The Synthesis, Structure, and Vibrational Spectra of Organomethyl Compounds

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1 Introduction

Although methyl derivatives are among the simplest organometallic derivatives known, their synthesis and characterization remain an active and intriguing field of study. Three recent reviews have dealt in part with the structure and bonding in methyl–metal compounds.[1] The following discussion will concentrate on the synthetic techniques and structural information available for these compounds. Table 1 summarizes data on selected physical properties and metal–carbon bond distances. Vibrational data have proved helpful in the structural characterizations. Two recent monographs[2] have treated the vibrational spectra of organometallic derivatives. This review will update these discussions with reference to methyl derivatives in addition to discussing those aspects of the vibrational studies relevant to the structural characterizations. Table 2 summarizes metal–carbon skeletal mode assignments for the methyl derivatives. In the following, for each family of elements, synthetic techniques are discussed first, followed by a comparison of the structures found for the solid, liquid and solution, and vapour states, respectively. Finally, vibrational data not included in the structural discussions are treated.

2 Group Ia

Methyl-lithium is formed in solution on mixing methyl halides and lithium using diethyl ether[3,4] or tetrahydrofuran[5] as solvents. Halide-free diethyl ether solutions have been prepared by reaction of lithium and dimethylmercury.[6] Solid methyl-lithium is precipitated on mixing benzene solutions of ethyl-lithium and methyl iodide at 5 to 10 °C.[7] Methylsodium[8] and methylpotassium[8,9] are

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Table 1 *The Melting Points, Boiling Points, and Metal–Carbon Bond Distances for* $(CH_3)_nM$ *Derivatives*

Compound	*Colour & Phase at Room Temp.*	*m.p.* (°C)	*Ref.*	*b.p.* (°C)	*Ref.*	M–C *Dist.*[a] (A)	*Ref.*
MeLi	colourless solid					2.31 (s)	11
MeNa	colourless solid						
MeK	colourless solid					3.22 (s)	9
MeRb	colourless solid					3.36 (s)	10
MeCs	colourless solid					3.53 (s)	10
Me_2Be	colourless solid					Polymer:	
						1.93 (s), b	21
						Monomer:	
						1.69 (v), t	21
Me_2Mg	colourless solid					Polymer:	
						2.24 (s), b	27
Me_3B	colourless gas	−159.85	25	−21.8	40	1.578 (v)	69
Me_3Al	colourless liquid	15.0	40, 41	125.3	40	Dimer:	
						2.125 (s), b	56
						1.956 (s), t	
						2.140 (v), b	71
						1.957 (v), t	
						Monomer:	
						1.957 (v), t	71
Me_3Ga	colourless liquid	−15.7	43, 46, 47	55.8	43, 46, 47		
Me_3In	colourless solid	89	46, 51, 53, 61			2.24 (s), b	56, 61
						2.16 (s), t	
Me_3Tl	colourless solid	38.5	52	147	52	2.30 (s), b	62
						2.22 (s), t	

Me_4Si	colourless liquid	−99	77, 90	26.54	78	1.888 (v)	96
Me_4Ge	colourless liquid	−87.8	86, 88	42.8	86	1.945 (v)	97
Me_4Sn	colourless liquid	−56	88	76.6	83	2.18 (v)	95
Me_4Pb	colourless liquid	−30	88, 98	109	80	2.238 (v)	98
Me_5As	colourless liquid	−6 to −7	103–105				
Me_5Sb	faint yellow liq.	−19	104, 105	126 to 127	104		
Me_3P	colourless liquid	−85.9	108	38.4	106, 108	1.846 (v)	122
Me_3As	colourless liquid	−87.3	108	50.4	106, 108	1.956 (v)	123
Me_3Sb	colourless liquid	−87.6	40, 108	80	40, 106, 115		
Me_3Bi	colourless liquid	−107.7	40, 108	109.3	40, 115	2.267 (v)	124
Me_2Se	colourless liquid		40, 108	58.2	131	1.943 (v)	126
Me_2Te	yellow oil			93.5	125		
MeCu	yellow solid		136				
MeAu	yellow solid		139–142				
Me_2Zn	colourless liquid	−29.2	40, 146	44	146, 149	1.94 (s)	150
						1.929 (v)	149
Me_2Cd	colourless liquid	−2.4	86, 147	105.7	40	2.112 (v)	149
Me_2Hg	colourless liquid			95	149	2.083 (v)	151
Me_4Ti	yellow solid		154				
Me_4Zr	red solid		156				
Me_4Cr	maroon oil	−60	160				
Me_5Nb	yellow soln. in diethyl ether		158				
Me_5Ta	yellow solid	0	158				
Me_6W	red solid	30	161				
Me_6Re	green solid	10	167				

