HETEROMETALLIC ALUMINIUM COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

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This review covers the heterometallic complexes of aluminium, excluding the many mixed oxides, and complements two companion reviews on the inorganic and organic complexes, respectively. There are nearly three hundred examples with metal atoms ranging from two to eighteen per unit, including aluminium and metals of both the hard and soft classification. Summaries of metal-metal distances are given in each section. The degree of complexity ranges from from dimers to polymers, with a wide range of ligand types and donor atoms. The most common sterochemistry about the aluminium centres is tetrahedral.

CONTENTS

0. ABBREVIATIONS

ac	acetate
acac	acetylacetonate
bht	3,5-di-iso-butyl-4-hydroxytoluene
Bu	Butyl
c	cubic
C_4H_3S	thiophen
C_5H_3	cyclopentadienide
$C_7H_{13}N$	1-azabicyclo[2.2.2]octane
$C_{10}H_8$	diphenyl
$C_{20}H_{14}$	triptycene
$C_{24}H_{24}$	[2.2.2]paracyclophane
cod	1,5-cyclooctadiene
cp.	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
cpb	pentabenzylcyclopentadienyl
dchd	bicyclohexyl-1,1-diol
dhat	1,2-dihydroxyantrachinoate
dhmp	1,4-dihydro-1,4-naphthylenate
dme	1,2-dimethoxyethane
dmf	N,N-dimethylformamide
dmp	2,6-dimethylphenolate
dmpe	bis(dimethylphosphine)ethane
dmpi	N,N-dimethylpiperazine
dmpm	bis(dimethylphosphine)methane
dox	1,4-dioxane

dpb	diporphyrin biphenylene
eb	1,4-epoxybutane
en	ethylenediamine
Et	ethyl
giy	glycolate
m	monoclinic
Me	methyl
mes	mesitylene (1,3,5-trimethylbenzene)
or	orthorhombic
Ph	phenyl
Pr	propyl
tbame	1,1,1-tris(((5'-bromo-2'-hydroxybenzyl)amino)methyl)ethane(3-)
tg	tetragonal
that	1,2,4-trihydroxyantrachinonate
thf	tetrahydrofuran
tl	toluene
tmeda	tetramethylethylenediamine
tr	triclinic
trg	trigonal

1. INTRODUCTION

The chemistry of aluminium is an active area of research particularly in the areas of catalytic activity and biochemistry. Up to end of June 1995 there have been numerous studies on the structure of aluminium published in the literature. These include almost five hundred coordination derivatives [1] and almost four hundred organometallic derivatives [2]. This review covers the aluminium compounds that contain at least one other metal atom, transition or non-transition, and they have been classified according to the total number of metal atoms present.

2. HETEROBINUCLEAR COMPOUNDS

The crystallographic and structural data for these compounds is presented in Table 1. There are over sixty such derivatives with several types of bridging, of which the distorted edge-shared tetrahedral is the most common. A yellow-brown compound [3] has two centres, C_3Al and FeC_7 connected only by a metal-metal bond, completing a tetrahedral environment about the aluminium(III) atom and eight coordination about the iron atom (Al-Fe = 251.0(2) pm).

There are two species [4,5] in which three hydride ions serve as a face-shared triple bridge between AlH_3Cl_2N and WH_5P_3 chromophores [4], or AlH_3C_2 and ReH_4P_3 chromophores [5]. The Al-H distances range from 168.4 to 190.8(52) pm in the former and from 176 to 210(8) pm in the latter. The mean Al-H-Al bond angles are 96.8° and 92°, respectively. The Al-Re distance of 250.1(2) pm [5] indicates a real metal-metal bond, but the Al-W distance [4] is not given.

Distorted edge-shared aluminium tetrahedra bridge through several donor atoms, for example: two hydrogen atoms [5-8], two deuterium atoms [9], two O-donor ligands [10-13], two N-donor ligands [14-16], two carbon ligands [17-21], a pair of chlorine atoms [22,23], bromine atoms [24], iodine atoms [25]; hydrogen plus a C-donor ligand [26,27], C-donor ligand plus a chlorine atom [27-30].

The shortest reported metal-metal bond is that of Al-Sm (229.2(6) pm [9], but for many examples the Al-M distances are not given. The mean Al-L(bridge) distances increase with covalent radii of the donor atoms in the sequence: 177 pm (H, 33 pm) < 181 pm (LO, 73 pm) < 190 pm (LN, 75 pm) < 210.5 pm (LC, 77 pm) < 221 pm (Cl, 99 pm) < 239 pm (Br, 113 pm) < 256 pm (I, 133 pm). There is a geometrical relationship between the Al-M distance and the Al-L-M bridge angle such that as the former increases the latter opens, for example in the series of doubly hydrogen bridged compounds the values are: 250.8(2) pm and 89(5)° [5]; 274.7(4) pm and 99(4)° [7]; 275.5(4) pm and 105(3)° [7]. For the doubly oxygen bridged compounds the values are: 277.8(4) pm and 94.3(4)° [12]; 329.8(7) pm and 107(4)° [13]; 341.1(6) pm and 105.5(3)° [13].

The structure of a red (Al,Ni) derivative [31] is shown in Figure 1. The aluminium atom is 49(2) pm out of the C(1)-C(2)-C(3)-C(4) plane with a dihedral angle of 20.44° between the plane and the C(1)-Al-C(4) plane. The aluminium is tetrahedrally coordinated while the nickel is eight coordinated (Table 1). The Al-Ni distance of 274.8(1) pm indicates a metal-metal bond.

There are two derivatives, yellow-green [32a] and yellow [32b] which contain aluminium and magnesium. A tetrahedral Al atom and a distorted trigonal bipyramidal Mg atom are connected through a hydrogen atom plus 9,10-dihydro-9,10-anthrylene [32a], with the hydrogen atom replaced by the oxygen atom of an ethoxy group in the yellow example [32b].

A five member ring incorporating five different elements has been found in two bimetal derivatives, Al + Li [33] and Al + Mn [34]. In the former, the ring is -LiPCAlCl-, and in the latter is -MnCOAlBr-. In both derivatives the aluminium has tetrahedral environments (AlC_3Cl and $AlBr_3O$, respectively). In the former the lithium is four coordinate (LiN_2ClP), and in the latter the manganese is six-coordinate (MnC_5Br).

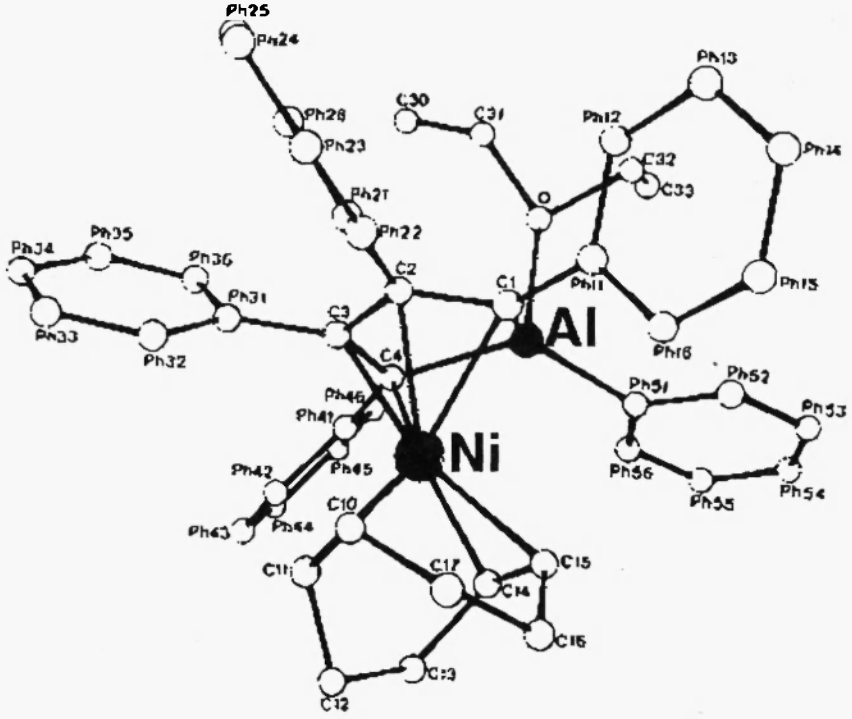

Fig.1 Structure of (cod)Ni(μ-C_4Ph_4)Al(Ph)(Et_2O) [31]

The molecule of another derivative [35] contains two metal centres connected by μ-chloro and μ-butadiene bridges. The chloride bridges Zr and Al unsymmetrically (Zr-Cl = 270.6(1) pm and Al-Cl = 222.6(1) pm) with a Zr-Cl-Al bridge angle of 112.2(1)°. The aluminium atom is close to tetrahedral geometry. The μ-butadiene bonds aluminium via one carbon atom (Al-C = 196.6(2) pm), while the zirconium is bonded by two carbon atoms (Zr-C = 234.8(2) pm and 252.5(3) pm), giving a C-Zr-C angle of 35.3(1)°. In addition, the zirconium carries two η^5-cyclopentadienyl rings.

The structure of a colourless orthorhombic (Al,Li) derivative [36] contains a six-membered heterocyclic ring, $Al(C\text{-}P)_2Li$, in which the chelating CH_2PMe_2 ligands coordinate to the "hard" lithium atom via their soft P atoms, and to the other "hard" aluminium(III) atom via their C atoms. A tetrahedral environment about lithium is completed by another chelate, $Me_2NCH_2NMe_2$, which coordinates through its N atoms (LiN_2P_2). The aluminium atom is also in a tetrahedral environment (AlC_4), and the Al-Li separation of 402.0(5) pm is too large to be considered a metal-metal bond.

There are several derivatives in which two metals are bridged by a single atom, for example: hydrogen atom [37-39], O-donor ligand [40,41,43], oxygen atom [42], N-donor ligand [44,45], C-donor ligand [46-48], and a chlorine atom [49-51]. The Al-L-M bridge angles range from linear (180°) to 66.7(1)° and correlates with the Al-M distance, such that as the latter increases the angle closes, at least for those examples for which data is given: 273.1(1) pm and 116(1)° (M = Ni) [38]; 264.9(2) pm and 84.65(23)° (W) [46]; 241.1(2) pm and 66.7° (Ir) [45]. The mean Al-L(bridge) bond distance increases with the covalent radius of the bridging atom in the sequence: 164 pm (H) < 181 pm (LO) < 194 pm (LN) < 218 pm (LC) < 227 pm (Cl). While the Al-O(bridge) distance found in this series is exactly the same as that found for doubly O-bridged derivatives, the values for N, C and Cl are longer than those of the corresponding doubly bridged examples (190 pm, 210.5 pm and 221 pm, respectively). By contrast, for the H-bridged derivatives the opposite is true (164 pm single and 177 pm double).

TABLE 1. Crystallographic and Structural Data for Heterobinuclear Aluminium Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M-L [pm]	Al-M [pm] Al-L-M [°]	L-M-L [°]	Ref
$(NEt_4).Ph_3Al$ $Fe(CO)_2cp]$ (yellow-brown)	m $P2_1/c$?	1050.7(3) 1525.4(4) 1889.2(4)	92.63(2)	AlC_3Fe	[b] C_{Ph} 202.3(6,10)	251.0(2)	[b] C,C 106.8(3,3.7) C,Al 112.0(2,3.7) C,C 95.4(3) C,cp 130.0(9,1.5))	3
				FeC_7Al	OC 173.2(8,1) C_{cp} not given			
$(Me_3P)_3H_2W(\mu\text{-}H)_3.$ $AlCl_2(NMe_3)$ (yellow)	or Pbca 8	1956.3(2) 1731.9(2) 1444.6(5)		AlH_3Cl_2N	μH 168.4(57) 190.0(69,8) N 206.7(8) Cl 219.7(5,7)	- 96.8(33,5.2)	H,H 76.7(27,7.4) H,N 95.5(21,2.7) 158.7(19) H,Cl 95.5(21,2.1) 157.8(20) N,Cl 95.1(3)	4
				WH_5P_3	μH 167.8(68,7) H 162.6(59,15) P 242.9(4,10)		μH,μH 73.6(29,4.0) μH,H 72.2(27) 132.3(31,10.2) H,H 63.5(27) μH,P 82.9(27,15.4) 148.7(27,8.4) H,P 73.3(21,6.4) 130.1(20) P,P 97.6(2,1.4) 142.8(1)	
$(PMePh_2)_3ReH$ $(\mu\text{-}H)_3.AlMe_2$ at 109K (pale yellow)	m $P2_1/a$ 4	1505.3(4) 1590.0(4) 1170.5(2)	92.59(1)	AlH_3C_2	μH 176(5) 202(6,9) C_{Me} 197.2(4,2)	250.1(2) 92(2,1)	H,H 76.2(2) H,C 116(1,16) C,C 109.7(2) μH,μH 83(3,7)	5
				ReH_4P_3	μH 160(6,13) H 158(3) P 236.7(1,15)		μH,H 89, 142(2,3) μH,P 84(3,13) 158(2,19) H,P 76(2,16)	
$(PMePh_2)_2ReH_4$ $(\mu\text{-}H)_2AlMe_2$ at 111K (pale yellow)	tr Pß 2	1781.5(8) 1038.6(4) 1109.4(4)	111.47(2) 86.08(2) 95.78(2)	AlH_2C_2	μH 179(8) 202(12) C_{Me} 195.0(9,4)	250.8(2) 89(5,3)	H,H 83(4) C,C 111.8(4)	5
				ReH_6P_2	μH 168(10,3) H 152(9,19) P 239.1(2,1)		H,H 64 - 154(4) H,P 76(4,10) 135(4,2) P,P 96.5(1)	
$\{(Me_3Si)N\}_2Al$ $(\mu\text{-}H)_2Li(Et_2O)_2$ (colourless)	tr Pß 2	1122.5(4) 1141.6(5) 1446.0(3)	90.15(3) 100.64(5) 112.07(2)	AlH_2N_2	μH 158.5(20,35) N 186.2(2,5)	- 96(1,0)	H,H 94.3 N,N 117.5(1)	6
				LiH_2O_2	μH 193(2,4) O 194.4(6)		H,H 74(1) O,O 120.6(3)	

