Me_2NH)_2]^{2+}[B_{10}H_{13}]_2^-$. The anions $[B_{10}H_{13},L]^-$ (ref. 20) and $B_{10}H_{13}^-$ (ref. 21) are both known. The tin complex can be formulated similarly as $[Me_3Sn]^+[B_{10}H_{13},Me_2NH]^-$ or $[Me_3Sn(Me_2NH)]^+[B_{10}H_{13}]^-$. The former is preferred as the infrared spectrum reveals only one SnC_3 stretching vibration, at 528 cm.$^{-1}$; the symmetrical stretching mode of a trigonal SnC_3 framework would be infrared-forbidden. Treatment of the tin complex with hydrogen chloride gave decaborane and chlorotrimethylstannane, but not quantitatively. The $\lambda_{max.}$ values (265 and 320 mμ) support the $[B_{10}H_{13},L]^-$ formula.[20] Heating the titanium complex for *ca.* 3 hr. at 220°/0·1 mm. yielded as the volatile products hydrogen, dimethylamine, and dimethylaminoborane $(Me_2NBH_2)_2$.

EXPERIMENTAL

Nitrogen was estimated by Kjeldahl's procedure. Amine was analysed by alkaline hydrolysis and steam-distillation into standard sulphuric acid. Alkoxide was estimated by hydrolysis and oxidation ($Cr_2O_7^{2-}$).[22] Titanium, zirconium, or hafnium were estimated gravimetrically as MO_2; samples (0·05—0·1 g.) were moistened with aqueous ammonia (2—3 ml.), evaporated to dryness at 80°, and ignited at 700—900°; with π-organometallic amides, the samples were first treated with fuming $HClO_4$ and the metals were precipitated as the hydroxides with aqueous ammonia.

Cyclopentadiene (π-C_5H_5H) (b.p. 41°) and methylcyclopentadiene (π-C_5H_5MeH) (b.p. 71·4°) were freshly prepared by pyrolysis of the commercial dimers. Last traces of CpH in π-C_5H_5MeH were removed by refluxing with $Ti(NMe_2)_4$ (*ca.* 2 g. per 100 g. hydrocarbon) and subsequent fractionation.

Tetrakis(dialkylamido)titanium(IV) and the zirconium(IV) were prepared by the method of Bradley and Thomas.[5] Conventional and rigorous precautions were taken to ensure exclusion of moisture and air at every stage.

The Synthesis of Tetrakis(dialkylamido)hafnium(IV).—These compounds have not previously been described, although some of their reactions have been briefly reported.[10]

The procedure was that described by Bradley and Thomas for the zirconium analogues.[5] n-Butyl-lithium (28·4 g., 4 mol.) in diethyl ether (500 ml.), dimethylamine (22·0 g., 4·4 mol.), and hafnium tetrachloride (35·5 g., 1 mol.) were used to prepare the lemon-yellow, low-melting, crystalline *tetrakis(dimethylamido)hafnium* (15·1 g., 38·4%), b.p. 54—56°/0·03 mm. (Found: Hf, 49·7. $C_8H_{24}HfN_4$ requires Hf, 50·3%).

n-Butyl-lithium (30·9 g., 4 mol.) in diethyl ether (600 ml.), diethylamine (40·0 g., 4·5 mol.), and hafnium tetrachloride (38·7 g., 1 mol.) afforded *tetrakis(diethylamido)hafnium* as a colourless liquid (40·0 g., 70·9%), b.p. 117°/0·04 mm. (Found: Hf, 38·3; N, 12·0. $C_{16}H_{40}HfN_4$ requires Hf, 38·2; N, 12·0%).

Reactions of Acidic Hydrocarbons with Metal Amides.—Two typical experiments are described. Further details are in Tables 1 and 2.

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[14] A. Anagnostopoulos and D. Nicholls, *J. Inorg. Nuclear Chem.*, 1965, **27**, 339.

[15] A. Anagnostopoulos and D. Nicholls, *J. Inorg. Nuclear Chem.*, 1966, **28**, 3045.

[16] J. F. Klebe, *J. Amer. Chem. Soc.*, 1964, **86**, 3399.

[17] G. A. Guter and G. W. Schaeffer, *J. Amer. Chem. Soc.*, 1956, **78**, 3546.

