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DI[TRIS(TRIMETHYLSILYL)METHYL]-ZINC AND -CADMIUM[†]

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SUMMARY

Tris(trimethylsilyl)methyllithium reacts with the anhydrous halides MCl_2 (M = Zn or Cd) to give the compounds $[(Me_3Si)_3C]_2M$, which show high thermal and chemical stability. They decompose only above 300°C, with formation of $(Me_3Si)_3CH$, and are not attacked by water in refluxing THF. The zinc compound can be steam-distilled without decomposition, and does not react with boiling concentrated hydrochloric acid or with bromine in carbon tetrachloride.

INTRODUCTION

Some tris(trimethylsilyl)methyl-metal derivatives show remarkable thermal stability and appear to be reluctant to undergo substitution reactions at the metal centre. For example, the compound $(Me_3Si)_3CSiCl_3$ does not react with boiling methanolic silver nitrate, and the compounds $(Me_3Si)_3CSiR_2X$ (R = Me or Ph, X = Cl or Ph) give no substitution products even on treatment with boiling MeONa-MeOH, although a fragmentation occurs slowly [1,2]. The compound $[(Me_3Si)_3C]_2Hg$ is known to be decomposed by UV light to give radicals $[(Me_3Si)_3C^\cdot]$[3] but it is decomposed by heat only above its melting point of 290°C, and is unaffected by HCl in boiling ethanol, by bromine in boiling carbon tetrachloride or by refluxing dichloroacetic acid [4]. We have now made the corresponding zinc and cadmium derivatives from tris(trimethylsilyl)methyllithium and the anhydrous chlorides MCl_2 (M = Zn or Cd) and have found them also to be thermally stable and unusually unreactive.

[†] No reprints available.

EXPERIMENTAL

The $(Me_3Si)_3C$ group is denoted by Tsi in this section. TsiLi was made by metallation of TsiH with methyllithium [5] and solutions were standardised by weighing the $(Me_3Si)_4C$ formed by reaction with chlorotrimethylsilane. Good yields (85%) were obtained when the THF solvent was distilled from lithium aluminium hydride before use and when the excess of chloromethane was removed from the methyllithium solution by heating under reflux for 0.5 h. or by bubbling argon through the solution.

Anhydrous zinc chloride was obtained by treating the hydrated salt with thionyl chloride. Both zinc and cadmium chlorides were dried to constant weight at 110°C before use.

Di[tris(trimethylsilyl)methyl]zinc

TsiH (2.0 g 8.7 mmol) in dry THF (55 ml) was added dropwise to MeLi (10 mmol) in ether (17 ml); the mixture was stirred for 20 h. at 20°C and then heated under reflux for 0.5 h. Anhydrous $ZnCl_2$ (0.68 g 5.0 mmol) in ether (100 ml) was added dropwise to the refluxing solution and the mixture was heated under reflux for a further 5 h. Solvent was removed and the residue was extracted with boiling toluene. Cooling of the toluene solution gave di[tris(trimethylsilyl)methyl]zinc, m.p. 304-5°C; yield 0.76 g, 33% based on TsiH (Found: C, 45.0; H, 10.0. $C_{20}H_{54}Si_6Zn$ calcd. C, 45.4; H, 10.2%).

In another experiment, the reaction mixture, after removal of solvent, was mixed with hexane and the slurry was treated with saturated ammonium chloride solution. The organic layer was then dried ($MgSO_4$) and the product was precipitated from the organic layer by addition of methanol; yield 42%.

Di[tris(trimethylsilyl)methyl]cadmium and -mercury

$(Tsi)_2Cd$ was obtained analogously from TsiLi and cadmium(II) chloride, and recrystallised from n-heptane; m.p. 291°C; yield 22% based on TsiH (Found: C, 41.6; H, 9.4. $C_{20}H_{54}CdSi_6$ calcd.: C, 41.8; H, 9.4%). $(Tsi)_2Hg$ was made similarly; m.p. 291°C (lit.[4] 263-5°C); yield 35%.

Reactions of di[tris(trimethylsilyl)methyl]zinc

(a) With methanol and water.