[a] v, vapour-state measurement; s, solid-state measurement; b, bridging metal–carbon bond distance; t, terminal metal–carbon bond distance

Table 2 *Metal–Carbon Skeletal Mode Assignments* (cm^{-1}) *for Monomeric* $(CH_3)_nM$ *Derivatives*

		Mode Description[a]				
Compound	ν_a(MC)	ν_s(MC)	δ(CMC)			*References*
Me^{6}Li		558				18
Me^{7}Li		530[b]				18
Me$_2$Be	1081	[c]		[c]		21
Me$_2$Zn	613	511		157		148
Me$_2$Cd	536	473		140		148
Me$_2$Hg	540	518		160		148
Me$_2$Se	912	585		625		132
Me$_2$Te	843	524		531		132
Me$_3{}^{10}$B	1177	680	341		321	63, 72—74
Me$_3{}^{11}$B	1149	680	341		321	63, 72—74
Me$_3$Al	760	530	[d]		170	64
Me$_3$Ga	577	521.5	[d]		162.5	46, 68, 75
Me$_3$In	500	467	[d]		132	46, 75
Me$_3$P	711	657	315		288[e] 269[e]	119
Me$_3$As	587	574	265		249[e] 222[e]	111
Me$_3$Sb	513	513		188[f]		75, 120
Me$_3$Bi	460	460		171[f]		2, 120
Me$_4$Si	696	598	239		202	78 99—101
Me$_4$Ge	595	558	195		175	80, 100–101
Me$_4$Sn	529	508		157[f]		83, 100, 101
Me$_4$Pb	476	459		120[f]		101, 102
Me$_4$Ti	577	489		180[f]		155
Me$_5$As	458[g]	388[g]	297[h]		265[h]	103
	570[h]	519[h]		113		
Me$_5$Sb	456[g]	414[g]		104[g]		105
	516[h]	456[h]	213[h]		195[h]	
				239		
Me$_6$W	482[i]					161
Me$_6$Re	500[i]					167

[a] ν, stretching mode; δ, deformation mode; a, asymmetric mode; s, symmetric mode.
[b] Estimated mode.
[c] Not observed.
[d] $\delta_{\parallel}$, not observed.
[e] The δ(CMC) mode of E symmetry is split into two bands.
[f] The two expected δ(CMC) modes are accidentally degenerate.
[g] An axial mode.
[h] An equatorial mode.
[i] Since the band was observed in the infrared spectrum, it has T_{1u} symmetry.

formed by reaction of the respective metals with dimethylmercury. Methylpotassium has also been prepared by reaction of K/Na alloy and dimethylmercury as well as by a metathetical reaction between methyl-lithium and potassium t-butoxide.[9] The methyl derivatives of rubidium and caesium have been prepared by reaction of methyl-lithium with rubidium t-butoxide and caesium 2-methylpentan-2-olate, respectively.[10] The Group Ia methyl derivatives all react spontaneously and violently with oxygen and with water, and decompose on heating.