[18] B. Siegel, J. L. Mack, J. U. Lowe, and J. Gallaghan, *J. Amer. Chem. Soc.*, 1958, **80**, 4523; J. Gallaghan and B. Siegel, *ibid.*, 1959, **81**, 504.

[19] N. N. Greenwood and N. F. Travers, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 169; *J. Chem. Soc.* (*A*), 1967, 880.

[20] B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, 1962, **1**, 622.

[21] M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Amer. Chem. Soc.*, 1960, **82**, 1825.

[22] D. C. Bradley, F. M. Abd-el Halim, and W. Wardlaw, *J. Chem. Soc.*, 1950, 3450.

Cyclopentadiene (6·18 g., 3 mol.) was added to tetrakis(dimethylamido)titanium (7·0 g., 1 mol.) in benzene (10 ml.) at 0°. An exothermic reaction ensued. The reaction mixture was refluxed (*ca.* ½ hr.). Dimethylamine (1·30 g., 92·8%) was liberated. The volatile materials were removed under reduced pressure. The residue afforded a red liquid, solidifying to a low-melting red solid, identified as *cyclopentadienyltris(dimethylamido)titanium* (5·50 g., 72%), b.p. 95°/0·05 mm. (Found: N, 16·9; Ti, 19·4%; *M* 227. $C_{11}H_{23}N_3Ti$ requires N, 17·1; Ti, 19·5%; *M* 245·2).

Cyclopentadiene (3·66 g., 3 mol.) was added to a solution of tetrakis(dimethylamido)zirconium (4·95 g., 1 mol.) in benzene (15 ml.) at 5°. An exothermic reaction ensued. Finally, an orange solution was obtained which was refluxed for 2 hr. Dimethylamine (1·60 g., 96·4%), liberated during reaction, was trapped at −78°. The volatile materials were removed at 35°/0·05 mm. and the residue (5·73 g., 100%) was sublimed at 110—120°/0·05 mm. Yellow, glistening crystals (3·10 g., 54·1%), identified as *bis(cyclopentadienyl)bis(dimethylamido)zirconium* (Found: N, 8·8; Zr, 29·9%; *M*, 305. $C_{14}H_{22}N_2Zr$ requires N, 9·0; Zr, 29·5%, *M*, 309·5), were obtained.

TABLE 2

Reactions of $M(NR_2)_4$ with hydrocarbons and characterisation of π-organometallic amides

Compound	Reagents	Reflux time (hr.)	Yield [a] (%)	Found N(%)	Found M(%)	Found *M* [d]	Formula	Required N(%)	Required M(%)	Required *M*
$(\pi\text{-}C_5H_5)Ti(NMe_2)_3$	$Ti(NMe_2)_4 + 3(\pi\text{-}C_5H_5)H$	½	72	16·9	19·4	227	$C_{11}H_{23}N_3Ti$	17·1	19·5	245
$(\pi\text{-}C_5H_5)Zr(NMe_2)_3$	$Zr(NMe_2)_4 + (\pi\text{-}C_5H_5)H$	2	33 [b]	16·5	31·7	—	$C_{11}H_{23}N_3Zr$	14·6	31·6	—
$(\pi\text{-}C_5H_5)_2Zr(NMe_2)_2$	$Zr(NMe_2)_4 + 3(\pi\text{-}C_5H_5)H$	2	54 [c]	8·8	29·9	300	$C_{14}H_{22}N_2Zr$	9·0	29·5	310
$(\pi\text{-}C_5H_5)_2Hf(NMe_2)_3$	$Hf(NMe_2)_4 + 4(\pi\text{-}C_5H_5)H$	2	60	7·0	44·7	401	$C_{14}H_{22}N_2Hf$	7·1	45·0	397
$(\pi\text{-}C_5H_5)Ti(NEt_2)_3$	$Ti(NEt_2)_4 + 5(\pi\text{-}C_5H_5)H$	2	82	12·2	14·5	325	$C_{17}H_{35}N_3Ti$	12·7	14·5	329
$(\pi\text{-}C_5H_5)_2Zr(NEt_2)_2$	$Zr(NEt_2)_4 + 3(\pi\text{-}C_5H_5)H$	12	64	7·5	25·2	375	$C_{18}H_{30}N_2Zr$	7·6	24·9	366
$(\pi\text{-}C_5H_5)_2Hf(NEt_2)_2$	$Hf(NEt_2)_4 + 4(\pi\text{-}C_5H_5H$	12	72	6·0	39·2	440	$C_{18}H_{30}N_2Hf$	6·2	39·4	453
$Me\text{-}(\pi\text{-}C_5H_4Me)Ti(NMe_2)_3$...	$Ti(NMe_2)_4 + 2Me\text{-}(\pi\text{-}C_5H_3MeH)H$	2	70	16·0	18·8	270	$C_{12}H_{25}N_3Ti$	16·2	18·5	259
$[Me\text{-}(\pi\text{-}C_5H_4Me)]_2Zr(NMe_2)_2$	$Zr(NMe_2)_4 + 3Me\text{-}(\pi\text{-}C_5H_3MeH)H$	2	67	8·0	27·5	340	$C_{16}H_{26}N_2Zr$	8·3	27·0	338
$IndZr(NMe_2)_3$	$Zr(NMe_2)_4 + 2IndH$	15	20	12·0	26·5	—	$C_{15}H_{25}N_3Zr$	12·4	26·9	—