$cp_2Ti(\mu\text{-}H)_2$	or	1232.2(2)		AlH_2Cl_2	μH	185(7,15)	274.7(4)	H,H	78(3)	7
	Pbca	1509.0(3)		Cl	Cl	216.1(5,12)	99(4,2)	H,Cl	103(2,8)	
$Al(Et_2O)Cl_2$ [c]	16	3794.1(7)		O	O	195.6(7)			136(2)	
								H,O	80, 158(2)	
								Cl,Cl	110.1(2)	
				$TiC_{10}H_2$	μH	178(3,6)		Cl,O	95.3(3,9)	
					C_{Cp}	231(1,3)		H,H	80(3)	
second molecule [c]					μH	164(5,18)	275.5(4)	H,H	78(3)	
				AlH_2Cl_2	Cl	215.2(5,9)	105(3,3)	H,Cl	98(2,1)	
				O	O	197.9(8)			126(2,3)	
								H,O	80, 158(2)	
								Cl,Cl	109.1(2)	
					μH	181(6,10)		Cl,O	94.7(3,1.0)	
					C_{Cp}	233(1,5)		H,H	70(2)	
				$TiC_{10}H_2$						8
$cp_2W(\mu\text{-}H)_2AlMe_3$	or	1316.6(13)		AlC_3H_2	μH	202(16,6)	311.0(3)		not given	
	Pmcn	898.1(7)			C_{Me}	not given				
at 107K	4	1107.3(8)		$WC_{10}H_2$	μH	146(17,24)				
					C_{Cp}	not given		H,H	60(7)	
$(C_5H_3Bu^t_2)_2Sm$	m	1326.7(3)		AlD_3N_2	μD	190(10,10)	229.2(6)	μD,μD	70	9
	$P2_1/a$	1124.7(2)			D	140(10)		μD,D	113(-,9)	
$(\mu\text{-}D)_2Al(tmeda)D$	4	2476.7(6)	105.02(1)		N	212(2)		μD,N	102.3, 142.4	
								D,N	93.6(-,2.6)	
(dark green)									160.8 [d]	
				$SmC_{10}D_2$				N,N	82.4(8) [d]	
					μD	180(10,20)		not given		
					C	278(3,6)				
$(thf)_2Li$	m	1649(3)		AlO_3Cl	μO	176.4(4,3)	-	μO,μO	91.9(1)	10
$(\mu\text{-}Et_3CO)_2$	$P2_1/c$	1065(1)	106.97(11)		O	169.6(4)	93.8(2,1)	μO,O	116.3(2,6)	
$Al(Et_3CO)Cl$	4	2005(3)			Cl	219.9(4)		μO,Cl	110.0(1,7)	
								O,Cl	110.9(1)	
(colourless)				LiO_4	μO	196.7(8,2)		μO,μO	80.3(3)	
					O	199.1(8,13)		μO,O	120.2(4,5.4)	
								O,O	97.5(3)	
$(Et_2O)Li$	m	1378.9(1)		AlO_3C	μO	180.7(2,2)	-	μO,μO	88.0(1)	11
$(\mu\text{-}Ph_2MeCO)$	$P2_1/c$	1967.6(2)	105.389(7)		O	173.6(2)	94.7(2,3)	μO,O	115.6(1,1.1)	
Al(bht)Me	4	1783.5(2)			C_{Me}	196.9(4)		μO,C	115.0(2,4.2)	
								O,C	107.2(2)	
(colourless)				LiO_3	μO	191.6(7,6)		μO,μO	81.8(3)	
					O	193.3(7)		μO,O	138.0(4,9.8)	
(acac)Cu	tr	1110.7(6)	100.77(5)	AlO_4	μO	181.5(9,4)	277.8(4)	μO,μO	90.2(4)	12
$(\mu\text{-}Me_3SiO)_2$	Pß	1495.6(5)	94.41(5)		O	171.1(9,3)	94.3(4,1)	μO,O	112.5(4,4)	
$Al(Me_3Si0)_2$ [c]	2	1973.9(6)	107.0(3)	CuO_4	μO	197.3(8,0)		O,O	114.3(4)	
					O	189.4(9,1)		μO,μO	81.3(3)	
(blue violet)				AlO_4				μO,O	91.4(4,2)	
								O,O	95.8(4)	
					μO	180.2(9,3)	278.4(4)	μO,μO	91.1(4)	
					O	168.3(9,5)	94.2(4,2)	μO,O	111.9(5,1.2)	
				CuO_4				O,O	115.7(5)	
					μO	199.4(8,4)		μO,μO	80.4(3)	
					O	189.1(8,2)		μO,O	92.6(4,7)	
								O,O	94.5(4)	

$(dmp)_2(thf)_2Yb$	m	2388.1(9)		AlO_2C_2	μO 184.6(10,0)		O,O 85.1(6)	13
$(\mu\text{-}dmp)_2AlMe_2$	C2/c	1203.5(7)	118.74(2)		C_{Me} 199.6(29,0)		C,C 113.9(16)	
	4	1867.6(6)		YbO_6	μO 230.6(8,0)		O,C 113.7(8,6)	
(colourless)					O_{dmp} 205.6(12)		μO,μO 65.6(4)	
					O_{thf} 237.1(9)		μO,O 93.0(4,12.8)	
							O,O 82.9(4,7)	
$(dmp)_2(thf)_2Nd$	m	2318.5(2)		AlO_2C_2	μO 191.0(8,0)	341.1(6)	O,O 87.4(5)	13
$(\mu\text{-}dmp)_2AlEt_2$	C2/c	1312.8(1)	117.658(7)		C_{Et} 199.1(18)	105.5(3)	C,C 110.5(15)	
	4	1890.5(2)		NdO_6	μO 244.7(7,0)		O,C 114.4(7,1)	
(red)					O_{dmp} 215.3(9)		μO,μO 61.5(3)	
					O_{thf} 249.3(7)		μO,O 95.5(3,15.8)	
							O,O 82.5(3,1.0)	
$LiAl(\mu\text{-}NCBu^t_2)_2$	or	1709.8		AlN_4	μN 187(2,0)	255(4)	μN,μN 98.5	14
	Pnma	1501.1			N 178(2,0)	83.9	N,N 103.8	
$(NCBu^t_2)_2$	4	1591.2		LiH_2N_2	μN 195(2,0)		μN,μN 93.7	
					H 237			
(pale yellow)								
$(thf)_2Li(\mu\text{-}NMe_2)$	m	1126.9(7)		AlN_4	μN 190.1(4,5)	-	μN,μN 98.5(2)	15
$Al(Me_2N)_2$	$P2_1/n$	1538.0(10)	92.42(5)		N 184.6(4,10)	85.6(3,2)	μN,N 111.2(2,1.4)	
	4	1377.2(10)					N,N 112.7(2)	
(pale yellow)				LiO_2N_2	μN 213.1(9,1)		N,N 85.1(3)	
					O 199.5(9,10)		O,O 97.8(4)	
							N,O 119.0(4,6.1)	
$(Bu^t)_2Al$	m	3778(2)		AlN_2C_2	μN 193.5(3,3)		C,C 113.5(1)	16
$\{\mu\text{-}N(H)CPh_3\}_2Li$	C2/c	1063.5(4)	98.19(3)		C_{Bu^t} 202.9(3,1)			
	8	1923.7(7)		LiC_4N_2	μN 202.5		not given	
(colourless)					C 224.4-257.0(7)			
$cp^*_2Sm(\mu\text{-}Et)_2AlEt_2$	tr	1567.51(33)	64.785(10)	AlC_4	μC 210.6(5)		C,C 109.3(2)	17
	Pß	1801.41(22)	73.559(14)		C_{Et} 203.2(6)			
	6	1905.86(29)	66.253(14)	SmC_{12}	μC 266.2(4)		not given	
(deep red)					C_{cp^*} 271.2(2)			
$cp_2Yb(\mu\text{-}Me)_2AlMe_2$	or	1786.6(5)		AlC_4	μC 213.1(20,35)	301.4(6)	μC,μC 113.3(8)	18
	$Pna2_1$	797.3(3)			C_{Me} 200.3(25,12)	78.9(7,1.2)	μC,C 106(1,5)	
	4	1087.2(3)					C,C 118(1)	
				YbC_{12}	μC 258.6(23,24)		μC,μC 87.1(6)	
					C_{cp} 260.7(26,66)		μC,cp 106.8(-,2.3)	
							cp,cp 133.1	
$cp_2Zr(\mu\text{-}CCPh)$	tr	976.0(1)	67.53(1)	AlC_4	μC 210.3(4.0)	-	μC,μC not given	19
$\{\mu\text{-}C(Ph)CMe\}AlMe_2$	Pß	1645.3(2)	84.40(1)		C_{Me} 195.5(8,3)	84.8(4,1.6)	C,C 117.4(4)	
	4	1707.6(2)	81.22(1)	ZrC_{13}	μC 240.5(10,65)		C,C not given	
(pale yellow)					C 216.3(3)			e
					C_{cp} not given		cp,cp 129.3	
$cp_2Zr(\mu\text{-}MeCCSiMe_3)$	m	1569.6(3)		AlC_4	μC 207.1(6)	-	μC,μC 104.8(2)	20
	$P2_1/c$	911.9(1)	95.56(1)		211.6(6)	83.9(2,1.6)	μC,C 107.2(3,2.5)	
$(\mu\text{-}CCSiMe_3)AlMe_2$	4	1917.2(2)			C_{Me} 194.7(8,1)		C,C 122.1(4)	
				ZrC_{13}	μC 239.7(6.81)		μC,μC 87.5(2)	
(light brown)					C 215.8(6)		μC.C 32.0(2)	
					C_{cp} not given		119.5(2)	

$cp_2Zr\{\mu$-MeCC(C_6H_{11})}{μ-CC(C_6H_{11})}$AlMe_2$ (yellow)	m $P2_1/c$ 4	1224.5(2) 841.8(1) 2627.2(1)	90.59(1)	AlC_4 ZrC_{13}	μC 209.8(4) 211.7(5) C_{Me} 195.9(5,0) μC 240.3(4,65) C 219.2(5) cp 222.7(-,3)	- 83.1(2,1.8)	μC,μC 105.3(2) μC,C 108.5(2,1.1) C,C 119.2(2) μC,μC 88.4(1) μC,C 31.5(2) 119.8(2) e cp,cp 129.2(1)	20
$cp_2Hf\{\mu$-MeCC-(C_6H_{11})}{μ-CC-(C_6H_{11})}$AlMe_2$	m $P2_1/c$ 4	1222.4(1) 840.3(1) 2611.4(2)	90.77(1)	AlC_4 HfC_{13}	μC 208.9(6,2) C_{Me} 195.5(7,10) μC 237.1(6,61) C 212.0(6) C_{cp} 249.8(10,30)	300.4(2) 84.4(2,1.6)	μC,μC 103.5(2) μC,C 108.4(3,1.9) C,C 118.8(3) μC,μC 87.5(2) μC,C 31.7(2) 119.3(2)	21
$[(C_6H_3Me_3)_2Zr(\mu$-Cl)$_2AlCl_2]$ $[Al_2Cl_7]$ (red)	m $P2_1/c$ 4	948.2(2) 1170.7(3) 2837.7(8)	90.06(2)	$AlCl_4$ $ZrC_{12}Cl_2$ $AlCl_4$ dimer	μCl 219 Cl 210 μCl 269.6 C 254 μCl 228 Cl 210	- not given	not given not given	22
$cp_2Yb(\mu$-Cl)$_2AlCl_2$	m $P2_1/n$ 4	1818.4(3) 1292.3(2) 1036.4(2)	?	$AlCl_4$ $YbC_{10}Cl_2$	μCl 218.6(1,1) Cl 209.6(1,2) μCl 275.6(1,4) C 258.4(3,25)	365 94.4(4,1)	μCl,μCl 97.71(5) μCl,Cl 111.6(1,1.0) Cl,Cl 111.92(6) Cl,Cl 73.36(3)	23
$[C_6H_3Me_3)_2Zr(\mu$-Br)$_2AlBr_2]$ $[Al_2Br_7]$ (dark red)	m $P2_1/c$ 4	978.0(5) 1220.6(7) 2980.0(10)	90.08(3)	$AlBr_4$ $ZrC_{12}Br_2$ $AlBr_4$ (dimer)	μBr 244(2,4) Br 217(2,12) μBr 282(1,0) C 254(4,10) μBr 247(2,1) Br 224(2,17)	- 93.5(8,5) 113(1)	μBr,μBr 94(1) μBr,Br 110(1,7) Br,Br 118(1) Br,Br 78.8(3) Br,Br 110-119	24
$[(C_6H_3Me_3)_2Zr(\mu$-Br)$_2AlBr_2]$ $[Al_3OBr_8]$ (red)	m $P2_1/n$ 4	1303.8(3) 1564.7(5) 1918.8(7)	99.77(2)	$AlBr_4$ $ZrC_{12}Br_2$ $AlBr_3O$ trimer $AlBr_3$ x2 trimer	μBr 234(1,2) Br 224(1,1) μBr 282.2(5,13) C 254(2,12) μO 176(2) Br 226(1,2) μO 182(2,4) μBr 252(1,13) Br 222(1,1)	- 92.4(2,7) 125(1,4) - 72.5(3)	μBr,μBr 98.0(3) μBr,Br 110.3(3,3.4) Br,Br 116.0(4) Br,Br 77.2(1) μO,μBr 88.2(8,3.0)	24

$[(C_6H_6)_2Zr(\mu\text{-}I)_2$	tg	1485.7(5)	AlI_4	μI	256(2,1)	-	μI,μI	97.6(6)	25
$AlI_2(Al_3I_{10})\cdot$	$P4_12_12$	-		I	250(2,3)	89.6(5,2)	μI,I	110.7(8,3.1)	
C_6H_6	8	3957(1)					I,I	115.4(7)	
			$ZrC_{12}I_2$	μI	299.5(9,17)		I,I	79.6(2)	
(dark red)				C	253(8,13)				
							C,C	132.6[e]	
			AlI_4			-			
			trimer	μI	259(3,2)	108.9(8,0)	μI,μI	106.7(9)	
			AlI_4 x2	I	248(3,1)		μI,I	108.9(9,3.2)	
			trimer	μI	272(3,1)		I,I	114.4(9)	
				I	249(3,4)		μI,I	105(1,4)	
							I,I	114(1,2)	
$cp_2Zr(\mu\text{-}H)$	m	829.8(2)	AlC_3H	μH	167(3)	-	not given		26
$(\mu\text{-}C_6H_8)Al(Bu^i)_2$	$P2_1/c$	2432.8(3)		μC	210.1(4)	106(2)			
	4	1166.0(2)		C_{Bu}	198.3(5,14)	79.7(1)			
			$ZrC_{12}H$	μH	195(3)				
				μC	238.9(4)		not given		
				C	215.5(4)				
				C_{cp}	not given				
$cp_2Zr(\mu\text{-}H)$	m	1703.0(2)	AlC_3H	μH	171(4)	-			26
$(\mu\text{-}$	$P2_1/c$	836.2(1)		μC	216.4(5)	105(2)	not given		
$PhCCPh)Al(Bu^i)_2$	4	2082.1(5)		C_{Bu}	195.6(6,2)	78.3(1)			
			$ZrC_{12}H$	μH	192(4)				
(colourless)				μC	240.1(4)		not given		
				C	218.4(4)				
				C_{cp}	not given				
$cp_2Zr(\mu\text{-}H)$	m	1674.9(3)	AlC_3H	μH	185	-	μH,μH	95.6	27
$(\mu\text{-}C_6H_4)Al(Bu^i)_2$ c	$P2_1/n$	1383.3(1)		μC	209(1)	101.3	μC,C	108.0(5,8)	
	8	2017.8(2)		C_{Bu}	201(2,7)	79.4(3)	C,C	117.9(7)	
			$ZrC_{12}H$	μH	190		μH,μC	83.7	
				μC	243.6(9)		μH,C	117.6	
(colourless)				C	216.6(9)		μC,C	33.9(4)	
				C_{cp}	247-254				
			AlC_3H	μH	180	-			
				μC	208	105.9	μH,μC	92.8	
				C_{Bu}	199(1,6)	79.1(3)	μC,C	109.5(5,1.2)	
				μH	181		C,C	116.1(5)	
			$ZrC_{12}H$	μC	242.5(9)				
				C	216.0(9)		μH,μC	82.1	
				C_{cp}	247-254		μH,C	116.1	
				μC	208.2(3)		μC,C	34.1	
$cp_2Zr(\mu\text{-}Me)$	m	915.1(1)	AlC_4	μC_{Me}	210.1(5)	80.5(1)	μC,μC	113.4(2)	27
$(\mu\text{-}C_6H_4)AlMe_2$	$P2_1/n$	1402.2(1)	104.56(1)				μC,C	106.8(2,2.8)	
	4	1441.5(1)		C_{Me}	195.9(5,7)	78.3(1)	C,C	116.3(2)	
(white)				μC	248.1(3)		μC,μC	87.8(1)	
			ZrC_{13}	C	216.5(3)		μC,C	33.8(1)	
				μC_{Me}	255.9(5)			121.5(1)	
				C_{cp}	not given				

$cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Al(Me_3CCH_2)_2$ (red)	m $P2_1/c$ 4	944.3(8) 1557.3(4) 1535.8(4)	100.30(8)	AlC_3Cl	μC/Cl 223.6(2,23) C 197.8(4,4)	304.0(1) 81.1(1,1.7)	μC/Cl,C 104.66(8) μC/Cl,C 108.5(1,7) C,C 117.8(2)	28
				$TiC_{11}Cl$	μC/Cl 243.7(2,57) C_{cp} 236.9(5,35)		μC/Cl,C 93.09(6)	
$cp_2Zr\{(\mu\text{-}CH(CH_2Bu^t))(\mu\text{-}Cl)Al(Bu^i)_2$ at 173K (red orange)	m $P2_1/n$ 4	1977.9(3) 1405.5(3) 908.6(2)	90.12(2)	AlC_3Cl	μC 208.7(2) μCl 235.6(1) C_{Bu} 197.4(2,4)	308.2(1) 77.20(2) 93.07(9)	μC,μCl 98.89(7) μC,C 111.1(1,6) μCl,C 107.6(1,1.4) C,C 118.5(1) μC,μCl 90.69(6) μCl,cp 105.3(1,3)[e] μC,cp 106.5(1,1.2)[e] cp,cp 124.3(2)	29
				$ZrC_{11}Cl$	μC 215.8(2) μCl 257.6(1) C_{cp} 250.0(3,17)			
$cp_2Zr(\mu\text{-}Me_3SiCCPh)(\mu\text{-}Cl)AlMe_2$	m C2/c 8	1814.6(6) 973.1(1) 2721.8(3)	102.97(2)	AlC_3Cl	μC 212.1(3) μCl 226.4(1) C_{Me} 196(1)	- 79.9(2) 87.0(2)	μC,μCl 106.1(2)	30
				$ZrC_{12}Cl$	μC 245.3(3) C 218.6(3) μCl 263.8(1) C_{cp} not given		μC,μCl 86.9(2) μCl,C 119.5(1)	
$(ood)Ni(\mu\text{-}C_4Ph_4)Al(Ph)(Et_2O)$ (red)	m $P2_1/n$ 4	1199.48(8) 1697.58(13) 1877.21(14)	97.958(3)	AlC_3O	μC 195.7(3,3) C_{Ph} 197.5(3) O_{Et} 197.7(3)	274.8(1) 82.3(1,2)	μC,μC 88.1(1) μC,C 127.5(1,2.2) μC,O 107.0(1,1.0) C,O 98.1(1)	31
				NiC_8	μC 221.2(3,8) C 209.7(3,3) C_{cod} 209.6(3,14)		μC,μC 75.9(1) μC,C 39.3(1,2.6) 69.6(1,3) C,C 38.4(1,2)	
$(thf)_3Mg(\mu\text{-}H)(\mu\text{-}dhan)AlEt_2$ (yellow green)	m $P2_1/n$ 4	1170.7(1) 1868.7(2) 1401.64(5)	94.299(3)	AlC_3H	μH 162(3) C 203.6(4) C_{Et} 198.2(5,2)	- 139(2)	C,C 111.3(2,1.3) C,H 108(1,3)	32a
				MgO_3HC	μH 196(3) C 219.5(4) O_{thf} 207.1(3,35)		O,O 86.3(1,1) 120.6(1) O,H 83.8(9,7) 159.9(9) O,C 112.9(1,13.6) H,C 100.8(9)	
$(thf)_3Mg(\mu\text{-}OEt)(\mu\text{-}dhan)AlEt_2$ (yellow)	m $P2_1/a$ 4	4039.9(3) 878.7(1) 1047.3(1)	96.781(6)	AlC_3O	μO not given C " C_{Et} "		not given	32b
				MgO_4C	μO " O " C "		μO,O 136 μO,C 144 O,C 109	

(tmeda)Li(μ-Cl) {μ- $P(Me)_2C(SiMe_3)_2$} $AlMe_2$ at 238K (colourless)	m $P2_1/n$ 4	891.5(1) 1886.7(2) 1655.8(2)	92.52(1)	AlC_3Cl	μCl C C_{Me}	227.6(2) 204.7(4) not given	- 94.5(1)	μCl,C	105.4(1)	33
				LiN_2ClP	μCl P N	236.9(6) 266.9(7) not given		μCl,P	93.6(2)	
$(CO)_4Mn(\mu\text{-}Br)$ $\{\mu\text{-}OCMe\}AlBr_2$ (yellow)	m $P2_1/c$ 4	683.5(2) 1637.4(6) 1227.8(4)	94.18(2)	$AlBr_3O$	μBr O Br	231.3(7) 181(1) 224.5(7,26)	- 92.3(2)	μBr,O μBr,Br Br,Br O,Br Br,C C,Cl μCl,Cl μCl,C Cl,Cl Cl,C Cl,C C,C cp,cp	97.3(5) 112.9(3,5) 114.6(3) 108.9(5,2.3) 89.8(3,2.6) 177.2(6) 90.1(9,2.6) 177.7(9,7) 105.6(1,4) 102.2(1) 110.1(1) 116.0(1,1.5) 87.4(1) 35.3(1) not given	34 35
				MnC_5Br	μBr C OC	258.0(4) 195(2) 185(2,6)				
$cp_2Zr(\mu\text{-}C_4H_6)$ $(\mu\text{-}Cl)AlCl_2$	m $P2_1/n$ 4	912.4(1) 1504.0(1) 1173.7(1)	96.60(1)	$AlCl_3C$	μCl Cl C	222.6(1) 213.7(1,2) 196.6(2)	- 111.2(1)			
				$ZrC_{12}Cl$	μCl C C_{cp}	270.6(1) 243.7(2,89) 250.9(2,42)				
(tmeda)Li $(\mu\text{-}PMe_2CH_2)_2AlMe_2$	or $Cme2_1$ 4	1065.2(3) 1620.9(5) 1276.1(1)		AlC_4	C C_{Me}	203.3(4,0) 200.8(7,3)	402.0(6)	C,C	109.5(2,6.0)	36
				LiN_2P_2	N P	211(1,1) 260.6(5,0)		N,N P,P N,P	87.3(5)[d] 105.7(3) 115.9(3,1.7)	
$cp_3Zr(\mu\text{-}H)AlEt_3$	or Pcmn 4	804.2(2) 1328.6(6) 1904.7(7)		AlC_3H	μH C_{Et}	177 193.8(9,25)	- 180	μH,C C,C	106(-,4) 104.4(3) 123.8(6)	37a
				$ZrC_{15}H$	μH C_{cp}	188 258.5(8,43)		μH,cp cp,cp	95.5(-,9.7)[e] 119.1(-,1.1)[e]	
$cp_2Lu(\mu\text{-}H)$ $AlH_3(NEt_3)$	m $P2_1/a$ 4	1327.8(4) 969.7(3) 1409.9(4)	94.22	AlH_4N	μH H N	181(14) 153(20,8) 213.1(13)	323.4(5) 127(8)	μH,H μH,N H,H 57, 100, 131(8) H,N 90(5,5), 139(8)	112(9,3) 102(5)	37b
				$LuC_{10}H$	μH C_{cp}	181(14) 231(-,1)[e]		cp,cp	129[e]	
$(C_7H_{13}N)(Me)_2$ $Al(\mu\text{-}H)Ni(cdt)$ (yellow)	or Pbca 8	2206.0(2) 1426.1(1) 1307.5(2)		AlC_2HN	μH N C_{Me}	157(3) 206.0(2) 198.1(3,2)	273.1(1) 116.2(2)	C,C H,N C,C	116.4(1) 86(1) 37.7(2,1.7)	38
				NiC_6H	μH C	165(3) 211.4(4,76)				

(dmpi)Li(μ-H)Al(Bu^t)$_4$	m $P2_1/n$ 4	1085.0(2) 1635.2(3) 2008.2(4)	100.30(2)	AlC_3H	μH 159(3) C 203.7(3,3) C_{Bu} 203.0(3)	- 152(2)	μH,C 104(1,7) C,C 114.2(1,8.6) μH,N 135.3(9,8.6) N,N 75.9(3)[d]	39
{(Me$_3$Si)$_2$CH}$_2$ (colourless) at 153K				LiN_2H	μH 176(3) N 204.9(8,5)			
(thf)Li(μ-$C_{16}H_{23}O_6$)Al(Me)$_2$Cl at 173K	m $P2_1/n$ 4	963.1(2) 1754.4(1) 1518.7(4)	?	AlC_2OCl LiO_5	μO 180.4 C 203.6(-,19) Cl 217.6 not given			40
{(Me$_3$Si)$_2$CH}$_2$(Me)Al(μ-OC$_2$H$_4$OMe)K(dme) (colourless)	m $P2_1/c$ 4	1236(1) 1856(1) 1586.5(9)	92.24(4)	AlC_3O KO_4	μO 181.0(2) C_{Me} 201.4(3) C 205.9(3,1) μO 263.7(7,2) O 273.1(6,39)	- 123.6(1)	μO,C 106.6(1,9) C,C 112.2(1,2.6) O,O 64.7(1,3.3)[d] 115.7(1,23.8)	41
Br$_3$Al(μ-O)W(Bu^{t}CH$_2$)$_3$Br	or Pbca 8	1864.3(6) 1599.6(5) 1709,2(6)		$AlBr_3O$ WC_3OBr	μO 179(1) Br 224.8(9,12) μO 177(1) C 211(2,3) Br 242.8(3)	- 172(1)	μO,Br 105.8(6,3.8) Br,Br not given C,C 120(1,1) C,O 89.7(8,3.0) C,Br 90.3(6,2.7) O,Br 177.4(5)	42
Et$_2$Al{μ-OC(Me)P(Ph)$_2$N(Bu^t)}Fe(CO)cp (brown-black)	tr Pß 2	1047.4(2) 1568.7(3) 970.7(1)	97.98(1) 115.01(1) 71.81(1)	AlC_2ON FeC_7O	μO 184.2(2) N 193.6(2) C_{Et} not given μO 196.9(2) C 198.3(3) O 172.9(3) C_{cp} 208.4[e]	- 118.08(9)	C,C 113.4(2) O,N 92.22(8) O,C 41.53(8)	43
{(Bu^{t}N)(Bu^{t}NH)Si(Me)}Na(μ-NBu^t)AlMe$_2$	or Pbca 8	1067(3) 1558(4) 2681(7)		AlN_2C_2 NaN_2	μN 191(1) N 186(1) C_{Me} 199(1,1) μN 248(1) N 252(1)	- 105.9(4)	μN,μN 81.9(4) C,C not given μN,N 70.6(3)	44
Me$_2$Al{μ-(Ph$_2$PCH$_2$Si(Me)$_2$)$_2$N}Ir(MeCCH$_2$)	m $P2_1/c$ 4	1882.3(6) 970.1(2) 2135.9(8)		AlC_2N IrP_2NC	μN 197.0(5) C_{Me} 197.0(8,10) μN 237.3(5) C 201.4(6) P 228.3(2,11)	241.1(2) 66.7(1)	C,C 108.2(3) C,N 119.1(2,7) C,Ir 120.3(2,1.1) N,Ir 64.7(1) P,P 161.86(5) N,C 168.8(2) P,C 93.6(2,2.2) P,N 88.1(1,4)	45

$Me_2ClAl(\mu\text{-}CH)$ $WCl(PMe_3)_3$	m $P2_1/c$ 4	966.89(24) 1198.68(30) 1997.14(51)	103.059(20)	AlC_3Cl	μC 211.3(6) C_{Me} 205.1(5,34) Cl 215.2(2)	264.9(2) 84.65(23)	μC,C 108.6(2,2.6) C,C 113.14(21) μC,Cl 110.79(18) C,Cl 107.8(1,8)	46
				WP_3CCl	μC 180.7(6) Cl 252.0(2) P 248.2(2,29)		P,P 91.5(1,2) P,C 92.1(2,8.8) P,Cl 85.4(1,3.5) C,Cl 172.23(19)	
$cp^*_2Yb(\mu\text{-}Et)AlEt_2(thf)$ (green)	or $P2_12_12_1$ 4	1334.5(2) 1962.9(3) 1237.2(2)		AlC_3O	μC not given C " O_{thf} "		not given	47
				YbC_{12}	μC 285.4(18) C 293.9(1) C_{cp^*} 267.9(17)		cp^*,cp^* 142.8[e]	
$cp^*_2(H)Ta(\mu\text{-}C_2H_4)AlEt_3$ at 220K	m $P2_1/c$ 4	1487.7(5) 1245.5(7) 1501.7(4)	101.08(13)	AlC_4	μC 225(2) C_{Et} 198(2,1)		μC,C 37.4(6) μC,H 72.6	48
				$TaC_{12}H$	μC 231(2) C 218(2) H 177 C_{cp^*} 244(2,5) 212.5(-,5)[e]		cp^*,cp^* 138.9[e]	
$cp_2ClZr(\mu\text{-}Cl)AlCl_3$ (pale yellow)	m C2/c 8	2556.8(9) 1271.0(3) 984.5(2)	101.47(2)	$AlCl_4$	μCl 223.4(3) Cl 209.8(4,3)	- 126.06(7)	μCl,μCl 105.5(1,2.6) Cl,Cl 113.1(2,1.9)	49
				$ZrC_{10}Cl_2$	μCl 260.5(2) Cl 240.6(3) C_{cp} 248.0(8,29) 217.7[e]		μCl,Cl 92.3(7)	
$(dmpe)_2(H)(CCMe_3)Ta(\mu\text{-}Cl)AlMe_3$ (orange)	m $P2_1/c$ 4	985.87(24) 2227.99(63 1479.65(40)	103.479(20)	AlC_3Cl	μCl 231.0(2) C_{Me} 195.7(8,3)	- 149.85(9)	μCl,C 103.6(3,4.5) C,C 114.6(4,1.0)	50
				TaP_4HCCl	μCl 275.8(2) C 185.0(5) H 179.6(49) P 256.9(2,56)		P,P 78.7(1,6.8) 123.02(6) P,H 61.6(16,7) P,C 93.4(1,1.5) P,Cl 86.2(1,3.5) H,C 100.4(16) H,Cl 82.1(16)	
$[C(_{24}H_{24})Sn(\mu\text{-}Cl)AlCl_3][AlCl_4]$ (colourless)	m $P2_1/n$ 4	1743.1(3) 1273.8(3) 1761.7(3)	99.86(1)	$AlCl_4$	μCl not given Cl "		not given	51
				SnC_xCl	μCl 307.3(2)		C,C 117.7(-,2.2)[e]	
				$AlCl_4$	C 260.8(-,74)[e] not given		not given	

$(dmpe)_2(Ph_2Bu^t$	m	2114.7(4)		AlC_3O	μCO	186.2(9)		P,P	88.6(1,11.0)	52
$SiCO)Ta(\mu\text{-}CO)$	C2/c	1335.7(2)	105.14(1)		C_{Et}	not given		P,C	94.4(1,10.9)	
$AlEt_3$	8	3278.0(6)						C,C	73.4(4)	
				TaP_4C_2	μOC	193(1)				
(red) at 226K					C	189.4(9)				
					P	256.4(3,73)				
$(PMe_3)_3Cl(CO)W$	m	1041.97(17)		$AlCl_3O$	O	175.1(3)		O,Cl	107.3(1,2.1)	53
$(\mu\text{-}HCCO)AlCl_3$	$P2_1/c$	1289.65(25)	105.88(2)		Cl	212.0(2,3)		Cl,Cl	111.6(1,1.1)	
	4	1931.94(45)		WC_3P_3Cl	C	202.2(5,13)		C,C	33.99(17)	
(orange)					OC	198.4(4)			71.35(17)	
					P	253.8(1,33)			109.32(18)	
					Cl	247.6(1)		P,P	93.0(1,6)	
								C,P	94.7(1,20.8)	
								C,Cl	86.01(13)	
									161.0(1,3.6)	
								P,Cl	83.1(1,3.9)	
(tmeda)(thf)Li	m	860.2(2)		AlC_4	C	203.5(4)	458.8(7)	C,C	109.5(2,4.9)	36
$(-Me_2PCH_2)AlMe_3$	$P2_1$	1551.1(3)	111.80(2)		C_{Me}	201.0(5,5)				
	2	923.9(2)		LiN_2OP	P	259.3(7)			[d]	
(colourless)					O_{thf}	190.4(8)		N,N	87.7(3)	
at 238(5)K					N	211.9(8,3)		N,O	113.9(4,2.8)	
								N,P	115.2(4,4.9)	
								O,P	108.9(3)	
$cpFe\{\mu\text{-}C_5H_4CH_2\text{-}$	m	1296.9(2)		AlC_3N	N	206.2(5)		C,C	113.5(3,7)	54
	$P2_1/a$	1310.33(2)	91.45(2)		C_{Me}	195.7(7,4)		C,N	105.0(2,8)	
$(Me_2)N\}AlMe_3$ [c]	8	2041.1(3)		AlC_3N	N	205.3(5)				
					C_{Me}	196.0(7,13)		C,C	114.2(3,2.1)	
(yellow)					C_{cp}	not given		C,N	104.1(2,4)	
				FeC_{10}					not given	
$[Co(\mu\text{-}dpb)$	tr	1309.5(4)	87.47(1)	AlN_4O	N	200.2(4,6)	437.0(1)		[f]	55
$Al(EtO)]C_7H_8$	Pß	1683.6(3)	70.40(3)		O_{Et}	178.9(3)		N,N	88.2(1,1.4)	
	2	1698.6(3)	85.90(2)					N,O	100.6(1,3.3)	
				CoN_4	N	195.6(4,7)			[f]	
								N,N	90.1(1,1.2)	
$(CO)_5Cr(\mu\text{-}PPh_2)$	m	1183.9(4)		AlC_2NP	μP	248.5(1)	-	C,C	116.62(15)	56
$Al(Me_3SiCH_2)_2(Me_3N)$	$P2_1/n$	1851.7(5)	90.32(2)		N	204.9(3)	124.64(4)	C,N	106.0(1,1.8)	
	4	1615.8(4)			C	196.5(4,2)		C,P	112.4(1,4.2)	
(yellow)					μP	248.2(1)		C,C	89.5(1,4.2)	
				CrC_5P	OC	188.0(4,33)		C,P	91.0(1,4.4)	
									174.20(12)	

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Crystallographically independent molecules are present.
d. Five member metallocyclic ring.
e. Centroids of the carbon ring.
f. Six member metallocyclic ring.