Crystalline methyl-lithium[11] and methylsodium[9] have been reported to be tetrameric with interpenetrating tetrahedra of metal and carbon atoms. This contrasts with the structures found for crystalline methyl-potassium,[9] -rubidium,[10] and -caesium,[10] all of which have a hexagonal structure of the NiAs type with isolated methyl anions and alkali-metal cations.

Both colligative property measurements[6] and n.m.r. studies[12–14] using diethyl ether and tetrahydrofuran as solvents indicate that methyl-lithium retains the tetrameric solid-state structure in solution. This conclusion is supported by vibrational data for halide-ion-free, diethyl ether solutions of methyl-lithium, with Raman bands at 486, 299, 209, and 171 cm^{-1} assigned to the cluster modes of the tetrameric units.[15] Raman spectra of diethyl ether solutions of methyllithium containing halide ions, however, showed none of these bands; halide ions appeared to destroy the tetrameric clusters.[15] The variable-temperature n.m.r. studies[12–14] have been used to examine the mechanisms of methyl group exchange and have led to the conclusion that, while there is an absence of rapid intramolecular exchange of lithium atoms, the tetramers appear to dissociate into dimers in an exchange process of the form (1).

$$Li_4R_4 = 2Li_2R_2 \tag{1}$$

While a tetrameric species is found in ether solutions, a hexameric species is likely to predominate in hydrocarbon solvents.[16]

I.r. studies show that the strong tendency of methyl-lithium to associate is also found in the vapour state.[17] Monomeric methyl-lithium has been produced in an argon matrix through the reaction of methyl radicals and lithium atoms.[18]

The low carbon–hydrogen stretching mode frequencies of tetrameric methyllithium (2840 and 2780 cm^{-1}) have been reported to be characteristic of methyl groups involved in electron-deficient bonding.[17] The fact that the carbon–hydrogen stretching mode frequencies of monomeric methyl-lithium (2820 and 2780 cm^{-1}) are in the same region, however, implies little change in the carbon–hydrogen bond strength on association of monomers in the solid state.[18]

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3 Group IIa

Dimethylberyllium has been prepared from beryllium dichloride and methylmagnesium halides in diethyl ether[19,20] or dimethyl sulphide[21] solutions under anhydrous conditions, or by reaction of beryllium with dimethylmercury.[21–24] The former method has been reported to be useful for preparing large quantities of dimethylberyllium, while the latter method is more useful for preparing small quantities of this compound.[25] Dimethylmagnesium has been prepared by adding dioxan to a diethyl ether solution of a methylmagnesium halide. This precipitates any methylmagnesium halide or magnesium dihalide that is present and leaves dimethylmagnesium in solution.[26–28] It is also formed on adding dimethylmercury to a magnesium diethyl ether mixture[28] or to pure magnesium.[24,29,30] Both dimethylberyllium and dimethylmagnesium are extremely oxygen- and water-sensitive.[25,27,31,32] In addition, both beryllium and organoberyllium compounds are extremely toxic.[23] Attempts to prepare dimethyl-calcium, -strontium, and -barium have failed.[33]

Both dimethylberyllium[31] and dimethylmagnesium[27] are polymeric in the solid state. In a recent i.r. and Raman study of solid dimethylmagnesium, it was also concluded that there are some indications of direct interactions between the magnesium atoms.[34]

The fact that the low-temperature n.m.r. spectrum of dimethylberyllium in diethyl ether exhibits one signal indicates that dimethylberyllium is not associated in this solvent, since an associated structure would produce two signals due to the presence of both terminal and bridging methyl groups.[23] Dimethylmagnesium, however, does give two signals in the low-temperature n.m.r. spectrum of a diethyl ether solution, indicating that dimethylmagnesium is associated to some extent in this solvent.[35] I.r.[36] and ebullioscopic[37] studies also show that dimethylmagnesium is associated in diethyl ether with the degree and extent of association being concentration-dependent. I.r. data indicate that in tetrahydrofuran, however, dimethylmagnesium is not associated.[36]