$(Tsi)_2Zn$ was incompletely soluble in boiling methanol, and was recovered unchanged after 8 h. In another experiment $(Tsi)_2Zn$ (0.3 g) and water (1 ml) were heated under reflux in THF (5 ml) for 2 h. The solvent was removed, and the residue extracted with n-pentane. The solution was dried ($MgSO_4$) and pentane evaporated to leave a white solid (0.25 g), which was shown by its m.p. and NMR spectrum to be starting material. $(Tsi)_2Zn$ also distilled out unchanged from boiling water when steam was passed into the mixture.

(b) With acetyl chloride.

$(Tsi)_2Zn$ (0.4 g) in benzene (20 ml) was treated with acetyl chloride (0.2 g) in benzene (25 ml) in the presence of a catalytic amount of lithium bromide. The mixture was heated under reflux for 7 h and after a further 16 h at 20°C the solvent was removed and the residue extracted with boiling pentane. $(Tsi)_2Zn$ (0.31 g), identified by m.p. and NMR spectrum, was recovered.

Table 1

Spectroscopic properties of $[(Me_3Si)_3C]_2M$

M	Zn	Cd	Hg
NMR (τ)[a]	9.45	9.52	9.46
IR ν(M-C)[b] (cm^{-1})	375	368	365
% Total ion current in mass spectra[c]			
P^+	0.5	5.8	1.4
$[P-Me]^+$	4.0	12.4	5.7
$[(Me_3Si)_3CM]^+$	5.0	8.7	1.4
$[\{(Me_3Si)_2(Me_2Si)C\}_2M]^{2+}$	2.6	1.8	0.5
$[(Me_3Si)_3C]^+$	-	5.8	3.9
$[C_9H_{24}Si_3]^{+}$[d] m/e 216	27.8	8.7	14.9
$[C_8H_{21}Si_3]^+$ m/e 201	26.5	19.1	11.7
M^+	-	-	1.8
Me_3Si^+	9.9	14.7	19.1
Others	22.2	23.0	39.5
Total containing M	12.1	28.7	10.8

a In toluene, with solvent peak at τ 7.67 as reference.

b In Nujol mull.

c At 70 eV; sample temp., 50°C; source, 200°C. P^+ = parent ion.
The mass spectrum of $[(Me_3Si)_3C]_2Hg$ has also been described in ref.[4].

d The isotope pattern shows that this group of ions may be more complex than is indicated.

(c) With bromine.

$(Tsi)_2Zn$ (0.4 g) did not react with Br_2 (0.1 g), with or without a little aluminium bromide, in boiling CCl_4 (50 ml) during 8 h.

(d) With hydrogen chloride.

$(Tsi)_2Zn$ failed to react with boiling concentrated hydrochloric acid (12 M) during 0.5 h. There was also no reaction when HCl gas was passed through $(Tsi)_2Zn$ dissolved in boiling ethanol or ether. In all cases, $(Tsi)_2Zn$ was recovered in good yield.

(e) Thermal decomposition.

$(Tsi)_2Zn$ was heated in a sealed ampoule for 16 h at 340-370°C. The residue was treated with benzene and the solution was separated from the metallic mirror and shown by GLC and NMR spectroscopy to contain unchanged $(Tsi)_2Zn$ and TsiH.

Reactions of di[tris(trimethylsilyl)methyl]cadmium

$(Tsi)_2Cd$ was recovered after (a) heating under reflux for 7 h with acetyl chloride in benzene, (b) treatment with methanol at 58°C for 20 h in toluene, (c) heating under reflux with aqueous THF, and (d) heating under reflux in THF for 9 h with a stoichiometric quantity of cadmium(II) chloride. In this last experiment no TsiCdCl was detected. Some cadmium metal was deposited when a sample of $(Tsi)_2Cd$ was heated in a sealed tube for 16 h at 300-320°C; the solution obtained by dissolving the residue in pentane was shown by GLC and NMR analysis to contain TsiH and $(Tsi)_2Cd$.