A bidentate carbonyl group serves as a bridge in a red monoclinic derivative [52] (Al-O-C-Ta). The aluminium is tetrahedral and the tantalum is pseudo-octahedral. An orange Al/W derivative [53] has three meridional PMe_3 ligands, a carbonyl, a chloride and one η^2-$HC{\equiv}COAlCl_3$ unit giving a WC_3P_3Cl chromophore. A colourless Al/Li derivative [36] utilizes a bidentate Me_2PCH_2 ligand to form a two atom bridge, Al-C-P-Li, with both metals in tetrahedral geometries.

The structure of a yellow Al/Fe complex is shown in Figure 2. The coordination geometry around the aluminium is distorted tetrahedral The cyclopentadienyl rings in the ferrocene moiety are in the eclipsed conformation.

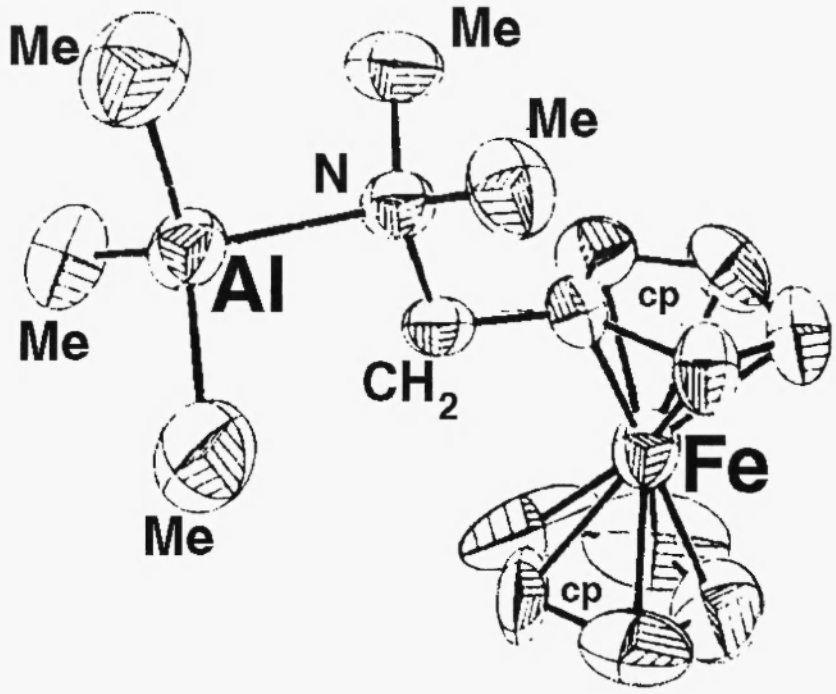

Fig.2 Structure of cpFe{μ-$C_5H_4CH_2(Me_2)N$}$AlMe_3$ [54]

A heterobimetallic cofacial di-porphyrin structure [55] shows no metal-metal interaction (Al-Co = 437.0(1) pm) and both porphyrin moieties are eclipsed (a = 29.8°). The cobalt is four coordinate, square planar CoN_4. The aluminium is five coordinate, with an axial ethoxy group located outside the N_4 cavity. The aluminium atom lies 36.5(1) pm from the plane of the four nitrogen atoms and towards the direction of the ethoxide ligand.

The data in Table 1 reveal that there is only one example in which the aluminium atom is six coordinate [4], four examples of trigonal bipyramidal coordination [5,7-9] and one square pyramidal Al(III) [55]. The rest all have aluminium with a tetrahedral coordination, which is also the most common for the coordination [1] and organometallic derivatives [2]. The range of heterometal atoms is considerable, including both transition and non-transition metals, with a variety of sterochemistries, often quite complex or unusual. One example has a two coordinate sodium atom, NaN_2 [44]; two examples have three coordinate lithium, LiO_3 [11] and LiN_2H [39]; several examples have a four coordinate heterometal atom [6,10,12,14,15,33,36,41,45,55], five coordinate [32,40,42,46], six coordinate [13,16,34, 52,56] and seven coordinate [5,38,50,55]. There are also examples with eight coordinate heterometal atoms, such as WH_5P_3 [4], ReH_6P_2 [5] and NiC_8. Iron "open sandwich" compounds, FeC_5, are also found with two additional ligands FeC_5C_2 [3]) or three additional ligands FeC_5C_2O [43] to give seven or eight coordination, respectively. Full "sandwich" compounds are, however, more common [7-9,17-30,35,47-49,54]. There is one example with zirconium as the heterometal atom in which it carries three η^5-cyclopentadienyl ligands and is also H-bridged to an AlC_3 moiety [37].

The heterometallic aluminium compounds show a variety of colours, for example: colourless with Li (x3), Zr (x3), K, Sn and Yb (one each); yellow with Zr (x3), Li, Mg, Fe and Re (two each), W, Ni, Cr and Mn (one each); red(orange) with Zr (x5), Ta (x2), Ti, Ni, Sm and Nd (one each); green with Sm; blue-violet with Cu; Brown with Zr; white with Zr. The Al/Zr bimetallic derivatives exhibit the widest range of colours.

There are four examples [7,12,27,50] which contain two crystallographically independent molecules in the same crystal, with differing degrees of distortion in the M-L and L-M-L parameters. This is typical of the general class of distortion isomerism [57].

The mean Al-L bond distance in the four coordinate examples increases with the covalent radius of the coordinating atom in the sequence: 179 pm (LO) < 188 pm (LN) < 199 pm (LC) < 213 pm (Cl) < 223 pm (Br, 113 pm) < 250 pm (I, 133 pm). The mean Al-L(bridge) values follows also this trend: 172.5 pm (H) < 181 pm (LO) < 190 pm (LN) < 212 pm (LC) < 225 pm (Cl) < 236 pm (Br) < 256 pm (I). In general the mean bonding distances for unidentate ligands are shorter than those of the corresponding bridging ligands.

The sixty or so derivatives listed here, together with the eighty or so dimeric coordination complexes [1] and over one hundred and sixty organoaluminium dimers [2], illustrate the rich diversity of the aluminium dimeric compounds. In all three classes, four coordinate (tetrahedral) aluminium is by far the most common. A summary of mean Al-L bond distances for the four coordinate hetero- and homobimetallic dimers is given in Table 1A. Only the most common donor atoms in the heterobimetallic series are listed, for comparison. The Al-L bond distances show a tendency to increase in the order:- homo- < hetero- < organo-bimetallic.

A summary of the Al-M distances is given in Table 1B. It should be noted that there are several examples for which the full data have not been published. The heterometal atom ranges from the typical transition metal, a number of lanthanides, and a range of non-transition metals. The Al-M distances vary from a definite bonding distance (229.2(6) pm) to a distance that rules out any bonding (458.8(7) pm.

TABLE 1A. Summary of the Al-L(atom) Bond Distances (pm) for Four Coordinated Binuclear (Homo- and Heterometallic) Aluminium Derivatives[a]

COORD. ATOM	Cov. Rad. [pm]	Heterometallic Coord. Cpds. this paper	Homometallic Coord. Cpds. [ref 1]	Organoaluminium Compounds [ref 2]
LO	73	179(11,9)	170(3,3)	189(22,11)
μLO		181(2,4)	182(6,1)	187(5,9)
LN	75	188(10,8)	181(2,1)	191(7,7)
μLN		190(3,4)	194(4,4)	197(5,24)
L(C)	77	199(8,7)		197(14,7)
μLC		212(3,13)		221(25,2)
Cl	99	213(4,4)	210(3,4)	212(10,6)
μCl		226(7,9)	226(4,2)	233(8,12)
Br	113	223(8,4)	225(5,5)	-
μBr		236(5,12)	242(5,9)	249
I	133	250(3,3)	248(1,1)	-
μI		256	265	-
μH	30	173(18,29)	168(1,1)	179(14,8)

Footnotes: *a. The first number in parenthesis is the difference between the shortest and the mean values, the second number is the difference between the highest and the mean.*

TABLE 1B. Summary of the Al-M Distances [pm].

Al-M	Distance [reference]	Al-M	Distance [reference]
-Sm	229.2(6) [9]	-Ir	241.1(2) [45]
-Re	250.1(2) [5]	-Fe	251.0(2) [3]
-Li	255(4) [14]; 402.0(6), 458.8(7) [54]	-W	264.9(2) [46]; 311.0(3) [8]
-Ni	273.1(1) [38]; 274.8(1) [31]	-Ti	274.7(4), 275.5(4) [7]; 304.0(1) [28]
-Cu	277.8(4), 278.4(4) [12]	-Hf	300.4(2) [21]
-Yb	301.4(6) [18]; 329.8(7) [13]	-Zr	308.2(1) [29]
-Lu	323.4(5) [37b]	-Nd	341.1(6) [13]
-Co	437.0(1) [56]		

3. HETEROTRINUCLEAR COMPOUNDS

There are forty five heterotrinuclear aluminium derivatives for which the crystallographic and structural data are listed in Table 2. There are two types of compound, one containing two aluminium atoms plus one other metal (30 examples, Table 2A), and the other with one aluminium and two atoms of another metal (15 examples, Table 2B). There are no examples with three different metal atoms present.

From the structural point of view the derivatives are complex and difficult to categorize. The pale yellow Al^{III}_2/W^{IV} derivative [58] has a W-(CAl_2Me_4Cl) fragment involving a W=C: unit linked by a three centre, two electron, bond to the aluminium atoms of the $[Me_2Al(\mu\text{-}Cl)AlMe_2]^+$ moiety. The Al-C distances are slightly asymmetric at 198.4(5) and 204.3(5) pm, with the Al-C-Al angle of 97.06(23)°. While this angle is obtuse, the Al-Cl-Al angle is acute (78.88(9)°) and each aluminium atom is tetrahedrally coordinated (AlC_3Cl).

There are several derivatives [59-68] in which a "central" metal atom (Mg^{II} [59-63], Pd^{II} [64], Ti [65], W^{VI} [66] and Y^{III} [67]) edge shares with a tetrahedral aluminium unit on each side. The bridging atoms are varied as indicated: two C-donor ligands [59], two O-donors [60-63], two chlorine atoms [64], or two N-donors [66]. There are also mixed bridges containing O- and N-donors [60], or O- and C-donors [65,67]. The most common central metal atom is magnesium and the most common bridge atom is oxygen. The coordination number of the central atom varies from 4 (MgC_4 [59], MgO_4 [60], MgO_2N_2 [60], $PdCl_4$ [64] and WN_4 [66]), to 5 (TiO_4C [65]) and 6 (MgO_6 [61-63] and YO_4C_2 [67]).

The mean Al-L bond distances, both terminal and bridging, increase with the covalent radius of the donor atom in the sequence: 172 pm (LO) < 197 pm (LC) < 207.5 pm (Cl) and 180.5 pm (LO) < 195 pm (LN) < 208 pm (LC) < 221 pm (Cl); respectively. As usual, terminal bonds are tighter than bridging bonds.

There is a correlation between the Al-L-M bridge angle and the covalent radii of the bridge atom. The angle closes as the radius increases, for example: 93.9° to 103.3° (average 99°) for LO > 88.7° to 90.2° (average 88.6°) for LN > 77.7° to 87.7° (average 83.2°) for LC. The Al-Mg distances range from 270.4(2) to 304 pm, and the Al-Y distance has a mean value of 322.2(3) pm which precludes an M-M bond.

Several examples [69-76] have a central "open sandwich" Ti(III) unit edge-shared with two tetrahedral aluminium atoms in a similar manner to that outlined above. Again, the Al-X bond distances, terminal or bridging, increase with covalent radius of X in the order: 208 and 219 pm (Cl) < 223 and 233 pm (Br) < 247 and 257 pm (I). The Al-X-Ti bridge angle closes as the Al-X value increases and as the covalent radius of X: 92.8° and 219 pm (Cl) > 90° and 233 pm (Br) > 87.3° and 257 pm (I).

An "open sandwich" yttrium moiety is linked to two tetrahedral aluminium atoms by bridging methyl and tertiary butoxide ligands in another example [77]. The mean Al-Y distance of 312.7(2) pm indicates there is no direct metal-metal bond. The Al-O-Y and Al-C-Y bridge angles of 98.4(2)° and 84.6(2)°, respectively, follow the trend mentioned above. A zirconium sandwich moiety (cp_2Zr) and a tetrahedral aluminium(III) atom are connected by a chlorine atom [78], and also via a both carbon atoms of a -CH_2-CH- link to the zirconium atom, giving a five member dimetallocyclic ring. The other aluminium bridged to the ring aluminium via the CH of the ring linkage, and hence also to the zirconium through both carbon atoms of the ring. The Al..Zr separation of 314.5 pm also rules out

any metal-metal bonding. A sandwiched zirconium in another, yellow, complex [79] is connected to two three coordinate aluminium(III) atoms, AlC_3, by a single two carbon bridge ($Zr\text{-}CH_2\text{-}CH(Al)_2$). The Al..Al separation about the -CH end of the bridge is 312.3(2), which excludes a metal-metal bond.

An Al_2/Rh derivative [80] has a normal three leg "piano stool" geometry about the rhodium, with an unbridged Rh-Al bonding distance of 245.81(8) pm, which is the shortest Al-M distance in the heterotrimeric derivatives. The aluminium atoms are then connected to each other via a single chlorine atom with non-equivalent Al-Cl distances of 241.9(1) and 232.2(1) pm. The Al-Cl-Al bridge angle is 113.60(4)° which places the second Al atom at a considerable distance from the rhodium atom.

A trimetallic Al_2Mn derivative [81] is shown in Figure 3. The molecule was described as a polycyclic heterocycle, incorporating a five member ring fused to a bicyclo-[2.2.2]octane framework. The Al..Al separation is 301.9(4) pm with Al-C-Mn and Al-O-Mn bridge angles of 84.2(6)° and 138.3(4)°, respectively.

