

AMIDO DERIVATIVES OF METALS AND METALLOIDS XII*. FURTHER REACTIONS WITH PROTIC COMPOUNDS

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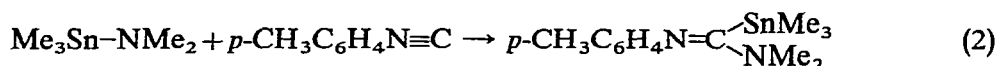
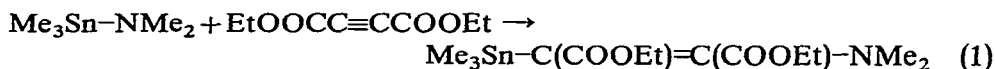
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SUMMARY

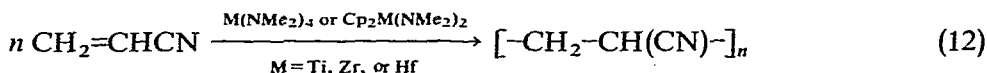
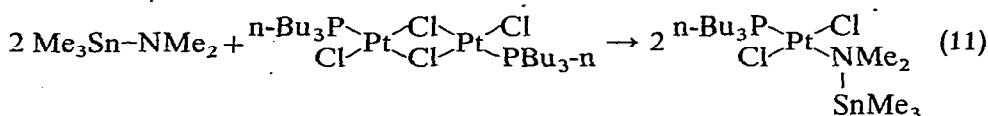
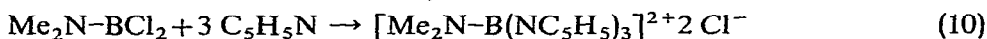
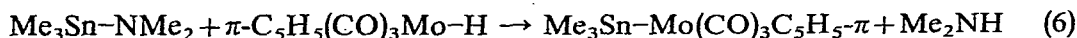
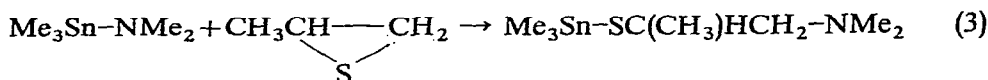
(Dimethylamido)trimethyltin, $\text{Me}_3\text{SnNMe}_2$ reacts with pentafluorobenzene in refluxing benzene to give trimethyl(pentafluorophenyl)tin, $\text{Me}_3\text{SnC}_6\text{F}_5$. This is the first example of such an amine elimination reaction involving an aromatic hydrocarbon. Amides of titanium(IV) [*e.g.* $\text{Ti}(\text{NMe}_2)_4$] or zirconium(IV) were found not to react with $\text{C}_6\text{F}_5\text{H}$; but the amine-elimination reaction furnished the following derivatives from appropriate organometallic dimethylamides: $\text{Ti}(\text{NCH}_2\text{CH}_2)_4$, $\text{Cp}_2\text{-Zr}(\text{NCH}_2\text{CH}_2)_2$ ($\text{Cp} = \pi\text{-C}_5\text{H}_5$), $\pi\text{-(MeC}_5\text{H}_4\text{)Ti(C}\equiv\text{CPh)(NMe}_2)_2$, $\text{Cp}_2\text{M(C}\equiv\text{CPh)}_2$ ($\text{M} = \text{Zr, or Hf}$), $[\pi\text{-(MeC}_5\text{H}_4)]_2\text{Zr(C}\equiv\text{CPh)}_2$, $\text{CpNb(NMe}_2)_3$, $\text{Me}_3\text{SnC}\equiv\text{C(CH}_2)_2\text{-Pr-i}$, $\text{Me}_3\text{SnC}\equiv\text{CC(Me)=CH}_2$, and $\text{Me}_3\text{SnC}\equiv\text{C(CH}_2)_3\text{C}\equiv\text{CSnMe}_3$.