DISCUSSION

Di[tris(trimethylsilyl)methyl]zinc and -cadmium show the high thermal stability already found [3][4] for the mercury analogue. Differential scanning calorimetry shows that the three compounds melt sharply within 10° of each other, suggesting that intermolecular forces are determined mainly by the large alkyl groups. Support for this comes also from melting points of mixtures: $(Tris)_2Cd$ + $(Tris)_2Hg$ 286-8; $(Tris)_2Zn$ + $(Tris)_2Cd$ 285-7; $(Tris)_2Hg$ + $(Tris)_2Zn$ 285-7°C.

The three compounds begin to decompose at about the same temperature (<u>ca</u>. 300°C); the only products so far identified are metal and $(Me_3Si)_3CH$, which is also a major product in the decomposition of $(Me_3Si)_3CMMe_3$ (M = Ge or Sn) [6]. Fairly high thermal stability is shown by other trimethylsilyl-substituted methyl-metal compounds. For example, $(Me_3SiCH_2)_2Hg$ [7] and $[(Me_3Si)_2CH]_2Hg$ [4][8] decompose only slowly at 160°C, whereas $Bu^t{}_2Hg$ is completely decomposed in 0.5 h at 40°C [9]. Bis(trimethylsilylmethyl)cadmium is, however, like many other dialkylcadmiums, extensively decomposed at 140°C [10], so that the stability of $[(Me_3Si)_3C]_2Cd$ is exceptional.

There has been considerable discussion about the precise order of metal-carbon bond strengths in dialkyls R_2M (M = Zn, Cd, or Hg); see e.g. ref.[10]. Data obtained so far are insufficiently precise to establish the order for the tris(trimethylsilyl)methyl compounds: what evidence there is [Table 1] suggests that the M-C bonds are very similar in the three compounds. Thus, the asymmetric M-C stretching frequencies are almost the same, and about 100 cm^{-1} lower than in the methyl [11], trimethylsilylmethyl [10] or bis(trimethylsilyl)methyl [8] compounds. In the mass spectra the proportion of the ion current carried by metal-containing ions has sometimes been taken as a measure of the ease with which the M-C bond is broken. In our compounds $[(Me_3Si)_3C]_2M$ the cadmium derivative appears to give more metal-containing ions than does the mercury compound. In contrast, for the compounds $(Me_3SiCH_2)_2M$ only 10% of the ion current is carried by M-containing species when M = Cd, but 50% when M = Hg [10]. For bis(trimethylsilyl)methyl compounds $[(Me_3Si)_2CH]_2M$ the proportion of the current carried by metal-containing species for M = Cd is similar to that for M = Hg [8].

The generally accepted mechanism for decomposition of dialkylmercury(II) compounds R_2Hg involves rate-determining dissociation to the radicals R· and ·HgR followed by very rapid decomposition of ·HgR to Hg and R· [12]. This does not seem to us compatible with the high thermal stability of $[(Me_3Si)_3C]_2Hg$, since we can see no reason why the homolytic dissociation of $[(Me_3Si)_3C]_2Hg$ into radicals should be unusually slow; indeed, it might be expected to be accelerated by relief of steric strain. The high stability of $[(Me_3Si)_3C]_2Hg$ would be consistent with mechanisms for thermal decomposition of R_2Hg involving either direct elimination of R_2 or a chain process including as one step attack of R· on R_2Hg to give RR and RHg· (which would then decompose rapidly to R· and Hg), since in each case the formation of the R-R bond would be sterically inhibited for bulky R groups.

The most unusual feature of the chemistry of di[tris(trimethylsilyl)-methyl]zinc and -cadmium is their ability to withstand boiling in aqueous THF. Thus, dimethyl- and diethylzinc react with water at 20°C or below, and ready reaction with diethylzinc is the basis of a method for quantitative determination of water [13], whereas $[(Me_3Si)_3C]_2Zn$ can be distilled unchanged in steam. The hydrolytic stability is associated with the presence of the third trimethylsilyl group; bis(trimethylsilylmethyl)zinc and -cadmium are both readily hydrolysed and oxidised, and the compound $[(Me_3Si)_2CH]_2Cd$ is converted quantitatively by water and methanol into $(Me_3Si)_2CH_2$ [8].

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