[a] Quoted for purified materials. [b] Yield of crude product, 97·4%. [c] Yield of crude product, 100%. [d] Determined isopiestically, in C_6H_6, with a Mechrolab vapour-pressure osmometer.

Reaction between Metallocene Dichlorides and Lithium Dimethylamide.—Dimethylamine (9·0 g., 3·8 mol.) was added dropwise at −10° with constant stirring to a solution of n-butyl-lithium (7·0 g., 2·09 mol.) in light petroleum (b.p. 40—60°, 200 ml.). Lithium dimethylamide was precipitated. After the addition of dimethylamine was completed, the mixture was stirred for a further ½ hr. The excess of dimethylamine was then removed by displacement with nitrogen. A suspension of titanocene dichloride (13·0 g., 1 mol.) in toluene (200 ml.) was then added to the lithium dimethylamide in light petroleum at 0° during ½ hr. with constant stirring. The mixture became dark-brown, was refluxed (6 hr.), and finally was filtered. The filtrate was concentrated under reduced pressure and then distilled to give a dark-brown, viscous liquid (3·47 g., 25%), b.p. 120—128°/0·2 mm., which was identified as *bis(cyclopentadienyl)bis(dimethylamido)titanium* (Found: N, 10·45; Ti, 17·2%; *M*, 265. $C_{14}H_{22}N_2Ti$ requires N, 10·5; Ti, 18·0%; *M*, 266·2).

Similarly, from dimethylamine (7·50 g., 2·2 mol.), n-butyl-lithium (10·07 g., 2·08 mol.), and zirconocene dichloride (22·0 g., 1 mol.), there was obtained a yellow solid (23·41 g.). This, on sublimation at 110°/0·04 mm., gave biscyclopentadienylbis(dimethylamido)zirconium as yellow crystals (19·96 g., 85·7%) (authentic infrared and ^1H n.m.r. spectrum).

Reactions of Hexamethyldisilazane with Various Metal Amides.—Tetrakis(dimethylamido)titanium (6·33 g., 1 mol.) and hexamethyldisilazane (25·0 g., >4 mol.) were heated at 110—120° for 48 hr. The volatile materials were removed under reduced pressure, and the residual brown, viscous liquid (7·70 g.) was distilled to afford tetrakis(dimethylamido)titanium (0·80 g.), and *tris(dimethylamido)[bis(trimethylsilyl)amido]titanium* (5·10 g., 53·1%), b.p. 110—120°/0·02 mm., as a yellow liquid, which immediately solidified to an orange-yellow, low-melting solid (Found: N, 16·2; Ti, 14·3%; *M*, 355. $C_{12}H_{36}N_4Si_2Ti$ requires N, 16·4; Ti, 14·1%; *M*, 340·5).

Tetrakis(dimethylamido)zirconium (5·54 g., 1 mol.) and hexamethyldisilazane (20 ml., ⪢4 mol.) were heated at 140° for *ca.* 24 hr. Liberated dimethylamine was trapped at −78°. The reaction mixture was freed from volatile materials under reduced pressure. The residue was a brown semi-solid (10·40 g.), which on sublimation (at 120—140°/0·04 mm.) gave white crystals of *bis(dimethylamido)bis[bis(trimethylsilyl)amido]zirconium* (7·80 g., 75·3%) (Found: N, 10·9; Zr, 18·6%; *M*, 530. $C_{16}H_{48}N_4Si_4Zr$ requires N, 11·2; Zr, 18·2%; *M*, 500).