INTRODUCTION

Organometallic amides (*e.g.*, LMNMe_2 , where L represents the sum of all ligands other than one NMe_2 group attached to the metal or metalloid M) have proved to be remarkably reactive compounds. The principal reaction types may be classified as follows: (i) 1,2-insertion reactions¹⁻³, (ii) 1,1-addition^{1,3}, (iii) 1,3-insertion^{1,4}, (iv) 1,4-insertion^{1,4}, (v) reactions with protic compounds⁵, (vi) reactions with metal hydrides⁶, (vii) metathetical exchange reactions with inorganic complexes⁷, (viii) metathetical exchange reactions with organic compounds⁸, (ix) dehydrochlorination reactions⁹, (x) reactions with bases¹⁰, (xi) reactions with Lewis acids¹¹, and (xii) polymerisation initiation reactions¹². These are exemplified by eqns. (1)–(12), for the sake of simplicity for the case of the tin amide $\text{Me}_3\text{SnNMe}_2$ [unless this is unreactive, *i.e.* eqns. (10) and (12)].



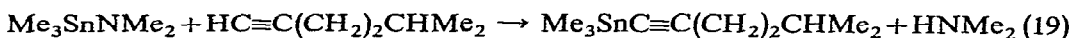
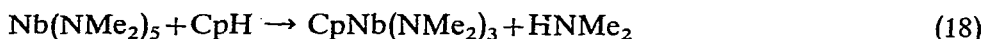
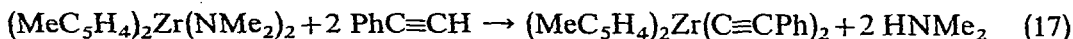
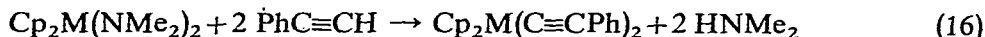
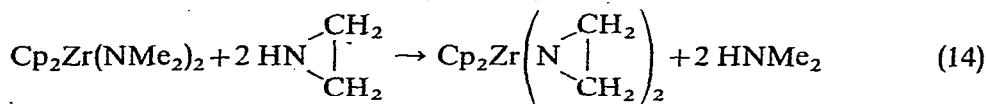
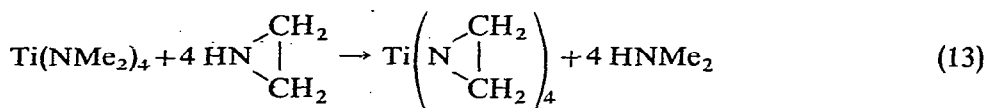
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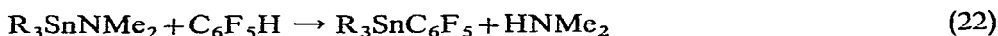
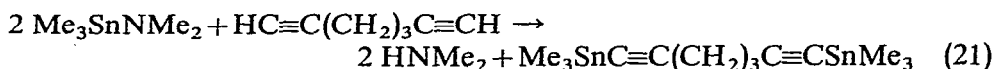


With regard to reaction type (v), hydrocarbon acids which have previously proved reactive in the sense of eqn. (5), other than cyclopentadiene, have been: $\text{RC}\equiv\text{CH}$ ⁵, $\text{HC}\equiv\text{CH}$, indene, CX_3H ($\text{X} = \text{Cl, Br}$)¹³, CH_2N_2 ¹⁴, MeNO_2 ⁵, Me_2CO , and $\text{RR}'\text{CHCN}$.

DISCUSSION

Compounds containing protic hydrogen often undergo amine elimination when treated with a metal amide (see above). Such reactions are now extended [eqns. (13)–(22)] to a cyclic amine, monosubstituted acetylenes, a diacetylene, and pentafluorobenzene.

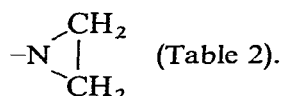




These reactions proceed under mild conditions and are of preparative value for obtaining a wide range of functionally-substituted organometallic compounds.