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It has been suggested that monomer, dimer, trimer, and higher polymers are all present in dimethylberyllium vapour, with the last degree of association becoming important only near saturation conditions.[30] In a more recent i.r. study, it was concluded that the monomer is the major constituent in the vapour phase under non-saturated conditions and that under saturated conditions the monomer is still the principal species with only small amounts of other polymeric species being present.[21] The predominance of the monomer in the vapour was attributed to the possibility that hyperconjugation is able to compete successfully with polymerization as a stabilization process.[21] In an electron diffraction study of dimethylberyllium vapour, however, it was concluded that the beryllium–carbon bond distances offer no indication of hyperconjugation.[38]

As was true for methyl-lithium, there is little difference between the carbon–hydrogen stretching mode frequencies for monomeric[21] and polymeric[39] dimethylberyllium. The methyl deformation mode frequencies, however, are slightly higher for the bridging methyl groups in the polymer than for the terminal methyl groups in the monomer. Although detailed i.r. and Raman data have been reported for solid, polymeric dimethylmagnesium,[34] no such data have been reported for the monomer.

4 Group IIIb

Trimethylboron has been prepared by reaction of boron trifluoride with methylmagnesium halides[40] or trimethylaluminium with tributyl borate.[25] Although spontaneously flammable, it can be stored as a solid complex on reaction with trimethylamine,[25] and regenerated by treatment with slightly more than the theoretical amount of dry hydrogen chloride. Trimethylaluminium is formed on reaction of aluminium with dimethylmercury[41] or methyl iodide,[42] is spontaneously flammable in air,[43-45] and reacts violently with water.[43] Trimethylgallium, which is also spontaneously flammable in air,[43,45,46] has been prepared by reaction of gallium with dimethylmercury[46-49] as well as by reaction of gallium trichloride[44,48] or gallium tribromide[50] with trimethylaluminium. Both solid trimethylindium and trimethylthallium decompose violently in air or water;[45,51,52] trimethylthallium is also photosensitive.[52] Trimethylindium has

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been prepared by reaction of indium with dimethylmercury[46,51,53] for several days with small quantities of iodine, mercury dichloride, or magnesium acting as a catalyst.[46] More recently, up to 100% yields of trimethylindium have been prepared using reaction times of a few hours, by treatment of activated indium with dimethylmercury.[54,55] Trimethylthallium has been prepared from thallous halides, methyl-lithium, and methyl iodide; to avoid explosive decomposition of this solid, it has been purified by distillation under reduced pressure.[52]

Single-crystal *X*-ray studies of trimethylaluminium at −170 °C have shown the presence of a dimeric structure with two bridging methyl groups.[56–58] This solid-state structure is also supported by ^{27}Al n.q.r. data.[59] The trimethyl derivatives of gallium, indium, and thallium as solids are isomorphous. The i.r. and Raman spectra of solid trimethylgallium have been reported to suggest the presence of an associated structure.[60] A single-crystal *X*-ray study of trimethylindium has shown it to consist of tetrameric units with these units interacting more weakly through additional methyl bridges.[61] More recently, however, it has been noted that each trimethylindium molecule is planar in the solid state and that the 'pseudo-tetramer' should be viewed as bonded together very weakly, if at all.[56] Although trimethylthallium might also be considered to be tetrameric, the differences in the intra- and inter-tetrameric Tl · · · Tl bridge bond lengths (5.46 ± 0.01 and 5.63 ± 0.01 Å, respectively) are even smaller than those in trimethylindium (5.235 and 5.66 Å, respectively). Therefore, the structure of solid trimethylthallium may be even more properly considered as polymeric with asymmetric but approximately linear Tl · · · CH_3 · · · Tl units, and one nonbridging methyl group attached to each thallium atom.[62]