Synthesis and Reactions of Dimethylamidotris(isopropoxy)titanium.—Dimethylamine (9·3 g., 2·4 mol.) was added dropwise to a solution of n-butyl-lithium (5·48 g., 1 mol.) in light petroleum (b.p. 60—80°, 100 ml.) at −10°; stirring was continued for a further ½ hr. Tris(isopropoxy)titanium chloride (22·3 g., 1 mol.) in benzene (50 ml.) was added during ½ hr., while stirring and cooling to keep the temperature below *ca.* 5°. There was obtained a yellow solution over a white precipitate. This was filtered off and the filtrate was concentrated under reduced pressure to afford a yellow liquid (20·0 g.) (Found: N, 4·1; OPr^i, 75·1; Ti, 17·7%). Distillation of a portion (19·0 g.) afforded a fore-run (7·25 g.), b.p. 40—46°/0·02 mm. (Found: N, 4·8; OPr^i, 69·2; Ti, 17·3%); and *dimethylamidotris(isopropoxy)titanium* (11·0 g.), b.p. 48—50°/0·02 mm. (Found: N, 4·5; OPr^i, 68·8; Ti, 17·5. $C_{11}H_{27}NO_3Ti$ requires N, 5·2; OPr^i, 65·8; Ti, 17·8%).

Dimethylamidotris(isopropoxy)titanium (11·07 g., 1 mol.) and cyclopentadiene (6·2 g., 2·32 mol.) were refluxed for *ca.* 2 hr. Dimethylamine was liberated and the residue furnished *cyclopentadienyltris(isopropoxy)titanium* (8·0 g., 67%), b.p. 69°/0·1 mm. (authentic i.r. spectrum).

Reactions of Metal and Cyclopentadienylmetal Amides with Alcohols.—t-Butyl alcohol (5·28 g., 3 mol.) was added to a benzene solution (20 ml.) of tetrakis(dimethylamido)-titanium (5·33 g., 1 mol.) at 0°. The mixture was refluxed (2 hr.). Volatile materials were removed under reduced pressure. A yellow liquid (5·65 g.), believed to be (i.r.) a mixture of $Ti(NMe_2)_4$ and $Ti(OBu^t)_4$, b.p. 47—53°/0·1 mm. (Found: N, 2·0; Ti, 14·6. Calc. for $C_{14}H_{33}NO_3Ti$: N, 4·5; Ti, 15·4%), was collected.

A mixture of tetrakis(diethylamido)titanium (4·94 g., 1 mol.), t-butyl alcohol (3·27 g., 3 mol.), and benzene (30 ml.) was refluxed for *ca.* 3 hr. The volatile fractions were removed, and the orange residual liquid (4·95 g.) was distilled. Three fractions were collected: crude tetrakis-(t-butoxy)titanium (2·0 g.), b.p. 44—53°/0·03 mm. (authentic i.r.); a middle cut (0·9 g.), b.p. 54—55°/0·03 mm. (Found: N, 1·69; Ti, 14·2%); and impure *bis-(t-butoxy)-bis(diethylamido)titanium* (0·65 g.), b.p. 76—79°/0·03 mm. (Found: N, 7·8; Ti, 14·5%. $C_{16}H_{38}N_2O_2Ti$ requires N, 8·3; Ti, 14·2%). The residue (0·6 g.) in the flask was essentially $Ti(NEt_2)_4$ (authentic i.r.).

Isopropyl alcohol (2·50 g., 3 mol.) was added dropwise to a benzene (40 ml.) solution of cyclopentadienyltris(dimethylamido)titanium (3·41 g., 1 mol.). The mixture was refluxed for *ca.* 2 hr., and the liberated dimethylamine (1·72 g., 91·4%; authentic i.r.) was trapped at −78°. Solvent was removed under reduced pressure, and distillation of the residue afforded the pale yellow, slightly viscous liquid *cyclopentadienyltris(isopropoxy)titanium* (3·02 g., 75%), b.p. 59—60°/0·015 mm. (Found: C, 57·5; H, 9·0%; *M*, 302. $C_{14}H_{26}O_3Ti$ requires C, 57·9; H, 9·0%; *M*, 290).