Upon adding excess of ethyleneimine to tetrakis(dimethylamido)titanium [eqn. (13)] or dicyclopentadienylbis(dimethylamido)zirconium [eqn. (14)], the corresponding aziridides were obtained. By contrast, similar reactions with acyclic secondary amines gave¹⁵ mixed compounds of the type $(\text{Me}_2\text{N})_n\text{Ti}(\text{NR}_2)_{4-n}$; the difference in the two systems no doubt has a steric origin. It was thought possible that ethyleneimine might be polymerised by the amides, by analogy with their effect on alkylene sulphides¹², although epoxides do not react.

The titanium aziridide is a non-volatile, hygroscopic, orange solid, whereas the white zirconium compound can be sublimed at $100^\circ/0.005 \text{ mm}$. The NMR spectra of these compounds show a singlet for



Reactions (15)–(17) provide a convenient route to the Group IVA transition metal acetylides; which are of interest as rare examples, for these elements, of complexes containing metal–carbon σ -bonds. Although the products of these reactions were not analytically pure, their formulation and structures were substantiated by

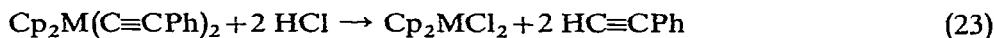
TABLE 1

IR DATA ON GROUP IVA METAL ACETYLIDES^a

Compound	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})	$\nu(\text{C}=\text{C})$ (cm^{-1})
$(\text{MeC}_5\text{H}_4)\text{Ti}(\text{C}\equiv\text{CPh})(\text{NMe}_2)_2$	2080 m	1595 m
$\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})_2$	2073 s	1592 s
$\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CPh})_2$ (see ref. 16)	2070 s	1590 s
$\text{Cp}_2\text{Hf}(\text{C}\equiv\text{CPh})_2$	2083 s	1593 m
$(\text{MeC}_5\text{H}_4)_2\text{Zr}(\text{C}\equiv\text{CPh})_2$	2078 s	1598 m

^a m = medium; s = strong.

IR (Table 1), NMR (Table 2), and mass (Table 3) spectra, and by a cleavage reaction [eqn. (23)].



While this work was in progress, the preparation of similar titanium acetylides (by a sodium salt elimination) was reported¹⁶.

The ^1H NMR spectra of the methylcyclopentadienyl derivatives were consistent with structures (I) and (II). Singlets corresponding to protons of the ring methyl and the phenyl group were present. The ring protons gave a group of 6 lines,

TABLE 2

CHEMICAL SHIFTS (τ) OF SOME NEW COMPOUNDS^a

Compound	$\tau(\text{Ph})$	$\tau(\text{Cp})$	$\tau\left(\begin{array}{c} \text{CH}_2 \\ \\ \text{N} \\ \\ \text{CH}_2 \end{array}\right)$ or $\tau(\text{NMe}_2)$	$\tau(\text{Me})$
$\text{Ti}(\text{NC}_2\text{H}_4)_4^b$			8.16(s)	
$\text{Cp}_2\text{Zr}(\text{NC}_2\text{H}_4)_2^b$		3.95(s)	7.95(s)	
$\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CPh})_2^c$	2.77(s)	3.62(s)		
$\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})_2^d$	2.73(s)	3.58(s)		
$\text{Cp}_2\text{Hf}(\text{C}\equiv\text{CPh})_2^d$	2.83(s)	3.77(s)		
$(\text{MeC}_5\text{H}_4)\text{Ti}(\text{C}\equiv\text{CPh})(\text{NMe}_2)_2^e$	2.75(m)	4.18(m)	6.9(s)	7.75(s)
$(\text{MeC}_5\text{H}_4)_2\text{Zr}(\text{C}\equiv\text{CPh})_2^d$	2.83(s)	3.88(m)		7.67(s)
$\text{CpNb}(\text{NMe}_2)_3^b$		3.99(s)	6.86(s)	

^a s=singlet; m=multiplet. ^b In C_6H_6 . ^c See ref. 16. ^d In CS_2 (using TMS as standard). ^e In C_6D_6 (using TMS as standard).