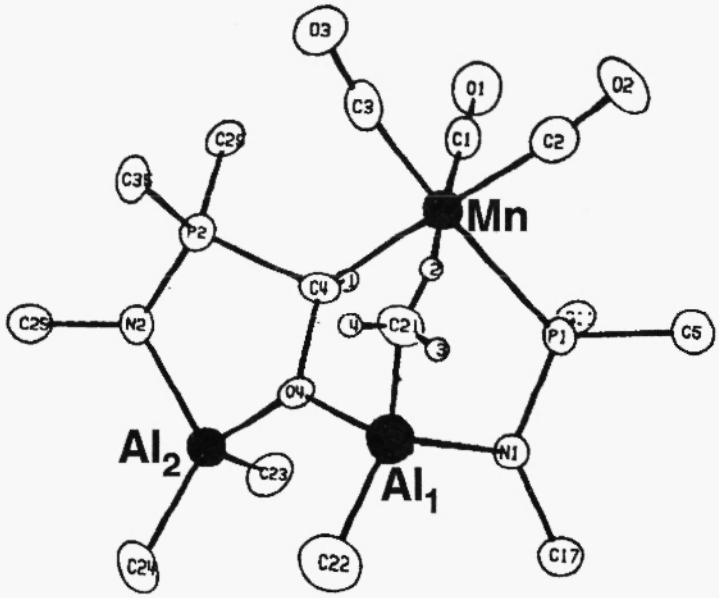

Fig.3 Structure of $(CO)_3Mn\{CHOAl(Me_2)N(CMe_3)PPh_2\}\{Ph_2PN(CMe_3Al(HCH_2)Me$ [81]

A red Al_2/Fe complex [82] has two dimethylaluminium units bridged one chlorine atom (Al-Cl-Al = 78.4(1)°) and by one carbon atom of a cyclopentadienyl group of a ferrocene moiety (Al-C-Al = 91.0(3)°). Within the four member ring the bonding exhibits effects which may be attributed to the steric requirements of the ferrocenyl ligand. The angle of tilt of the two cyclopentadienyl rings is 8.3°. No significant Al..Fe interaction is present (310.0(3) pm).

The structure of an Al_2/Li derivative [83] is shown in Figure 4, where it can be seen that the two $Me_2AlN(CMe)_4$ moieties are bridged by the chlorine atom, and both pyrrole rings are penta-haptocoordinated to the lithium atom (Table 2A).

There are fifteen derivatives (Table 2B) which contain one aluminium and two other metal atoms, and in these examples the aluminium is at the centre of the system, unlike the Al_2M examples (Table 2A) where the aluminium atoms are more a part of the ligands around M. The Sm_2Al complex molecule [84] contains two bent sandwich units of $(C_5H_4Bu^t)_2Sm$ connected by a pair of hydrogen bridges and, in addition, are bridged by another two pairs of hydrogen atoms from aluminohydride groups. The symmetry of this molecule is C_2, and it is shown in Figure 5. The aluminium atom bonds to each samarium atom via asymmetric triple hydrogen bridges, one μ-H and two μ_3-H. The Al-Sm and Sm-Sm distances of 304.4(3) pm and 371.2(1) pm are too long to suggest any metal-metal bonding. The aluminium atom is six coordinate, AlH_4N_2.

TABLE 2. Crystallographic and Structural Data for Heterotrinuclear Aluminium Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromo-phore	M-L [pm]	Al-M [pm] Al-L-M [°]	L-M-L [°]	Ref
A: 2 Al + M								
$(\eta^2\text{-}C_2H_4)(Me)(PMe_3)_2(\mu_3\text{-}C)Al_2(\mu\text{-}Cl)Me_4$ (pale yellow)	tr Pß 2	1038.52(17) 1455.43(49) 871.72(21)	78.401(22) 68.546(16) 78.534(21)	AlC_3Cl WC_1P_2	μ_3C[b] 201.4(5,30) μCl 237.6(3,5) C_{Me} 194.8(9,4) μ_3C 181.3(6) η^2C 218.4(7,3) C_{Me} 221.1(6) P 249.9(2,3)	- var[c]	μ_3C,Cl[b] 91.8(1,9) μ_3C C 118.2(2,2.9) Cl,C 102.7(2,2.8) μ_3C,C 109.7(2,3.3) μ_3C P 94.9(1,9) C,C 134.6(2,1.0) C,P 79.0(1,7) 115.7(1,1) P,P 159.08(5)	58
$Mg\{(\mu\text{-}Me)AlMe_2\}_2$	tr Pß 2	695.5(2) 1080.2(2) 1028.7(2)	102.35(2) 105.03(1) 92.49(1)	AlC_4 MgC_4	μC 210.2(9,21) C_{Me} 196.5(10,8) μC 220.7(10,15)	270.4(4,2) 77.7(2,6)	C,C 119.6(3,4) μC,μC 105.7(3,2) Al,Al 178.5(1)	59
$Mg\{(\mu\text{-}OBu^t)_2AlMe_2\}_2$ (colourless)	m C2/c 4	1861.4(2) 905.7(2) 2978.1(5)	122.87(2)	AlO_2C_2 MgO_4	μO 181.1(5,4) C_{Me} 194.3(8,0) μO 194.2(4,1)	283.6(2) 98.1(2,1)	μO,μO 85.3(2) μO,C 112.7(4,1.2) μO,μO 78.4(2) 126.0(2) Al,Al 179.3(2)	60
$Mg\{(\mu\text{-}OEt)(\mu\text{-}NPr^i_2)AlMe_2\}_2$ (colourless)	m $P2_1/c$ 4	1143.3(2) 1655.7(4) 1482.4(3)	90.47(2)	AlC_2ON MgO_2N_2	μO 180.5(8) μN 194.4(1) C_{Me} 198(1,0) μO 193.1(9,0) μN 216.2(8,0)	287.5(5) 88.7(4) N 100.6(4) O	μO,μN 89.6(4) μO,C 110.1(6,8) μN,C 117.4(5,3.2) μO,μO 109.7(4) μN,μN 145.5(4) μO,μN 80.1(3,2) 120.9(3,1.1) Al,Al 150.1(2)	60
$(PrOH)_3Mg\{(\mu\text{-}OPr)_2Al(PrO)_2\}_2$ (colourless)	m $P2_1/c$ 2	1250.9(2) 1766.3(4) 2005.9(2)	106.11(2)	AlO_4 MgO_5	μO 170.6(7,27) O 177.2(5,7) μO 208.1(5,27) O 215.0(7,23)	289.0(4,7)	not given Al,Al 141.6(1)	61
$(\mu\text{-}dox)Mg\{(\mu\text{-}OMe)_2AlMe_2\}_2$[d] (colourless)	or Pnnm 2	1342(2) 1074(2) 730(2)		AlO_2C_2 MgO_5	μO 183(2,3) C_{Me} 201(2,0) μO 205.5(10,5) O 224(2,0)	293(1) 98.0(4,7)	μO,μO 87.8(3) μO,μO 76.11(26)	62

$(thf)_2Mg$	m	933.4(8)		AlO_4	μO 175(2,3)	295(2,2)	μO,μO 89.3(8,1.2)	63
$\{(\mu\text{-}OPh)_2$	$P2_1$	3296(2)	95.57(6)		O 170(2,4)	99.0(7,2.8)	μO,O 112.2(9,5.8)	
e	4	1685.3(10)					O,O 115.8(9,1.1)	
$Al(OPh)_2\}_2$				MgO_6	μO 211.5(20,35)		μO,μO 71.2(6,4)	
					O_{thf} 211(2,2)		99.3(6,4.3)	
							μO,O 92.7(8,6.1)	
							O,O 87.2(7)	
				AlO_4	μO 179(2,2)	304(2,5)	μO,μO 86.6(8,1.4)	
					O 170(2,2)	100.4(7,1.6)	μO,O 113.1(8,4.4)	
							O,O 114.8(10,7)	
				MgO_6	μO 210(2,5)		μO,μO 71.4(6,0)	
					O_{thf} 207(2,2)		101.1(6,1)	
							μO,O 92.5(7,3.6)	
							O,O 89.2(7)	
$Pd\{(\mu\text{-}Cl)_2$	m	658.3(3)		$AlCl_4$	μCl 221.2(2,1)	-	μCl,μCl 92.33(6)	64
$AlCl_2\}_2$	$P2_1/c$	734.2(3)	96.40(3)		Cl 207.5(2,5)	90.0(1)	μCl,Cl 111.8(1,1.8)	
	2	1303.3(5)					Cl,Cl 115.11(8)	
				$PdCl_4$	μCl 231.3(2,2)		μCl,μCl 87.23(4)	
$Ti\{(\mu\text{-}dchd)_{1.5}$	m	1221.8(1)		AlO_2C_2	μO 184.3(3,10)	-	not given	65
$(\mu\text{-}CHCH_3)_{0.5}$	$P2_1/n$	1881.9(2)	92.40(1)		C_{Et} not given	93.9(1)		
$AlEt_2\}_2$	4	1582.3(1)		AlC_3O	μO 187.2(3)	-	not given	
					μC 210.8(6)	87.7(2)		
(red)					C_{Et} not given			
				TiO_4C	μO 200.3(3,43)		μO,μC 87.3(2,1.3)	
					μC 193.3(6)			
					O 180.1(3)			
$W\{(\mu\text{-}NBu^t)_2$	m	1867.3(3)		AlN_2C_2	μN 199.1(8,1)	-	N,N 85.1(5)	66
$AlMe_2\}_2$	C2/c	918.7(1)	121.95(1)		C_{Me} 197.0(11,23)	90.1(3,1)		
	4	2016.8(3)		WN_4	μN 184.6(7,10)		N,N 93.7(3)	
(orange red)							117.8(3)	
$W\{(\mu\text{-}NBu^t)_2$	or	1066.0(1)		AlN_2Cl_2	μN	-	N,N 88.0(6)	66
e	$P2_12_12_1$	1538.7(3)			191.5(14,22)	90.2(6,6)		
$AlCl_2\}_2$	4	1699.0(6)		WN_4	Cl 209.8(9,4)		N,N 91.0(6)	
					μN 186.0(13,3)		119.4(5)	
(purple blue)				AlN_2Cl_2		-	N,N 87.6(5)	
					μN	89.6(5,4)		
				WN_4	194.3(13,22)		N,N 93.5(2)	
					Cl 210.0(9,14)		123.2(5)	
					μN 185.2(12,5)			
$(Me_3CO)(thf)Y$	or	1440.8(4)		AlC_3O	μO 184.1(6,0)	322.2(3,22)	μC,C 108.0(4,2.6)	67
$\{(\mu\text{-}OCMe_3)(\mu\text{-}$	$Pca2_1$	1721.6(3)			μC 204.9(11,4)	C 84.2(3,2)	μC,O 99.4(4,2)	
Me)	4	1218.6(2)			C_{Me} 197.3(11,10)	O	C,C 116.0(4,2.1)	
$AlMe_2\}_2$						103.3(3,1.1)	C,O 111.9(4,2.2)	
				YO_4C_2	μO 225.4(6,2)		O,O 99.4(2,13.5)	
(colourless)					μC 270.2(8,34)		151.1(2)	
					Me_3CO 200.5(4)		C,C 88.3(3)	
					O_{thf} 238.8(7)		O,C 81.9(3,13.5)	
							166.6(2,8.1)	

Yb[{(μ-N	tr	987.07(17)		AlC_3N	μN	196.3(5)	-	N,μC 106.1(-,1.6)	68
$(SiMe_3)_2$}	Pß	1293.48(17)	68.12(11)		μC	201.9(2,14)	N 80.5(7)	N,C 116.6(4)	
$(\mu\text{-Me})_2AlMe]_2$	2	1310.81(20)			C_{Me}	195.4(2)	C		
			83.19(15)	YbC_3N_2	μN	254.2(2,32)	69.9(7,4.0)	N,N 131.56(5)	
(yellow) at					μC	276.7(2,11)			
178K			84.39(14)			312.2(3,80)			
η^5-cpTi{$(\mu\text{-Cl})_2$	m	1371.0(4)		$AlCl_4$	μCl	218.5(2,16)		μCl,μCl 94.9(1,2)	69
$AlCl_2\}_2$	$P2_1/n$	1313.9(5)	106.90(2)		Cl	207.8(3.6)		Cl,Cl 116.8(1,1.14)	
	4	966.6(2)		TiC_5Cl_4	μCl	252.2(2,16)		μCl,μCl 80.4(1,2.1)	
					C_{cp}	239.8(8,40)			
						198[f]			
η^5-cpbTi	tr	1044.9(2)	95.62(2)	$AlCl_4$	μCl	219(1,1)		μCl,μCl 93.2(4,2)	69
{(μ-Cl)$_2$	Pß	1353.0(2)	103.89(2)		Cl	206(1,1)		C1,Cl 117.1(6,3)	
$AlCl_2\}_2$	2	1707.4(3)	112.70(2)	TiC_5Cl_4	μCl	253.6(8,19)		μC1,μCl 78.9(2,1.8)	
					C	232(2,7)		Cl,Cl 127.7(3,4.5)	
						199[f]			
η^6-C_6H_6Ti	m	1787.5(9)		$AlCl_4$	μCl	216.6(7,14)	-	μCl,μCl 98.1(3)	70
{(μ-Cl)$_2$	$P2_1/n$	1297.4(9)	91.64(8)		Cl	208.4(7,8)	91.2(2,1.2)	C1,Cl 115.1(3,5)	
$AlCl_2\}_2$ (red)	4	773.1(5)		TiC_6Cl_4	μCl	260.1(5,13)		μCl,μCl 77.9(1,2)	
					C	249			
						207[f]			
[η^6-C_6H_6Ti	m	984.9(2)		$AlCl_4$	μCl	217.1(3,7)		μCl,μCl 96.7(1,3)	71
{(μ-Cl)$_2$	$P2_1/b$	1406.7(3)			Cl	207.9(3,5)		C,Cl 113.3(1,2)	
$AlCl_2\}_2]C_6H_5$	4	1629.4(4)	90.46(2)	TiC_6Cl_4	μCl	260.6(2,27)		μCl,μCl 77.0(1,2)	
					C	250		127.8(1,5.0)	
(violet)						208.4[f]			
[η^6-C_6Me_6Ti	or	1833.9(6)		$AlCl_4$	μCl	217.3(6,15)	-	μCl,μCl 97.0(2,7)	72
{(μ-Cl)$_2$	$P2_12_12_1$	1412.9(5)			Cl	210.0(7,14)	92.9(2,4)	Cl,Cl 114.9(2,1.6)	
$AlCl_2\}_2]C_6H_5$	4	1131.8(10)						μCl,Cl 110.5(3,2.7)	
				TiC_5Cl_4	μCl	261.5(4,15)		μCl,μCl 78.1(1,1.9)	
(violet)					C			μCl,C 117.3(-,2.2)[f]	
					249.8(14,56)				
						205.5			
η^6-C_6H_6Ti	or	1563.4(3)		$AlCl_3C$	μCl	219.5(10,5)	-	μCl,μCl 94.5(4,4)	73
{(μ-Cl)$_2$	$Pna2_1$	1135.5(2)			Cl	208.5(10,5)	94.4(3,1.0)	μCl,Cl 109.0(5,1.5)	
$AlClEt\}_2$	4	1441.7(2)			C_{Et}	205(3,2)		Cl,C 115(1,3)	
				TiC_6Cl_4	μCl	260.1(7,28)		μCl,μCl 78.3(2,2.3)	
(purple)					C	249(2,5)			