The Raman spectrum of liquid trimethylboron is consistent with a monomeric structure and planar C_3B skeleton.[63] The vibrational spectrum of liquid trimethylaluminium is that expected for the methyl-bridged, dimeric structure[64,65] with the Raman spectrum indicating that at 25 °C, the amount of monomer in equilibrium with dimer must be less than about 2%.[64] The room-temperature n.m.r. spectrum of liquid trimethylaluminium, however, exhibits one signal rather than the two expected for the dimer.[66] The room temperature n.m.r. spectrum of trimethylaluminium in cyclopentane also shows one signal.[66] At lower temperatures, however, two signals were observed, thus confirming that the dimeric structure is

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present in solution and implying a similar structure for the pure liquid.[66] To explain the change in the spectrum as a function of temperature, an intramolecular rather than an intermolecular exchange process was suggested as being more likely. In another variable-temperature n.m.r. study of trimethylaluminium in cyclopentane,[67] it was concluded that a mechanism involving the rupture of the aluminium–carbon bond and the re-formation of this bond with another methyl group seemed most likely. More recently, however, in a variable-temperature n.m.r. study that used toluene as the solvent, and included data for not only trimethylaluminium but also for exchange between trimethylaluminium and trimethylgallium, it was suggested that the rate-determining step of the exchange process involved complete dissociation of the dimer into solvent-separated monomers that could then recombine according to the equilibrium (2).[48]

$$\begin{array}{ccccc} Me_6Al_2 & = & 2Me_3Al & = & Me_3Al+Me_3Al \\ \text{Dimer} & & \text{Solvent caged} & & \text{Solvent separated} \\ & & \text{monomer} & & \text{monomer} \end{array}$$

Molecular-weight measurements show trimethylaluminium to be dimeric in benzene[44] although it is monomeric in diethyl ether.[23] Vibrational data indicate that liquid trimethylgallium is monomeric,[46,68] while n.m.r. data support the presence of a monomeric structure in cyclopentane or benzene solutions.[50] Raman data are consistent with a monomeric structure for liquid trimethylindium.[46] Although it was initially reported that trimethylindium is tetrameric in benzene,[51] more recent studies using not only benzene[50,53] but also toluene, dichloromethane, and cyclopentane, indicate that it is monomeric in these solvents. Trimethylthallium is likewise monomeric in benzene.[52,62]

Trimethylboron is monomeric in the vapour state and a recent electron-diffraction study has shown the presence of a planar C_3B skeleton[69] with no evidence of hyperconjugative stabilization of the boron–carbon bonds. Although trimethylaluminium is dimeric in the vapour state at 70 °C, a dimer–monomer equilibrium has been found between 90 and 155 °C, while only the monomer has been detected in the Raman spectrum at 260 °C and a pressure of approximately 1 atm.[45,64,70] A gas-phase electron-diffraction study has been reported of both monomeric and dimeric trimethylaluminium.[71] The monomer has D_{3h} symmetry while the data for the dimer are consistent with a model of D_{2h} symmetry. Trimethyl-gallium,[46] -indium,[45] and -thallium[62] are all monomeric in the vapour phase. In the liquid and the vapour phases, there is free rotation of the methyl groups for all of the trimethyl derivatives of the Group IIIb elements.[46,63,64,71]

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Several vibrational studies have been reported for trimethylboron.[63,72–74] In assigning the vibrational spectrum of dimeric trimethylaluminium, attempts to distinguish between terminal and bridging methyl group modes have been complicated by extensive vibrational mixing of these modes.[65] Although vibrational data are also available for trimethylgallium[46,68,75] and trimethylindium,[46,75,76] it is lacking for trimethylthallium.