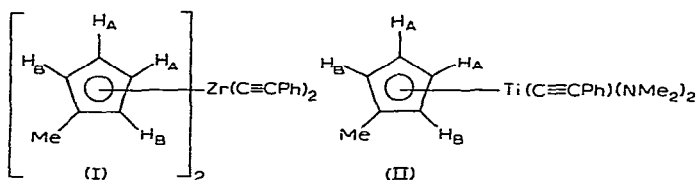
TABLE 3

MASS SPECTROSCOPIC RESULTS FOR METAL ACETYLIDES^a

$\text{Cp}_2^{90}\text{Zr}-$ $(\text{C}\equiv\text{CPh})_2$ (<i>m/e</i>)	$\text{Cp}_2^{180}\text{Hf}-$ $(\text{C}\equiv\text{CPh})_2$ (<i>m/e</i>)	Assignments of ions formed	$(\text{MeC}_5\text{H}_4)_2^{90}\text{Zr}-$ $(\text{C}\equiv\text{CPh})_2$ (<i>m/e</i>)	Assignments of ions formed
422	512	$\text{Cp}_2\text{M}(\text{C}\equiv\text{CPh})_2^+$	450	$(\text{MeC}_5\text{H}_4)_2\text{Zr}-$ $\text{M}(\text{C}\equiv\text{CPh})_2^+$
321	411	$\text{Cp}_2\text{M}(\text{C}\equiv\text{CPh})^+$	349	$(\text{MeC}_5\text{H}_4)_2\text{Zr}-$ $\text{M}(\text{C}\equiv\text{CPh})^+$
320		$\text{Cp}(\text{C}_5\text{H}_4)\text{M}(\text{C}\equiv\text{CPh})^+$		
220 ^b	310 ^b	Cp_2M^+	248 ^b	$(\text{MeC}_5\text{H}_4)_2\text{M}^+$
194		$\text{CpMC}_3\text{H}_3^+$	168	$(\text{C}_6\text{H}_6)\text{M}^+$

^a An intense peak at *m/e* 202, due to $(\text{C}\equiv\text{CPh})_2^+$, was observed in the spectra of all these compounds. ^b Most abundant peak, excluding $(\text{HC}\equiv\text{CPh})^+$.

the pattern of which was in agreement with an A_2B_2 coupling system. A similar pattern has recently been observed for $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ ¹⁷.



Mass spectra showed the monomeric parent molecular ion; the major metal-containing fragments are due to the loss of $(\text{PhC}\equiv\text{C})$.

Pentakis(dimethylamino)niobium and cyclopentadiene gave dimethylamine and a black intractable mass [eqn. (18)]. Attempts to sublime or distil the residue

resulted in its decomposition. However, the ^1H NMR spectrum (Table 2) of the residue in benzene is consistent with the formula $\text{CpNb}(\text{NMe}_2)_3$. Reactions involving the reduction of $\text{Nb}^{\text{V}} \rightarrow \text{Nb}^{\text{IV}}$ in other displacement reactions have been reported¹⁸.

Reactions of aminostannanes with acetylenes proceeded smoothly in good yield. In reaction (20), amine elimination was evidently preferred over the potentially competing 1,2-addition at $\text{C}=\text{C}$. The preparation of (3-methyl-3-buten-1-ynyl)trimethyltin (the product of reaction 20) (by a Grignard method in 37% yield) has previously been reported¹⁹. Reaction (21) (like that with acetylene⁵) proceeds directly to the second stage. A strong IR band at $\sim 2140\text{ cm}^{-1}$ in the spectra of these compounds is assigned to $\nu(\text{C}\equiv\text{C})$.