η^6-$C_6H_2Me_4Ti$	or	1994.9(6)		$AlCl_2I_2$	μCl	-	μCl,μCl 98.1(5)	74
$Al_2Cl_{4.75}I_{3.25}$	$Pna2_1$	914.6(4)			224.9(14,21)	92.8(4,2.5)	I,I 115.9(5)	
	4	1388.3(7)		$AlClI_3$	I 246.2(11,7)	-	μCl,μI 100.4(5)	
(dark violet)					μCl 220.0(13)	82.7(3)	I,I 115.6(5)	
					μI 244.4(12)			
				TiC_6Cl_3I	I 243.8(12,6)		μCl,μCl 78.7(3)	
					μCl		132.8(3)	
					267.1(10,39)		μCl,μI 81.6(2)	
					μI 290.4(6)		121.4(3)	
					C 250(3,3)			
η^6-$C_6H_6Ti\{(\mu\text{-}Br)_2$	or	1415.9(3)		$AlBr_4$	μBr 232.5(20,5)	-	μBr,μBr 97.6(3)	75
$AlBr_2\}_2C_6H_6$	Pnma	1774.6(9)			Br 224(2,1)	90.5(4,5)	Br,Br 114.5(4)	
	4	999.8(3)						
(violet)				TiC_6Br_4	μBr 274.9(7,21)		μBr,μBr 79.1(2)	
					C 249		131.2(3)	
					207[f]			
η^4-C_4Ph_4Ti	m	1463.4(4)		$AlBr_4$	μBr 233.6(7,41)	-	μBr,μBr 96.4(3,2)	76
$\{(\mu\text{-}Br)_2$	?	1170.4(3)	103.62		Br 221.6(7,5)	89.6(2,1.4)	Br,Br 117.1(4,2.5)	
$AlBr_2\}_2$	4	2070.9(4)					μBr,Br 110.4(3,3.4)	
				TiC_4Br_4	μBr 266.8(4,16)		μBr,μBr 82.2(1,1.5)	
(dark brown)					C 229(2,2)		μBr,C 85.2-138.9(5)	
					203[f]		C,C 37.5(7,4)	
							54.1(7,6)	
η^5-$C_5H_6Ti\{(\mu\text{-}I)_2$	m	1396.4(3)		AlI_4	μI 256.7(8,1)	-	μI,μI 98.2(2)	75
$AlI_2\}_2$	$P2_1/b$	1401.0(3)			I 248.9(8,2)	87.1(2,6)	I,I 115.8(3)	
	4	1192.6(2)	95.47(2)	TiC_5I_4	μI 297.2(4,27)		μI,μI 81.5(2)	
(black)					C 251		130.3(1)	
					208.4[f]			
				AlI_4	μI 256.9(7,8)		μI,μI 96.8(2)	
					I 249.4(7,2)	87.5(2,4)	I,I 113.8(3)	
				TiC_5I_4	μI 299.8(4,12)		μI,μI 79.7(2)	
					C 251		134.1(1)	
$(\eta^5$-$C_5H_4SiMe_3)$	m	1097.2(4)		AlC_3O	μO 184.1(4)	312.7(2,33)	μO,μC 97.1(2,1.0)	77
$Y\{(\mu\text{-}Me)$	$P2_1/c$	3167.7(5)	99.48(2)		μC 204.0(7,15)	O	μO,C 113.1(2,4.8)	
$(\mu\text{-}OCMe_3)$	4	849.8(3)			C_{Me} 196.4(6,5)	98.4(2,1.3)	μC,C 107.1(3,2.7)	
$AlMe_2\}_2$						C	C,C 117.1(3,5)	
				YC_7O_2	μO 228.0(4)	84.6(2,1.6)	μO,μO 132.5(1)	
(colourless)					μC 257.7(7)		μO,μC 73.9(2,1)	
					η^5C 264(3)		89.0(2,2.3)	
					235.6[f]			

$cp_2Zr(\mu\text{-}Cl).$	or	1497.6(2)		AlC_3Cl	μC 192.9(9)	314.5	μC,μCl 99.4	78
$(\mu\text{-}CH_2CH)Al_2Et_4$	$P2_12_12_1$	1860.7(5)			μCl 231.1	108.1	μC,C 97.8, 130.0	
	4	827.8(1)			C_{Et} not given		μCl,C 103.5(-,3.0)	
(yellow)							C,C 117.9	
				AlC_4	μC 195.6(9)		μC,C 117.8(-,9.9)	
					226.0(9)		C,C 124.4	
					C_{Et} not given			
				$ZrC_{12}Cl$	μC 231.4(9,62)		not given	
					μCl 268.6			
					C_{cp} 255.9(9,80)			
$cp_2Zr(\mu\text{-}Et).$	or	1141.6(3)		AlC_3	μC 199.8(5,1)	312.3(2)[a]	μC,C 116.8(3,8.8)	79
$Al_2Et_4(C_2H_3)$	$P2_12_12_1$	2043.7(5)			C_{Et} not given	102.9(2)	C,C 111.0(4,1.3)	
	4	1062.1(3)		ZrC_{12}	μC 239.3(4)		μC,C 75.7(3)	
(yellow)					C 225.1(6)			
					C_{cp} 251.2(7,33)			
$cpRu(PMe_3)_2Al_2.$	m	1569.6(2)		AlC_2Cl	μCl 241.9(1)	245.81(8)	μCl,C 98.2(2,2.8)	80
Me_4Cl_2	$P2_1/n$	1266.4(2)	108.32(1)		C_{Me} 203.4(5,46)	113.60(4)	C,C 112.2(2)	
	4	1254.4(2)					μCl,Rh 107.99(3)	
(yellow)							C,Rh 118.0(1,7.6)	
				AlC_2Cl_2	μCl 232.2(1)		μCl,Cl 100.57(4)	
at 173K					Cl 218.2(1)		μCl,C 110.2(1,8)	
					C_{Me} 194.6(4,10)		Cl,C 107.4(1,2.6)	
							C,C 119.5(2)	
				RhC_5P_2	P 225.4(1,7)		P,P 98.24(3)	
					C_{cp} 226.5(3,46)		P,Al 89.5(1,1.3)	
$(CO)_3Mn\{CHOAl$	or	1806.3(7)		AlC_2ON	μO 180.0(7)	301.9(4)[a]	μO,μC 107.5(5)	81
$(Me_3)N(CMe_3)$	Pbca	1844.6(8)			μC 202(2)	O 138.3(4)	μO,C 108.1(5)	
$PPh_2\}\{Ph_2PN$	8	2500.3(7)			N 180.4(8)	C 84.2(6)	μO,N 105.5(4)	
$(CMe_3)Al(HCH_2)Me$					C_{Me} 191.9(13)		μC,N 113.0(5)	
							C,N 120.0(5)	
							C,C 102.1(7)	
				AlC_2ON	μO 184.6(7)		μO,C 110.5(5,1.6)	
					N 190.3(9)		μO,N 90.6(4)	
					C_{Me} 195.2(12,11)		C,C 114.1(5)	
							C,N 114.4(5,4.2)	
				MnC_5HP	μC 245(2)		C,C 90.2(5,6.4)	
					H 191(12)		175.8(5,4)	
					OC		C,P 89.8(4,1.9)	
					179.9(15,21)		173.1(4)	
					P 237.6(3)		C,H 16(3), 90(3,13)	
							168(3)	
							H,P 94(4)	
η^5-cpFe	or	904.7(3)		AlC_3Cl	μC 207.1(8,45)	310.0(3)	μC,μCl 95.3(2,1.0)	82
$\{\eta^5$-	Pnma	1194.4(4)			μCl 233.5(4,75)	C 91.0(3)	μC,C 112.5(3,2.0)	
$C_5H_4Al_2Me_4Cl\}$	4	1539.5(4)			C_{Me} 194.1(8,1)	Cl 78.4(1)	μCl,C 104.0(3,4.3)	
							C,C 122.8(4,2.6)	
(red)				FeC_{10}	μC 209.0(8)		not given	
					C 204.4(7,37)			

[{(Me$_3$)$_3$N}(Me$_2$)Al(μ-Cl)Al(Me)$_2$.{N(CMe$_3$)$_4$}]Li	m P2$_1$/n 4	1049.7(1) 1271.4(2) 1796.3(3)	98.85(1)	AlC$_2$NCl	N μCl C$_{Me}$	190.6(3,1) 233.5(1,3) 194.6(6,8)	- 118.7(1)	C,C C,N C,Cl N,Cl N,N C,C	116.1(3,5) 114.9(2,2.2) 103.6(2,2.3) 101.0(1,1) 120.4(3) 116.2(3,4.4)	83
				LiC$_2$N$_2$	μN C	221.7(7,25) 228.9(7,55) 194.1(-,9)[f]				
B: Al + 2M										
[{(η^5-C$_5$HBu^t)$_2$Sm}$_2$(μ-H)μ-{(μ$_3$-H)$_2$Al(μ-H)$_2$(Me$_2$NC$_2$H$_4$NMe$_2$)]	m B2/b 8	1665.2(2) 1872.0(5) 1649.9(5)	91.77(2)	AlH$_4$N$_2$	μ$_3$H μH N	170 170 209.1(8)	304.4(3) 101.4(-,4.3)	μ$_3$H,μ$_3$H μ$_3$H,μH μ$_3$H,N μH,μH μH,N N,N	60.5 81.8(-,2.0) 107.6, 168.0 160.9 97.1(-,4.3) 84.4(5)[i]	84
				SmC$_{10}$H$_4$	μ$_3$H μH C	225(-,7) 215(-,1) 277(4) 249.9[f]	371.2(1) 114.6(-,3.5)	μ$_3$H,μ$_3$H μ$_3$H,μH	44.7 60.7(-,3)	
[{(η^5-cp)$_2$Y(μ-Cl)(μ$_5$-H)Y(η$_5$-cp)$_2$(μ-H)$_2$AlHNEt$_3$]C$_6$H$_6$	m P2$_1$/b 4	1453.8(3) 2072.1(7) 1179.3(3)	110.65(2)	AlH$_4$N	μ$_3$H μH H N	105(7) 160(8,9) 142(9) not given	324.5(3,1) 107(-,4)	μ$_3$H,μH μ$_3$H,H μH,μH μH,H μ$_3$H,N μH,N H,N	84(4,1) 100(4) 135(4) 113(4,5) 135(3) 88(3,4) 104(3)	85
				YC$_{10}$H$_2$Cl	μ$_2$H μH μCl C$_{cp}$	213(7) 243(8,2) 275.5(5,2) 236(-,1)[c]	395.1(3)[h] 136 91.6(1)	μ$_3$H,μH μ$_3$H,μCl cp,cp	50.4(-,2.2) 53.8 129[f]	
[(Me$_3$P)$_3$H$_3$W(μ-H)$_2$]AlH (yellow)	m P2$_1$/n 4	1020.4(1) 2152.3(5) 1654.0(2)	93.52(1)	AlH$_5$ WH$_5$P$_3$	μH H μH H P	189(8,9) 165(6) 168(7,5) not given 241.9(4,20)	269.2(5,2) not given	not given P,P	99.8(1,2.8) 141.5(1,2.3)	86
[(η^5-cp*)$_2$Ti(μ-H$_2$)$_2$AlH (yellow)	tr Pß 2	1188.1(4) 1895.1(8) 886.8(3)	93.04(3) 104.33(3) 79.26(3)	AlH$_5$ TiC$_{10}$H$_5$	μH H μH C$_{cp}$	not given " " 237.6(27) 207.0[c]	281.2(7,43) 547.9(3)[h]	Ti,Ti cp,cp	154.6(3,3.6) 145.5(-,1.3)[f]	87
[(η^5-cp)$_2$Ti(μ-H$_2$)$_2$AlMe	or F2dd 8	840.5(1) 2134.9(3) 2233.7(3)		AlH$_4$C TiC$_{11}$H$_2$	μH C$_{Me}$ μH C$_{cp}$	158(7,6) 194(2) 172(7,4) 236(1,1)	281.9(2) 117(2,1)	H,H H,C Ti,Ti H,H cp,cp	109(5,9) 110(3,11) 132 60(3,0) 136.7[f]	88

$[(\eta^5\text{-cp})_2Ti(\mu\text{-H})_2]_4AlCl$ (black)	or $P2_12_12_1$ 4	1041.4(1) 1199.8(2) 1600.8(1)		AlH_4Cl	μH 155(-,12) Cl 217.6(3)	277.1(3,1) 109(-,6.1)	H,H 77.5(-,2) 109.3(-,6.0) 166.3 H,Cl 95.4(-,1.1) 122.3(-,8)		89
				$TiC_{10}H_2$	μH 185(-,10) C_{cp} 234(1,4)		Ti,Ti 139.0(1) H,H 63.5 cp,cp 137.8(-,8)[f]		
$[\{(\eta_5\text{-cp})_2Ti(\mu\text{-H})_2\}_2Al(\eta^2\text{-}H_3BH_3)]$ (dark brown)	or Pnab 4	951.5(3) 944.9(3) 2205.1(4)		AlH_5	μH 175(10,5) H 180(10)	279.0(4) 113(5,3)	μH,μH 72(4) H,H 62(6) H,H 73(4)		90
				$TiC_{10}H_2$	μH 175(10,15) C_{cp} 235(3) 203.5(-,5)[f]		cp,cp 136.5[f]		
$[(\eta^5\text{-cp}Ti)_2(H)(H_2AlEt_2)(C_{10}H_7)]$ (red purple)	m C2/c 8	3331.0(4) 840.7(4) 1792.1(6)	117.89(2)	AlH_3C_2	μH 170 C_{Et} not given	313.4 135	H,H 109 not given		91
				$TiC_{10}H_2$	μH 169 180 C 235(-,4)	337.8[h] 138			
$[\{(\eta^5\text{-}cp_2Zr)_2(\mu\text{-H})\}(\mu\text{-}CH_2O)_2AlBu^i_2]$	tr Pß 2	1021.7(1) 1128.1(2) 1384.4(2)	100.37(1) 90.12(1) 106.36(1)	AlO_2C_2	μO 181.5(3) C_{Bu^i} not given	-	not given		92
				$ZrC_{11}HO$	μH not given μO 215.4(3,1) C 223.9(5,9) C_{cp} not given	138.3(2,4)	not given		
$[\{\eta^5\text{-}cp_2Zr(\eta^2\text{-}OCMe_2)\}_2(\mu\text{-}AlMe_2)(\mu\text{-Me})]$ (yellow)	m $P2_1/n$ 4	1057.4(1) 1645.6(2) 1676.3(2)	103.71(1)	AlO_2C_2	μO 180.8(3,4) C_{Me} 196.1(7,18)	- 149.9(1,1)	O,O 102.4(1) C,C 114.4(3)		93
				$ZrC_{12}O$	μO 215.0(2,2) μC 252.4(4,41) C 230.2(4,7) C_{cp} 225.0(-,8)[c]	152.4(2)	O,μC 74.2(1,4) O,C 37.8(1,1)		
$[\{\eta^5\text{-}cp_2Zr(\mu\text{-}OCCH_2CMe_3)\}_2(\mu\text{-}AlMe_2)(\mu\text{-Me})]$ (colourless)	m $P2_1/c$ 4	1020.89(1) 2021.4(3) 1842.1(2)	94.375(8)	AlO_2C_2	μO 181.2(4,7) C_{Me} 195.0(8,2)	- 156.1(2,3.5)	O,O 98.0(2) O,C 109.0(3)		94
				$ZrC_{12}O$	μO 218.1(4,2) μC 250.8(7,52) C 218.5(6,3) C_{cp} 222.4(-,15)[f]	481.7(1)[h] 147.8(3)	O,μC 75.9(2,0) O,C 37.6(3,2) cp,cp 129.7[f]		
$[\{\eta^5\text{-}cp_2Zr(\mu\text{-}OCCHCH_2CMe_3)\}_2(\mu\text{-}AlMe_2)(\mu\text{-Cl})]$ (colourless)	m $P2_1/c$ 4	1021.93(14) 2023.7(3) 1845.8(3)	94.303(14)	AlO_2C_2	μO 181.4(4,5) C_{Me} 194.6(8,5)	- 155.2(2,4.2)	O,O 98.6(2) O,C 109.6(3)		95
				$ZrC_{11}OCl$	μO 216.0(4,13) C 217.2(6,2) μCl 263 4(2,2) C_{cp} 221.1(-,11)[f]	486.4(1)[h] 134.87(7)	O,Cl 80.7(1,2) O,C 37.5(2,1) cp,cp 129.6[f]		

[{η^5-cp$_2$Zr(μ-O-CCHCH$_2$CMe$_3$)}$_2$ (μ-AlEt$_2$)(μ-H)] (colourless)	m C2/c 4	1821.9(2) 1036.44(9) 2027.39(2)	94.565(8)	AlO_2C_2 $ZrC_{11}HO$	μO C_{cp} μH μO C C_{cp}	181.2(3) 195.6(5) 201(4) 219.5(2) 218.8(4) 221.8(-,1)[f]	- 139.9(1) 397.6(1)[h] 163(2)	O,O O,C C,C H,O O,C cp,cp	94.4(1) 109.4(2) 116.8(2) 77(1) 37.0(1) 130.1[i]	95
[{η^5-cp$_2$Zr(μ-OCCHCH$_2$CMe$_3$)}$_2$(AlEt$_2$)·(μ-H)] (colourless)	m C2/c 8	1177.7(5) 1999.8(4) 3263.6(11)	96.83(6)	AlC_2HO $ZrC_{11}HO$ $ZrC_{11}O_2$	μH μO C_{cp} μH μO C C_{cp} μO C C_{cp}	170.4(34) 177.8(4) 194.9(9,16) 201.5(34) 219.4(4) 217.5(5) 221.0(-,4)[f] 217.7(4,17) 219.8(6) 222.6(-,4)[f]	- 147.8(20) 426.3(1)[h] 152.7(2)	H,O H,O O,C O,O O,C cp,cp	101.4(11) 86.2(10) 36.6(2) 77.0(1) 37.6(2) 130.8[f]	95
[Ir$_2$((2,6-Me$_2$C$_6$H$_3$N)$_2$CC}AlEt$_2$(2,6-Me$_2$C$_5$H$_3$NC)$_2$(impm)$_2$] (red-purple)	m $P2_1/c$ 4	1144.4(1) 1907.2(1) 2560.2(3)	102.91(1)	AlN_2C_2 IrC_2P_2	μN C_{gt} C C P	191.8(9,22) 199(1,2) 201(1,4) 195(1,3) 230.3(3,25)	- 278.61(6)[h]	N,N C,C N,C C,C P,P C,P	84.9(4)[i] 110.2(5) 115.0(5,3.6) 101.0(4.1.0) 100.9(1,7) 94.8(3,4.3) 145.7(3,11.8)	96

Footnotes: *a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.*
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Al-C-Al = 97.06(23)°; W-C-Al = 122.53(27) and 140.40(30)°; Al-C-Al = 78.85(9)°
d. Trimeric units in the complex held together by dioxane molecules to form an infinite polymer.
e. There are two crystallographically independent molecules.
f. Centroid of the carbon ring.
g. The Al-Al distance.
h. The M-M distance.
i. Five member metallocyclic ring.