5 Group IVb

The tetramethyl derivatives of the Group IVb elements are all stable towards air and water. Tetramethylsilicon has been prepared by reaction of methylmagnesium halides with silicon tetrachloride.[77,78] The Grignard reaction has also been used to prepare tetramethyl-germanium,[77,79–81] -tin,[80,82,83] and -lead.[83] The use of di-n-butyl ether rather than diethyl ether as the solvent can help to increase the yield of tetramethylgermanium[80,81] and decrease the problems involved in removing the solvent from tetramethyltin.[83] Tetramethylgermanium is also formed on reaction of germanium tetrachloride and trimethylaluminium,[84] dimethylzinc,[85] or dimethylcadmium.[86]

Solid tetramethylsilicon exhibits polymorphism. A metastable α-form (m.p., -102 °C) and a stable β-form (m.p., -99 °C), were originally characterized.[87–89] More recently, another metastable form (m.p., -107 °C) has been reported.[90] Although it was originally concluded that tetramethyltin does not exhibit polymorphism,[82] it has more recently been shown that it has a second solid phase that is unstable and obtained when the liquid is cooled through the freezing point of -56 °C.[91] The barrier to internal rotation of the methyl groups in the crystalline tetramethyl compounds decreases on going from silicon to lead.[88,92,93] A photoelectron study of these derivatives has been interpreted to show that it is unneces-

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sary to include the *d*-orbitals in any discussion of the bonding of these molecules.[94] All studies of the tetramethyl derivatives have assumed that the C_4M skeleton is tetrahedral in all phases. Such structures have been found in vapour-phase electron-diffraction studies of tetramethyl-silicon,[95,96] -germanium,[95,97] -tin,[95] and -lead.[95,98] Vibrational studies have also been reported for all four compounds.[78,80,83,99–102]

6 Group Vb

Only two pentamethyl derivatives of the Group Vb elements have been characterized, namely pentamethylarsenic[103] and pentamethylantimony.[104,105] The former has been prepared in dimethyl ether from methyl-lithium and trimethylarsenic dichloride, while the latter has been prepared in diethyl ether from methyl-lithium and trimethylantimony dibromide. A trigonal bipyramidal structure has been suggested for both compounds in all phases on the basis of i.r. and Raman data.

Trimethyl derivatives of all of the Group Vb elements have been reported. Trimethylphosphorus has been prepared by the reaction of phosphorus trihalides with methylmagnesium halides,[106,107] dimethylzinc,[107,108] or methyl-lithium.[109,110] Although it is an extremely volatile and toxic material that ignites spontaneously in air, it can be collected and stored as the solid silver iodide complex $[AgIPMe_3]_4$ and regenerated as needed by heating the complex.[107,109,110] Trimethylarsenic may similarly be prepared by reaction of arsenic trichloride with methylmagnesium halides[111] or dimethylzinc,[112] and stored as the solid complex $[Me_3As]_2PdCl_2$.[113] It can then be regenerated as needed by the thermal decomposition of this complex *in vacuo*.[49] Trimethylarsenic has also been prepared[114] by the action of trimethylaluminium on arsenic trioxide in toluene, and similarly trimethylantimony is obtained by the reaction of trimethyl-

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aluminium with antimony trioxide in hexane.[115] Trimethylantimony can be stored by treating with bromine to produce trimethylantimony dibromide,[116,117] and regenerated by distilling a mixture of trimethylantimony dibromide and finely granulated zinc using various solvents.[115–118] Trimethylantimony[40,106,116] as well as trimethylbismuth[40] have been prepared by reaction of the respective metal trichloride with methylmagnesium halides.

Vibrational data have been reported for all of these trimethyl derivatives.[75,111,119,120] The barriers to methyl group rotation have been determined using solid-state Raman data for trimethylphosphorus[119] and trimethylarsenic.[111] Although the trimethyl derivatives of the Group Vb elements are presumed to have a pyramidal structure in all phases,[121] detailed structural data derived only from microwave studies of the vapour are available for trimethylphosphorus[122] and -arsenic[123] and an electron-diffraction study of trimethylbismuth.[124]

7 Group VIb

Both dimethylselenium[125,126] and dimethyltellurium[127] are volatile and evil-smelling liquids that have been prepared by heating methyl iodide under reflux over a slurry of the respective metalloid powder in an alkaline solution of sodium formaldehydesulphoxylate.