Cyclopentadienyltris(dimethylamido)titanium (3·12 g., 1 mol.), isopropyl alcohol (4·58 g., 6 mol.), and benzene (5 ml.) were refluxed for *ca.* 1 hr. The liberated dimethylamine (1·60 g., 93%) was trapped at −78°. The residue gave tetrakis(isopropoxy)titanium (3·30 g., 91·2%), b.p. 45·5°/0·01 mm. (authentic i.r.).

t-Butyl alcohol (0·90 g., 2 mol.) in benzene (10 ml.) was added to a solution of bis(cyclopentadienyl)bis(dimethylamido)zirconium (1·88 g., 1 mol.) in the same solvent (15 ml.). A light-orange solution resulted, which was refluxed (1 hr.). Dimethylamine (0·50 g., 91·4%), liberated during reaction, was trapped at −78°. The solvent was distilled out at 20°/0·05 mm. to leave a light grey solid (2·22 g., 99·5%), which on sublimation gave white crystals of *bis-(cyclopentadienyl)bis-(t-butoxy)zirconium* (1·92 g., 86·1%), m.p. 148°, b.p. 110—120°/0·03 mm. (Found: C, 58·9; H, 7·9; Zr, 25·30%; *M*, 364. $C_{18}H_{28}O_2Zr$ requires C, 58·8; H, 7·7; Zr, 24·81%; *M*, 367·6).

Bis(cyclopentadienyl)bis(diethylamido)hafnium (2·0 g., 1 mol.), t-butyl alcohol (0·65 g., 2·0 mol.), and benzene (10 ml.) were refluxed for 3—4 hr. After removal of the volatile components, the residue furnished, as a sublimate at 110—120°/0·03 mm., the white crystals of *bis(cyclopentadienyl)bis-(t-butoxy)hafnium* (1·17 g., 58·2%) (Found: C, 47·3; H, 6·2; Hf, 39·1%; *M*, 440. $C_{18}H_{28}HfO_2$ requires C, 47·5; H, 6·2; Hf, 39·2%; *M*, 455).

Reactions of Metal and Cyclopentadienylmetal Amides with Thiols.—Tetrakis(dimethylamido)titanium (4·37 g., 1 mol.), ethanethiol (5·34 g., 4·4 mol.), and light petroleum (10 ml., b.p. *ca.* 40°) were refluxed for 1 hr. Dimethylamine was liberated and trapped at −78°. The volatile materials were removed at 20°/0·01 mm. to afford a dark red viscous mass (6·83 g.). This decomposed on heating, to afford ethanethiol (2·2 g., authentic i.r.).

Bis(cyclopentadienyl)bis(dimethylamido)zirconium (1·74 g., 1 mol.), 2-methylpropane-2-thiol (1·30 g., 2·5 mol.), and benzene (15 ml.) were refluxed for *ca.* 2·5 hr. Dimethylamine was liberated. The volatile fractions were removed under reduced pressure to leave a yellow solid (2·23 g., 99·2%). A sample (0·93 g.) was sublimed at 160—180°/0·05 mm. to give yellow, shining crystals of *bis(cyclopentadienyl)bis(2-methylpropane-2-thio)zirconium* (0·75 g., 80·6%) (Found: C, 54·0; H, 7·2; S, 15·9; Zr, 23·0%; *M*, 412. $C_{18}H_{28}S_2Zr$ requires C, 54·1; H, 7·1; S, 16·0; Zr, 22·8%; *M*, 400).

Bis(cyclopentadienyl)bis(dimethylamido)hafnium (0·96 g., 1 mol.), 2-methylpropane-2-thiol (0·65 g., 3·0 mol.), and benzene (10 ml.) were refluxed for 3—4 hr. Dimethylamine was liberated and trapped at −78°. The volatile materials were removed under reduced pressure and the product was sublimed at 140—160°/0·02 mm. to afford lemon-yellow crystals of *bis(cyclopentadienyl)bis(2-methylpropane-2-thio)-hafnium* (1·01 g., 85·7%) (Found: C, 44·4; H, 5·7; Hf, 36·4; S, 13·0%; *M*, 500. $C_{18}H_{28}HfS_2$ requires C, 44·4; H, 5·8; Hf, 36·6; S, 13·2; *M*, 487).