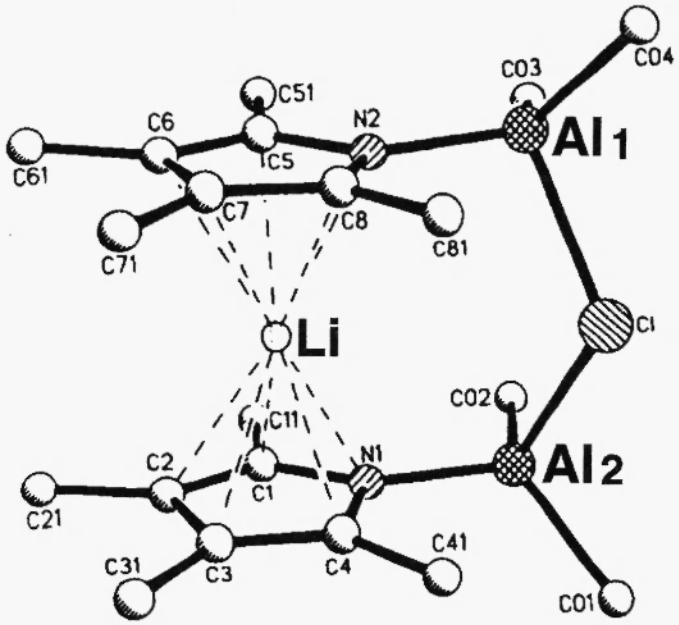

Fig.4 Structure of [{(MeC)$_4$N}(Me$_2$)Al(μ-Cl)Al(Me)$_2${N(CMe)$_4$}]Li [83]

A trimetallic derivative with two yttrium atoms [85] has two cp$_2$Y fragments doubly linked by one hydrogen and one chlorine atom. The aluminium ($AlH_3.NEt_3$) unit is then linked to each yttrium via a bridging hydrogen, and linked again via the same hydrogen linking the yttrium atoms, creating a μ_3-H linkage at the centre of a six member ring of -Al-H-Y-Cl-Y-H-.

There are five derivatives [86-90] in which the linkage between the W^{IV} [86] or Ti^{II} [87-90] and the Al^{III} atom is accomplished via a pair of hydrogen bridges, M(μ-H)$_2$Al(μ-H)$_2$M. The mean Al-H(bridge) distance of 169 pm is about 3 pm shorter than the Al-H(terminal) distance of 172 pm. The Al-W distance of 269.2(5) pm is the shortest Al-M bond found in this group of heterotrimers. The Al-Ti distance ranges from 277.1(3) to 281.9(2) pm and correlates with the Al-H-Ti bridge angle such that when the bridge opens the distance increases, for example: 277.1(3) pm and 109° [89], 279.0(4) pm and 113° [90], 281.9(2) pm and 117° [88].

In another seven derivatives, three metal atoms, Ti_2Al [91] or Zr_2Al [92-95], form six member metallocyclic rings with three bridging atoms. The M-L-M bridge angles range from 135° to 156.1(2)°. The mean Al-L(bridge) distances are 170 pm (L = H) and 181 pm (LO).

The structure of a red-purple derivative of In_2Al [96] is shown in Figure 6. The molecule has a "cradle" type of structure and an apparent Ir-Ir bond (278.61(8).

The heterotrimetallic aluminium derivatives contain the following heterometal atoms: Ti (15 examples), Zr (8), Mg (6), Y and W (3 each), Li, Pd, Rh, Ir, Mn, Fe, Yb and Sm (1 each). There are three derivatives [63,66,75] which contain two crystallographically independent molecules, examples of distortion isomerism [57].

The mean Al-L bond distances for the four coordinate (most abundant) aluminium derivatives increases with covalent radius of the donor atom in the order: 172 pm (LO) < 190 pm (LN) < 196.5 pm (LC) < 210 pm (Cl) < 223 pm (Br) < 247 pm (I). The mean Al-L(bridge) distance follows the same trend: 170 pm (H) < 182 pm (LO) < 204 pm (LC) < 225 pm (Cl) < 233 pm (Br) < 257 pm (I). The shortest Al-M, Al-Al and M-M distances in the heterotrimetallic derivatives are 245.81(8) (M = Zr [86]), 301.9(4) pm [81] and 278.61(6) pm (M = Ir [96]), respectively. These forty five examples relate to another fifteen homonuclear examples in the aluminium coordination compounds [1] plus almost thirty in the organoaluminium compounds [2], indicating the rich variety of the trimeric derivatives.

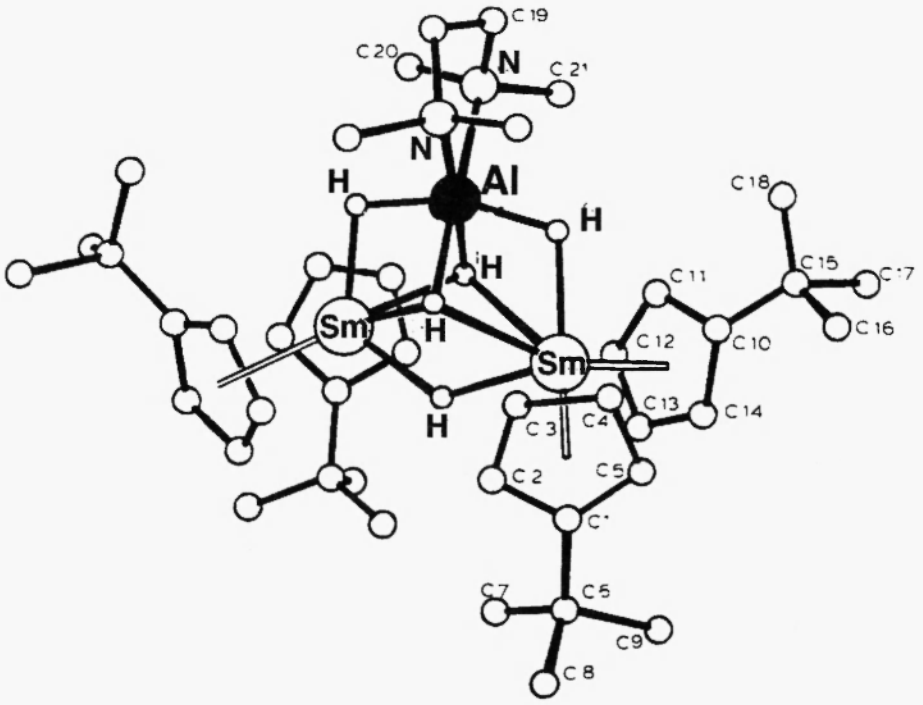

Fig.5 Structure of
$\{(C_5H_4Bu^t)_2Sm\}_2(\mu\text{-}H)\mu\text{-}\{(\mu_3\text{-}H)_2Al(\mu\text{-}H)_2(Me_2NCH_2H_4NMe_2)$ [84]

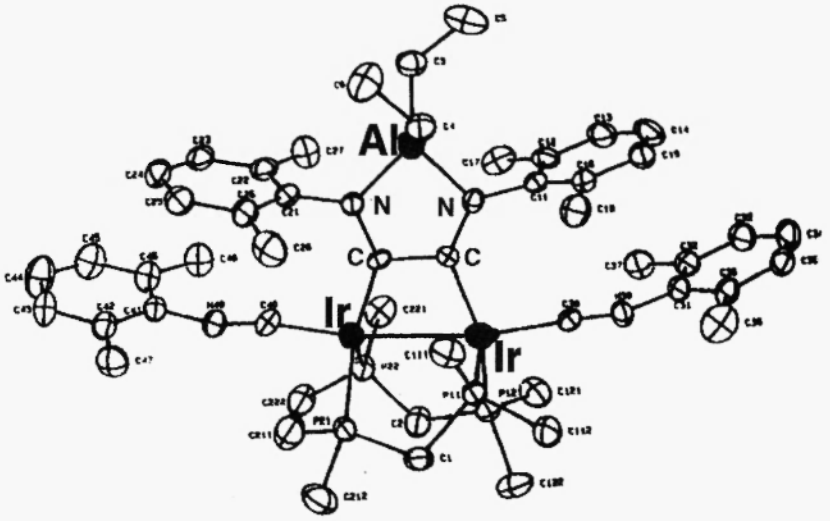

Fig.6 Structure of
$Ir_2\{(2,6\text{-}Me_2C_6H_3N)_2CC\}AlEt_2(2,6\text{-}Me_2C_6H_3NC)_2(dmpm)_2$ [96]

The shortest Al-Al distance found in the whole group (291.1(2) pm is much longer than the shortest value noted in this present study of heteronuclear aluminium complexes. Overall, however, it would seem that aluminium is usually found bonded with other metal atoms than with itself in these derivatives.

4. HETEROTETRANUCLEAR COMPOUNDS

Crystallographic and structural data for this class of compounds are gathered in Table 3. There are seventy derivatives which can be subdivided into three groups: those containing Al_3/M (11 examples), Table 3A; Al_2/M_2 (56 examples), Table 3B; A/M_3 (5 examples), Table 3C.

In the first group there are two derivatives [97] in which the structures are based on a cubane-like $[(AlN)_3(MN)]$ framework in which one aluminium is replaced by an alkali earth metal. The distortion of the cubic geometry increases with the coordination number of the heterometal atom (4-coord Mg, 6-coord Ca) (Table 3A).

The remaining eight derivatives [98-103] of this group have three tetrahedrally coordinated aluminium atoms, AlC_4 [98] and $AlCl_4$ edge-shared with a central M(III) atom [99-103].

The second group (Table 3B) is the most varied and complex from a structural point of view. In one example [104] two dimeric units of $cp_2TiAlEt_2$ are linked through a Ti-Ti bond intersecting a twofold symmetry axis. As indicated, each Ti atom is also coordinated to two π-cyclopentadienyl rings and one Al atom. Furthermore, the Al and Ti atoms of one dimer unit are at bonding distances from a carbon atom of each cyclopentadienyl ring of the other dimeric unit. The Ti-Al and Ti-Ti distances are 279.2(11) and 311.0(7) pm, respectively.

In a deep brown complex [105] the symmetry of the molecular core belongs to the D_{2h} group, and each benzene ring present may be formally assumed to act as a conjugated diene which is P-bonded to Pd atoms. Two tetrahedral Al(III)Cl_4 units are held together in the manner Cl_3-Al-Cl-Pd-Pd-Cl-$AlCl_3$. The Pd-Pd distance is 257.0(13) pm and the Cl-Pd-Pd angles are 177.8(5)°.

In an Al_2Mo_2 cluster compound [106] there is an eight member metallocyclic ring $(AlOMoO)_2$. In addition, two molybdenum atoms are bridged by acetate groups in a syn-syn arrangement due to the existence of a very strong Mo-Mo quadruple bond (207.9(1) pm). All the metal atoms are four coordinate, tetrahedral for the aluminium (AlO_4) atom and square planar for the Mo atom (Table 3B).

A red Al/Co complex [107] has a planar four member $(AlCo)_2$ ring, and all the ligands on the metal atoms are arranged as *trans* pairs. The mean Al-Co distance of 233.5(1) pm is much shorter than of Al-Al (266.3(3) pm) or Co-Co (383.5(1) pm). In another (red-brown) cluster [107] two (cpCoH) fragments, each η^5-bonded to the π-system of the bridging C_2 unit, are connected through a di-aluminoethene units over a twofold axis. The non-bonding distance of 350.3 pm between the two aluminium atoms is even longer than the distance between the cobalt atoms (333.8 pm). The mean Al-Co bond distance of 259.8(2) pm is about 26.3 pm longer than that found in the red cluster [107].

The structure of an Al/Zr cluster [110] indicates the presence of a planar central four member ring of two aluminium and two oxygen atoms about a centre of symmetry. Each oxygen coordinates to a bent $cp_2Zr(Me)$ metallocene unit. A similar four member $(AlO)_2$ central ring unit was found in a colourless Al/Sn cluster [111], in which both the aluminium and tin atoms are in pseudotetrahedral environments (Table 3B).

A cluster of Al_2Ga_2 [112] sits about a crystallographic centre of symmetry with a planar Al_2N_2 ring occupying the central cavity of the [14]aneN_4-aza crown ligand. Again, each metal atom is in a pseudoterahedral environment.

There are two derivatives [113,114] in which dinitrogen (N_2) forms a push-pull stabilized double bond (125 pm) with one end coordinated to CoP_3 [113] or WP_3Cl [14] chromophores and the other end part of an N_2Al_2 ring. There is a centre of symmetry within the Al_2N_2 ring. The M-N-N linkage is essentially linear (175.1(4)° [113] and 176.5° [114]).

The molecular structure of a yellow Al/Fe cluster [115] shows dimerisation occurring through a central $Al_2(NMe_2)_2$ ring which is planar. The aluminium atoms each have two exo substituents, one NMe_2 group and one $(CO)_4FeC(NMe_2)O$ group with trans orientation across the four member ring. The $C(NMe_2)O$ substituent on the $Fe(CO)_4$ fragment occupies an axial position. The aluminium atoms are pseudotetrahedral (AlN_3O) and the iron atoms are trigonal bipyramidal (FeC_5). An orange Al/Mn cluster [115] also contains an $Al_2(NMe_2)_2$ ring, but the substituent arrangement on this ring does not parallel the symmetrical arrangement found in the Al/Fe cluster [115]. One aluminium atom is bonded to two exo-NMe_2 groups while the second is bonded to only one exo-NMe_2 group plus a $Mn_2(CO)_9C(NMe_2)O$ group. The $C(NMe_2)O$ fragment is bonded to one Mn atom in an axial position of the $Mn_2(CO)_9$ fragment, and the four equatorial CO groups on each Mn centre form planes which are staggered with respect to each other. The Al-Al distance of 280.6(2) pm is about 10.7 pm shorter than the Mn-Mn distance of 291.3(1) pm.