Several studies have concluded that both compounds have a bent C_2M skeleton[126,128–131] in all phases. In a recent analysis of the vapour- and liquid-phase vibrational spectra of these compounds, however, it was concluded that the C_2M skeletons in both compounds are linear.[132] This conclusion has been criticized[133] as being based on a misinterpretation of poor quality vibrational data and ignoring the results of the above mentioned earlier studies.

8 Group Ib

Although trimethylgold is extremely unstable and has not been isolated, it has

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been suggested as an intermediate in the thermal decomposition of $Me_3AuP(C_6H_5)_3$ in a variety of solvents.[134] A molecular orbital study of trimethylgold in the same study reportedly shows that the Jahn–Teller-active structure of C_{3v} symmetry is not the most stable structure; rather, the T- and Y-shaped geometries are of lower energy and are therefore favoured. It was also suggested on the basis of the results obtained from the study of the gold compounds, that a T-shaped trimethylcopper intermediate might possibly be formed in the copper(I)-catalysed coupling reaction between dimethylcuprate and methyl iodide.

Methylcopper has been synthesized from copper nitrate and tetramethyllead,[135] copper iodide and methyl-lithium,[136] or copper acetylacetonate and dialkylaluminium ethoxides.[137] It is reported to be thermally unstable, to decompose explosively,[137] and to have a polymeric structure.[138] Methylsilver is formed as a precipitate on mixing methanol solutions of silver nitrate and tetramethyl-lead at low temperatures.[139–142] It shows extreme thermal instability and while it decomposes slowly between −80 and −50 °C, it is stable for only a few seconds at −30 °C. It is also potentially explosive.

9 Group IIb

Dimethylzinc has been prepared by treatment of methyl iodide with a zinc–copper couple[40,143] or with zinc dust and copper,[144] as well as by reaction of zinc with dimethylmercury,[41] or of zinc acetate and trimethylaluminium.[145,146] Dimethylcadmium has been synthesized from cadmium dihalides and methylmagnesium halides,[40,41,86,147] as well as from cadmium acetate and trimethylaluminium.[135] Dimethylmercury has been prepared by reaction of mercury dichloride with methylmagnesium halides.[138] These dimethyl compounds are highly toxic, and volatile liquids that are extremely air- and moisture-sensitive; except for dimethylmercury, which is stable towards air and water.[148]

Vibrational studies of these three compounds in all phases are consistent with a linear C_2M skeleton[148,149] and free rotation of the methyl groups, although the rotation becomes restricted in the solid state at very low temperatures.[138] Preliminary *X*-ray data reported for dimethylzinc are also consistent with the

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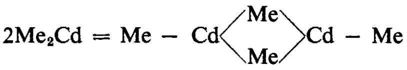
presence of a linear C_2Zn skeleton.[150] An attempted X-ray study of dimethylmercury resulted in a pattern indicative of an amorphous solid.[148] An electron-diffraction study of dimethylmercury vapour has also been reported.[151] Cryoscopic measurements of a benzene solution of dimethylcadmium show that this compound is monomeric.[41] Data derived from n.m.r. studies of dimethylcadmium solutions, however, indicate that there is appreciable intermolecular methyl group exchange between dimethylcadmium molecules.[152,153] A mechanism involving a methyl-bridged dimeric state has been suggested for the exchange process (3).[153]



$$2Me_2Cd = Me - Cd\overset{Me}{\underset{Me}{\langle\ \rangle}}Cd - Me \qquad (3)$$

10 Groups IIIa—VIII

An attempt has been reported to prepare methyl derivatives of scandium, yttrium, and lanthanum[33] from the respective metal trichlorides and methyl-lithium. Pyrophoric solids were produced that were only soluble in donor solvents. Although the constitution of these compounds was uncertain, it was speculated that they were tetrahydrofuran adducts of Me_3M ($M = Sc, Y, La$).