Aminosilanes and -germanes did not react with 5-methyl-1-hexyne. This is attributed to a combination of the lower basicity of the $\text{Si}-\text{N}$ or $\text{Ge}-\text{N}$ compounds (compared with $\text{Sn}-\text{N}$), combined with the relatively strong $\text{M}-\text{N}$ bonds.

The formation of the trialkyl(pentafluorophenyl)tin $\text{R}_3\text{SnC}_6\text{F}_5$ ($\text{R} = \text{Me}, \text{Et}$) by reaction (22) is surprising as (i) $\text{C}_6\text{F}_5\text{H}$ is an aromatic hydrocarbon, (ii) $\text{C}_6\text{Cl}_5\text{H}$ does not react⁵, and (iii) amine elimination [eqn. (22)] is favoured over nucleophilic substitution of fluoride by an $-\text{NMe}_2$ group (see ref. 4). The compound $\text{Me}_3\text{SnC}_6\text{F}_5$ has been independently prepared from the chloride Me_3SnCl and the appropriate Grignard reagent²⁰. Previously we have taken the view that a metal amide, such as $\text{LM}-\text{NMe}_2$, will react with a protic compound HA if the latter has high acidity and low $\text{p}K_{\text{a}}$ ⁵. However, we had not expected pentafluorobenzene to be particularly acidic, in this sense²¹ (e.g. not comparable with C_5H_6), because the conjugate base C_6F_5^- has no special stability (say compared with C_5H_5^-). The electron-attraction of the fluorine substituents is purely inductive. The present experiment suggests that the appropriate criterion for the reactivity of HA is its *kinetic* rather *thermodynamic* acidity. Pentafluorobenzene certainly is kinetically a strong acid, as shown by the high rate of hydrogen/deuterium exchange in basic media²¹.

Unexpectedly the Group IVA amides did not react with pentafluorobenzene. This may be due to the fact that the preparation of compounds having a $\text{Ti}-\text{C}$ (or $\text{Zr}-\text{C}$) σ -bond is not likely to be thermodynamically favourable. However, the compounds $\text{Cp}_n\text{M}(\text{C}_6\text{F}_5)_{4-n}$ ($n=2, 3$) are known.

In the following systems, the reagents did not react under the stated conditions; essentially quantitative recovery of starting materials was achieved in: (a) $\text{Me}_3\text{Si}-\text{NMe}_2$ and $\text{Bu}_3\text{GeNMe}_2$ with $\text{NC}\equiv\text{C}(\text{CH}_2)_2\text{CMe}_2$, stirred (2–5 h) at 100° ; (b) $\text{Me}_3\text{Sn}-\text{NMe}_2$ with $\text{C}_6\text{Cl}_5\text{H}$, reflux (2 h) in benzene; (c) Bu_3B with $\text{C}_6\text{F}_5\text{H}$, heated (2 h) at 100° ; (d) $\text{Me}_3\text{SiNMe}_2$ with $\text{C}_6\text{F}_5\text{H}$, heated (~ 4 h) at 150° ; (e) Bu_3SnOMe and Et_3SnH with $\text{C}_6\text{F}_5\text{H}$, stirred (~ 10 h) at 100° ; (f) $\text{Ti}(\text{NMe}_2)_4$ and $\text{Cp}_2\text{Zr}(\text{NMe}_2)_2$ with $\text{C}_6\text{F}_5\text{H}$, heated (1 h) at 100° ; and (g) $(\text{Et}_3\text{P})_2\text{PtHCl}$ with $\text{C}_6\text{F}_5\text{H}$, stirred (~ 5 h) in refluxing benzene.