Reactions between Metal Amides and Decaborane.—Tetrakis(dimethylamido)titanium (3·50 g., 1 mol.) was added dropwise to a suspension of decaborane (3·81 g., 2 mol.) in light petroleum (40 ml., b.p. *ca.* 40°) at 10°. A dark brown solid separated and no dimethylamine was liberated. Only a trace of hydrogen (0·15 mol.) was liberated. The mixture was set aside for 12 hr. and was filtered. The solid was washed (3 × 10 ml.) with light petroleum and then freed from solvent at 20°/0·01 mm. to afford a khaki-brown *solid* (7·30 g., 99·8%), identified as $Ti(NMe_2)_4,2B_{10}H_{14}$ (Found: C, 19·3; H, 10·0; N, 11·9. $C_8H_{52}B_{20}N_4Ti$ requires C, 19·9; H, 11·2; N, 11·9%).

When the reaction was repeated, but with reactants in 1 : 1 ratio, the same product was obtained with recovery of 1 mol. of tetrakis(dimethylamido)titanium.

(Experiment of Dr. T. A. George). Dimethylamino-trimethylstannane (9·42 g., 0·045 mole) in cyclohexane (20 ml.) was slowly added to decarborane (5·62 g., 0·045 mole) in the same solvent (80 ml.). An exothermic reaction ensued and furnished a white-yellow precipitate, which was filtered off, washed with cyclohexane (2 × 40 ml.), and recrystallised from dichloromethane. The resulting orange solid was identified as *trimethyltin-6-(dimethylamine)decaborane* $[Me_3Sn^+B_{10}H_{13}(HNMe_2)^-]$, m.p. 49—55° (Found: C, 20·3; H, 8·8; N, 5·9. $C_5H_{29}B_{10}NSn$ requires C, 18·1; H, 8·7; N, 4·2%), $\lambda_{max.}$ 265 and 320 mμ. Pyrolysis (200°/0·01 mm.) gave a transparent yellow glass (Found: C, 15·1; H, 8·9; N, 6·8; B, 41·2%). When the reaction was carried out in the molar ratio 2 : 1, the same product was obtained with recovery of 1 mol. of aminostannane.

Some Unsuccessful Reactions.—In the following systems the reagents did not appear to interact under the conditions stated; essentially quantitative recovery of starting materials was effected; (*a*) $(\pi\text{-}C_5H_5)_2TiCl_2$ with $2Me_3SiNMe_2$, reflux; (*b*) $Ti(NMe_2)_4$ with $4Ph_2PH$, reflux in light petroleum (b.p. 40—60°); (*c*) $Zr(NMe_2)_4$ with Ph_2PH, reflux in C_6H_6; (*d*) $(\pi\text{-}C_5H_5)_2Zr(NMe_2)_2$ with $(Me_3Si)_2NH$, reflux in C_6H_6; (*e*) $(Pr^iO)_3TiNPhC(\dot{:}O)OPr^i$ [from $(Pr^iO)_4Ti$ with PhNCO; see Part IX] with $\pi\text{-}C_5H_5H$, reflux in light petroleum; (*f*) $Ti(OPr^i)_4$ with $4PhC\vdots CH$, reflux in C_6H_6; (*g*) $Ti(OPr^i)_4$ with $\pi\text{-}C_5H_5H$, distillation; and (*h*) $Z(NMe_2)_4$ with $2C_7H_8$, reflux in C_6H_6.

Phenylacetylene (4·44 g., 4 mol.), tetrakis(dimethylamido)titanium (2·44 g., 1 mol.), and light petroleum (10 ml., b.p. 40—60°) were refluxed for *ca.* 4 hr. Dimethylamine (0·20 g.) was liberated and a black intractable mass was obtained.

Heptafluoropropane (1·07 g., 2 mol.) was allowed to react with bis(cyclopentadienyl)bis(dimethylamido)zirconium (0·97 g., 1 mol.) in toluene (10 ml.) in a Carius tube. No reaction was observed up to 45°/0·001 mm., but on further warming to 100°, decomposition of bis(cyclopentadienyl)bis(dimethylamido)zirconium occured with the formation of a black intractable solid. Unchanged heptafluoropropane (0·90 g., 84·1%) was recovered.

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