Tetramethyltitanium has been prepared from titanium tetrachloride and methyl-lithium at −80 °C using diethyl ether as the solvent.[154] It is very sensitive to air and water, undergoes thermal decomposition at temperatures above approximately −78 °C, and is presumed to be monomeric with a tetrahedral C_4Ti skeleton. This conclusion is supported by a vibrational study of tetramethyltitanium.[155] Tetramethylzirconium has been reported to be formed through the reaction of zirconium tetrachloride and methyl-lithium, and decomposes below −15 °C.[156]

The addition of a diethyl ether solution of methyl-lithium to $NbMe_2Cl_3$ or $NbMe_3Cl_2$, or to $TaMe_3Cl_2$ produced pentamethylniobium and pentamethyltantalum, respectively.[157,158] The former compound was produced as a yellow ether solution that decomposed above −30 °C. Its instability prevented isolation as a solid.[158] It was possible, however, to isolate solid pentamethyltantalum. Since this compound decomposes violently in air, it is dangerous to isolate more than a millimole, or to store it for more than a few hours at −78 °C, and it should never be stored in a partially decomposed state since further decomposition can

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be sudden and violent.[158] The photoelectron spectrum of pentamethyltantalum is consistent with a structure of D_{3h} symmetry.[159]

Tetramethylchromium has been prepared as a volatile, thermally unstable oil by reaction of chromium(IV) t-butoxide with methyl-lithium.[160] Although unaffected by water, it is sensitive to oxygen. Hexamethyltungsten is formed as an extremely volatile and thermally unstable solid that decomposes slowly on standing.[161] Extreme caution has been recommended in handling this compound since it reacts explosively with atmospheric oxygen and may also detonate, under certain circumstances, *in vacuo* or under nitrogen or argon.[162,163] It was originally prepared through the reaction of methyl-lithium and tungsten hexachloride in diethyl ether.[161] More recently, it has been noted[163] that the more stringent the precautions to exclude air from the solvents and reaction system, the poorer the yields. The reaction is therefore complex, and although oxygen is required to obtain the final solution, its role is obscure. A higher yield of hexamethyltungsten, allowing for the preparation of multigram quantities, has been reported,[163] in which trimethylaluminium and tungsten hexachloride react, followed by the removal of dimethylaluminium chloride with an amine. A photoelectron study has led to the conclusion that hexamethyltungsten has octahedral symmetry.[159,162]

In two different studies, dimethylmanganese was reported to be formed as an insoluble, yellow solid on reaction of MnI_2 and methyl-lithium in diethyl ether.[164,165] In a more recent study,[166] however, it was questioned whether this compound was actually prepared, on account of poor characterization and unsatisfactory analytical data that were reported for only manganese. Hexamethylrhenium has been synthesized as a very volatile solid that can be kept indefinitely at −20 °C, but which decomposes at approximately 10 °C. Although slowly decomposed by water, it is somewhat photosensitive, and extremely air-sensitive. In one case, it was observed to detonate violently on the addition of nitrogen to a sample *in vacuo*. Therefore, it must be handled with extreme caution.[157,167] It is prepared by reaction of trimethylaluminium with $ReO(CH_3)_4$.[167] An e.s.r. study suggested that hexamethylrhenium has a distorted, octahedral structure in petroleum or toluene.[168] A photoelectron study of this compound in the vapour state, however, shows a small and insignificant distortion of the structure from octahedral symmetry.[162]

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Reported synthesis of dimeric dimethylplatinum and tetrameric tetramethylplatinum have been shown to be incorrect, with the statement being made by one investigator that future synthesis of neutral methides such as tetramethylplatinum seems unlikely.[169]

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