EXPERIMENTAL

Reaction of tetrakis(dimethylamido)titanium with ethyleneimine

Ethyleneimine (0.70 g, 4.4 mol) in light petroleum (2 ml) was slowly added at 20° to a solution of tetrakis(dimethylamido)titanium (0.82 g, 1 mol) in the same solvent (5 ml). An orange solid immediately precipitated. After stirring (1 h), volatiles were removed under reduced pressure. The residue was washed with light petroleum

(5 ml) to afford orange tetraazirididotitanium (0.78 g, 98.7%), m.p. $> 110^{\circ}$ (decompn.). (Found: N, 25.7; Ti, 22.5. $C_8H_{16}N_4Ti$ calcd.: N, 25.9; Ti, 22.2%.) A sample of this product (0.3 g) decomposed when heated at $> 150^{\circ}/0.005$ mm.

Reaction of dicyclopentadienylbis(dimethylamido)zirconium with ethyleneimine

Ethyleneimine (0.46 g, 4 mol) was slowly added to dicyclopentadienylbis(dimethylamino)zirconium (0.83 g, 1 mol) in benzene (5 ml) at 20° . The reaction mixture was stirred (1 h), and then freed from volatiles under reduced pressure. The residue was sublimed at $100^{\circ}/0.001$ mm, to give white dicyclopentadienyldiazirididozirconium (0.60 g, 73.3%). (Found: N, 9.0; Zr, 30.2. $C_{14}H_{18}N_2Zr$ calcd.: N, 9.2; Zr, 29.9%.)

Reaction of (methylcyclopentadienyl)tris(dimethylamido)titanium and phenylacetylene

The titanium amide (1.0 g, 1 mol), phenylacetylene (0.39 g, 1 mol), and benzene (3 ml) were heated (~ 3 h) at 100° . Dimethylamine (90%) was liberated. Other volatiles were removed under reduced pressure. The residual darkbrown, viscous liquid, believed to be (methylcyclopentadienyl)bis(dimethylamido)(phenylethynyl)-titanium (1.20 g, 98.4%) decomposed when heated.

Reaction of dicyclopentadienylbis(dimethylamido)zirconium with phenylacetylene

Dicyclopentadienylbis(dimethylamido)zirconium (1.40 g, 1 mol) and phenylacetylene (0.92 g, 2 mol) were stirred (~ 1 h) together in refluxing THF (5 ml). Volatiles were removed under reduced pressure, and the dark-brown residue was triturated with light petroleum (5 ml). The light-brown solid, believed to be dicyclopentadienylbis(phenylethynyl)zirconium (1.55 g, 80.7%) was filtered off, washed with light petroleum, and dried. (Found: C, 69.7; H, 4.9; mol. wt. mass spectrosc., 422. $C_{26}H_{20}Zr$ calcd.: C, 73.7; H, 4.8%; mol. wt., 423.7.) A portion (0.8 g) of this product was treated with hydrogen chloride (0.14 g, 2 mol) in ether (1 ml) at 20° . The reaction mixture was stirred ($\frac{1}{2}$ h); then light petroleum (10 ml) was added. Dicyclopentadienylzirconium dichloride (0.5 g, 90.6%) was filtered off. The filtrate was concentrated to give phenylacetylene (0.26 g, 67.4%) (authentic IR spectrum).

The hafnium analogue (70%) was similarly prepared and characterised.

Reaction of bis(methylcyclopentadienyl)bis(dimethylamido)zirconium and phenylacetylene

Phenylacetylene (0.67 g, 2 mol) and bis(methylcyclopentadienyl)bis(dimethylamido)zirconium (1.10 g, 1 mol) were stirred (~ 3 h) together in refluxing diethyl ether (5 ml). Volatiles were removed under reduced pressure. The residue was triturated with light petroleum (15 ml), then filtered, to afford orange bis(methylcyclopentadienyl)bis(phenylethynyl)zirconium (1.2 g, 81.6%) m.p. $73-75^{\circ}$. (Found: Zr, 19.5%; mol. wt. mass spectrosc., 450. $C_{28}H_{24}Zr$ calcd.: Zr, 20.2%; mol. wt., 451.7.)

Reaction of pentakis(dimethylamido)niobium with cyclopentadiene

Pentakis(dimethylamido)niobium (1.5 g, 1 mol), cyclopentadiene (0.63 g, 2 mol), and benzene (5 ml) were stirred (1 h) together at 100° . Dimethylamine was evolved and other volatiles were removed *in vacuo*. The black residue decomposed when heated at $> 150^{\circ}/0.005$ mm.

Reaction of (dimethylamido)trimethyltin with 5-methyl-1-hexyne

(Dimethylamido)trimethyltin (2.59 g, 1 mol) was stirred (2 h) with 5-methyl-1-hexyne (1.4 g, 1.17 mol) at 100°. Distillation yielded the colourless (5-methyl-1-hexynyl)trimethyltin (2.62 g, 81.1%) b.p. 84°/8 mm. (Found: C, 46.2; H, 7.9%; mol.wt., 239. C₁₀H₂₀Sn calcd.: C, 46.4; H, 7.8%; mol.wt., 247.) IR: $\nu(\text{C}\equiv\text{C})$ 2133 cm⁻¹.

Reaction of (dimethylamido)trimethyltin with isopropenylacetylene

Isopropenylacetylene (0.9 g, 1.2 mol) was heated (2 h) with (dimethylamido)trimethyltin (2.38 g, 1 mol) at 40°. Dimethylamine was liberated. The residue afforded the colourless (3-methyl-3-buten-1-ynyl)trimethyltin (2.03 g, 77.5%), b.p. 57°/9 mm (lit.¹⁹ b.p. 40–42°/5 mm). (Found: C, 41.8; H, 6.3. C₈H₁₄Sn calcd.: C, 42.0; H, 6.2%.) IR: $\nu(\text{C}\equiv\text{C})$ 2158 cm⁻¹ and $\nu(\text{C}=\text{C})$ 1608 cm⁻¹.

Reaction of (dimethylamido)trimethyltin with 1,7-heptadiyne

(Dimethylamido)trimethyltin (5.64 g, 2.1 mol) and 1,7-heptadiyne (1.2 g, 1 mol), when heated (2 h) at 90°, afforded dimethylamine (1.06 g, 90.6%) and the colourless 1,7-bis(trimethylstannyl)heptadiyne (4.65 g, 85.5%), b.p. 94–95°/0.02 mm. (Found: C, 37.6; H, 5.8; mol.wt., 409. C₁₃H₂₄Sn₂ calcd.: C, 37.4; H, 5.8%; mol.wt., 417.7.) IR: $\nu(\text{C}\equiv\text{C})$ 2155 cm⁻¹.

Reactions of (dimethylamido)trialkyltins with pentafluorobenzene

Pentafluorobenzene (1.06 g, 1 mol) and (dimethylamido)trimethyltin (1.31 g, 1 mol) were stirred ($\frac{1}{2}$ h) together at 20° and then heated under reflux (1 h) with benzene (5 ml). Dimethylamine was liberated. Further volatiles were removed at 20°/10 mm, to yield the colourless trimethyl(pentafluorophenyl)tin (1.50 g, 71.9%) b.p. 80°/9 mm (lit.²⁰ b.p. 34–36°/0.01 mm). (Found: C, 32.9; H, 2.8. C₉H₉F₅Sn calcd.: C, 32.7; H, 2.7%.)

Similarly, pentafluorobenzene (1.29 g, 1 mol) and (dimethylamido)triethyltin (1.92 g, 1 mol) were stirred (~3 h) together in refluxing benzene (5 ml). The residue was distilled twice to give a colourless liquid (1.8 g, 62.9%), b.p. 52–53°/0.1 mm, characterised as triethyl(pentafluorophenyl)tin. (Found: C, 38.6; H, 4.0; F, 25.5%; mol.wt., 365. C₁₂H₁₅F₅Sn calcd.: C, 38.7; H, 4.1; F, 25.5%; mol.wt., 372.9.)

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