There are several derivatives [87,116-121] in which the linkage between the M and Al atoms is accomplished via a double hydrogen bridge $M(H)_2Al$, with the Al centres linked by $Al(X)_2Al$ bridges, where X = O [116,121], H [87,117-120], or N [121]. In one case [122] the bridges are $Li(O)_2Al$ and $Al(N)_2Al$. The coordination environment of each aluminium atom is a distorted bipyramid with three hydride and two O-donor ligands [116, five hydride ligands [87,117-119], three hydride and two O-donor ligands [120,121] or three N-donor and two 0-donor ligands. In each case the set

of two ligands occurs at the apices of the trigonal bipyramid. The Al-Al distances range from 264.4(14) to 291.1(5) pm (mean value 278.8 pm). The Al-M distances range from 239.3(4) pm (M = Mn) to 282.4(5) pm (M = Ti).

An Al/Cr cluster [113] contains dimeric units lying on an inversion centre. Each octahedral $(OC)_5CrPPh_2$ fragment is linked by a $-(CH_2)_4O-$ unit (formed by cleavage of thf) to the two $Al(CH_2SiMe_3)_2$ fragments. The central Al-O-Al-O ring is strictly planar with obtuse Al-O-Al angles of 100.3(6)° and acute O-Al-O angles of 79.7(5)°.

Two $cp_2TiH_2AlH_2$ units are linked by a tetramethylethylenediamine molecule in another tetramer [124]. The aluminium atom is bonded to a titanium atom by a double hydride bridge and has trigonal bipyramidal stereochemistry (AlH_4N). The Al-Ti distance is 278.8 pm and the mean Al-H-Ti bridge angle is 112(5)°.

The molecular unit of a yellow orange Al/Fe cluster [54] consists of two ferrocene moities connected via a N-Al-O-Al-N linkage. The linear geometry around the oxygen atom (180°) is crystallographically imposed since the O atom sits at a crystallographic inversion centre. Each aluminium atom is in a pseudotetrahedral environment (AlC_2ON). The Al..Fe separation of 594.4(1) pm is the longest reported for the heterotetrametallic derivatives of aluminium.

The structure of a red-purple Al/Ti derivative [91] is shown in Figure 7. The molecule has an imposed space group of $C_2(2)$ symmetry. Each titanium is η^5-bonded to a bridging C_5H_4, η^1-bonded to the other C_5H_4, and η^5-bonded to half of the $C_{10}H_8$ fulvalenide ligand. Both Ti atoms and C_5H_4 groups are bridged by hydridodiethylaluminium moieties. The Ti-Ti distance of 291.0 pm and the diamagnetism of the cluster point to a Ti-Ti single bond.

A colourless Al/Y cluster [125] consists of centrosymmetric dimer molecules $\{cp_2Y(\mu_3\text{-}H)(\mu\text{-}H)AlH_2(NEt_3)_2\}_2$. The Y and Al atoms are located in the bisector plane of the cp_2Y wedge-shaped sandwiches. The Al-Y distances of 330.8(11) and 410.8(11) pm, Y-Y distance of 370.0(4) pm and Al-Al distance of 678.0(9) pm all exclude any metal-metal bonding. Each aluminium atom is in a trigonal bipyramidal environment. Another colourless Al/Y cluster [125] contains two non-equivalent Al atoms, one tetrahedrally and the other trigonal bipyramidally coordinated. For metal atoms and four hydride anions form an eight member $(Y\text{-}H\text{-}Al\text{-}H)_2$ metallocycle. In addition, one μ_3-H anion bridges three metal atoms (2Y and Al). The Al-Y, Y-Y and Al-Al distances of 320.2(7), 356.5(8), 437.8(8) and 497.2(8) pm again exclude metal-metal bonding.

The colourless Al/Mg cluster [60] contains three orthogonal metal-(μ-O)-metal planes. The Al-Mg-Mg-Al backbone is almost linear with an Al-Mg-Mg angle of 178.44°. The Al and Mg atoms exist in distorted tetrahedral environments (AlO_2C_2 and MgO_4). A similar structure was found in six other colourless Al/Mg clusters [44,60,127-129]. Here the central Mg_2X_2 atoms form a coplanar heterocyclic four member ring. Each metal atom is tetrahedrally coordinated. A correlation is seen between the M-M distance and M-L-M angle, the latter opening as the former increases, for example: Al-Mg = 261.2(4) pm and Al-L-Mg = 77.1(2)° [129]; 280.0(2) pm and 86.7(2)° [60]; 289.5(6) pm and 96.2(4)° [60]; 330.7(2) pm and 105.2(2)° [44]. For Mg-Mg and Mg-L-Mg the values are: 273.5(3) pm and 82.0° [128]; 290.1(8) pm and 95.2(3)° [60]; 295.7(2) pm and 97.8(2)° [127]. There is one exception with an exceptionally long Mg-Mg bond of 410.1(8) pm the angle observed is 2.9(1)° [129] for which there is no immediate explanation.

The structure of a colourless Al/Sn derivative [130] is shown in Figure 8. The compound features discrete centrosymmetric dimeric complex units, with each tin atom η^6-coordinated to two neighbouring benzene rings of a triptycene ligand, but with different metal-ring distances of 290 and 338 pm. The angle between the two coordinated rings has decreased to 108.2.

The structure of dark red derivative [25] contains the dimeric $\{(\mu\text{-}Br)_3[(\eta^6\text{-}C_6H_6)Zr(\mu\text{-}Br)_2AlBr_2]_2\}^+$ cation, the dimeric $Al_2Br_7^-$ anion, and three solvating benzene molecules, one of which is on the twofold axis. In the complex cation two bridging bromine atoms are part of the tetrahedral $AlBr_4$ chromophore. Another three bridging bromine atoms are common to the two Zr(III) atoms. The Zr-Zr distance of 318.8(10) pm is essentially equal to the interatomic distance found in metallic zirconium of 320 pm.

Another bright red Al/Fe cluster [131] involves a *cis* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ moiety coordinated to two triethylaluminium acceptors through the oxygen atoms of two bridging carbonyl groups. The Fe-Fe bond distance is 249.1(8) pm. There are two Al/Sm clusters [84,134] which contain a heterocyclic eight member ring $(AlHSmH)_2$. There are also two μ_3-H atoms bridging three metal atoms (2Sm and Al). The mean Al-Sm, Sm-Sm and Al-Al separations are: 327, 413 and 506 pm, respectively. An A/Yb [135] and an Al/Y [136] cluster involve a $cp_2M(\mu_3\text{-}H)_2Mcp_2$ metallocycle connected to either $AlH_3.NEt_3$ [135] or AlH_3.thf [136] groups by both μ_3- and μ-bridging hydrogen atoms. The two Al-M distances and the M-M distance have the values: 326.0(2), 372.8(3) and 362.3(1) pm (M = Yb [135]); 324.2(3), 398.9(3) and 375.3(1) pm (M = Y [136]. All are too large to admit a metal-metal bond. In another colourless Al/Y cluster [137] both cp_2YCl wedge-like sandwiches are connected to each other by a double chlorine bridge, $cp_2Y(\mu\text{-}Cl)_2Ycp_2$.

TABLE 3A-C. Crystallographic and Structural Data for Heterotetranuclear Aluminium Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromo-phore	M-L [pm]	Al-M [pm] Al-L-Al Al-L-M [°]	L-M-L [°]	Ref
A: 3 Al + M								
(thf)Mg{HAl (Bu^t_3N)}$_3$ (colourless)	or Pbca 8	1710.7(2) 1730.5(4) 2022.0(5)		AlN_3H	μ_3N[b] 191.3(2,20) H 152(2,2)	- 89.2(1,8) 88.3(1)	N,N[b] 95.6(1,4.7) N,H not given	97
				MgN_3O	μ_3N 209.0(2,8) O_{thf} 200.2(2)		N,N 86.3(2) N,O 128(2)	
[(thf)$_3$Ca{HAl (Bu^tN)}$_3$].thf (colourless)	or Pbca 8	2048(1) 2038(1) 2051(1)		AlN_3H	μ_3N 191.3(10,41) H 135(2)	- 87.9(2,1.6) 91.7(1)	N,N 100.0(2,8.0) N,H not given	97
				CaO_3N_3	μ_3N 249.0(10,4) O_{thf} 253.9(10,13)		N,N 73.2(2,5) O,O 79.7(2,3) N,O 104.2(2,8.0) 167.6(2,4)	
Nd{(μ-Me)$_2$ $AlMe_2$}$_3$ at 163K	m P2_1/c 8	743.7(2) 1785.5(3) 3242.3(5)	92.109(14)	AlC_4	μC not given C_{Me} not given			98
				NdC_6	μC 259.2(13,29)			
d{(μ-Me)$_2$$AlMe_2$}$_3$. $(Al_2Me_6)_{0.5}$ at 163K	m P2_1/n 4	751.6(1) 1995.3(4) 1796.5(3)	97.22(1)	AlC_4	μC 224.9(11,13) C_{Me} 194.2(12,6)		not given	98
				NdC_6	μC 259.3(6,21)			
Nd{(μ-Me)$_2$ $AlMe_2$}$_3$. $(Al_2Me_6)_{0.5}$ at 163K	m P2_1/n 4	745.2(2) 1989.6(4) 1777.0(3)	96.61(2)	AlC_4	μC 214.3(11,21) C_{Me} 193.0(11,5)		not given	98
				YC_6	μC 250.8(7,6)			
[U{μ-Cl)$_2$ $AlCl_2$}$_3$].C_6H_6 (black)	tr Pß 2	947(2) 1081(2) 1679(2)	98.7(3) 86.5(3) 122.9(3)	$AlCl_4$	μCl 218.2(15,44) Cl 209.0(15,38)	- - 95.1(2,1.3)	μCl,μCl 98.4(2,1.4) Cl,Cl 116.5(2,10) μCl,Cl 110.1(2,4.0) μCl,μCl 75.1(1,8.3)	99
				VCl_6	μCl 287.8(7,40)			
[(η^6-C_5H_5)Sm {(μ-Cl)$_2$ $AlCl_2$}$_3$].1_tl (red)	m P2_1/c 4	1869.6(4) 1690.6(3) 1226.2(2)	100.81(2)	$AlCl_4$	μCl not given Cl "		not given	100
				SmC_6Cl_6	μCl 285(2) C 289(5)		not given	
(η^6-C_6H_5Me)Sm {μ-Cl)$_2$$AlCl_2$}$_3$ (yellow)	m P2_1/n 4	971.0(2) 1984.4(2) 1288.5(2)	103.85(1)	$AlCl_4$	μCl 219.3(4,12) Cl 207.9(4,11)		μCl,μCl 97.1(1,1.3) Cl,Cl 115.8(2,1.4)	101
				SmC_6Cl_6	μCl 283.4(3,60) C 290.7(9,51)		μCl,μCl 75.2(1,8.0) 138.5(1,5.3) μCl,C 68.7-155.7(2)	

$(\eta^6\text{-m-Me}_2\text{C}_6\text{H}_4)\text{Sm}$ $\{(\mu\text{-Cl})_2\text{AlCl}_2\}_3$ (yellow)	m $P2_1/n$ 8	1836(5) 1637(4) 2031(6)	114.11(2)	$AlCl_4$	μCl Cl	219.6(8,30) not given	- - 95.5(3,2.7)	μCl,μCl 97.4(3,2.8) Cl,Cl 117.5(1)	102
				SmC_6Cl_6	μCl C	282.6(8,36) 290(3,4)		μCl,μCl 74.9(2,6.9) 138.1(2,2.1)	
				$AlCl_4$	μCl Cl	217.5(1,15) not given	- 95.8(1,1.9)	μCl,μCl 97.5(1,1.9) Cl,Cl 117.6(1)	
				SmC_6Cl_6	μCl C	283.6(4,4.2) 288(2,15)		μCl,μCl 74.9(2,7.1) 138.0(2,5.2)	
$[(\eta^6\text{-C}_6\text{Me}_6)\text{Sm}$ $(\mu\text{-Cl})$ $\text{AlCl}_2]_3].1\_\text{tl}$ (yellow)	m $P2_1/c$ 4	1869.6(4) 1690.6(3) 1226.2(2)	100.8(2)	$AlCl_4$	μCl Cl	218.3(9,19) 208.0(11,6)	- - 95.9(3,1.9)	μCl,μCl 97.6(3,2.2) Cl,Cl 114.9(4,6) μCl,Cl 110.8(4,2.2)	103
				SmC_6Cl_6	μCl C	284.9(6,37) 289(2,7)		μCl,μCl 73.7(2,6.7) 136.1(2,2.5) μCl,C 71.5-154.5(4) C,C 28.3(7,8) 52.9(7,6.0)	
$(\eta^6\text{-C}_6\text{Me}_6)\text{U}$ $\{(\mu\text{-Cl})_2.\text{AlCl}_2\}_3$	tr Pß 2	9?1.6(5) 1?91.8(8) 9?3.0(4)	96.09(3) 118.9(3) 80.98(3)	$AlCl_4$	μCl Cl	218.6(8,20) 207.4(9,10)	376.2(4) - 95.9(2,1.9)	μCl,μCl 98.0(3,2.3) Cl,Cl 116.1(4,9) μCl,Cl 110.3(4,3.3)	103
				UC_6Cl_6	μCl C	289.5(5,27) 293(2,5)		μCl,μCl 73.6(1,9.2) 136.0(1,4.3) μCl,C 73.2-159.5(4) C,C 27.7(4,1.6) 51.7(6,5.7)	

B: 2Al + 2M

$[(\eta^5\text{-cp})_2\text{Ti}$ $\text{AlEt}_2]_2$	or Pbcn 4	950(2) 1460(3) 1940(3)		AlC_3	C_{Et} μC$_{ip}$	209(3) 211(3) 211(3)	279.2(11)	μC,C 113.2(1.4,1.2) C,C 110.0(1.4) C,Tl 124.4(1.0,2.1)	104
				TiC_{10}	μC$_{ip}$ C$_{cp}$	225(3) 236(3,12) 201[e]	311.0(7)[d]	cp,cp 135.2[e] Ti,Al 91.8	
$[C_6H_6PdAlCl_4]_2$ (deep brown)	m C2/c 4	1404(4) 1102(3) 1772(5)	52.4(3)	$AlCl_4$	μCl Cl	218.0(15) 212.0(15,20)		μCl,Cl 108.0(5,1.9) Cl,Cl 111.3(5,1.9)	105
				PdC_6Cl	μCl C	245.0(24) 277-351(2)	257.0(13)[d]	μCl,Pd 117.8(5)	
$[\{(\mu\text{-ac})_2\text{Mo}_2\}$ $\mu\text{-}(\text{OCHMe}_2)_2\text{Al}$ $(\text{OCHMe}_2)_2]_2$	m $P2_1/a$ 2	1817.8(5) 949.1(3) 1316.4(4)	109.706(9)	AlO_4	μO O	176.9(6,7) 160.3(15) 176.7(15)	121.3(3,1)	μO,μO 100.0(3) μO,O 111.0(6) O,O 111.6(7,6.5)	106
				MoO_4	μO O	212.9(10,6) 210.9(10,4)	207.9(1)[d]	μO,μO 163.0(2) μO,O 89.7(2,5) O,O 176.2(2)	
$\{\text{cp}^*(\eta^2\text{-C}_2\text{H}_4)\text{Co}$ $\text{AlEt}_2\}_2$ (red)	m $P2_1/c$ 2	848.6(1) 1798.9(7) 979.2(2)	106.89(1)	AlC_2	C_{Et}	199.6(3)	233.5(1,2) 266.3(3)[f]	Co,Co 110.4(1) Co,C 124.8(1,1.1) Al,C 68.9(1)	107
				CoC_7	not given				

$(cp^*CoH)_2\mu(Et_2Al$	m	2023.0(6)		AlC_3	μ_3C 208.8(4)	259.8(2,7)	μ_3C,Co 48.7(1)	107
$CH=CHAlEt_2$	C2/c	872.3(1)	106.24(2)		C_{Et} not given	79.3(1)		
	4	1992.2(4)		CoC_7H	μ_3C 198.9(4,5)	333.8[d]	μ_3C.Al 52.1(1)	
(red brown)					C 205.5(4,33)	114.2(2)	81.8(1)	
							μ_3C,H 88(2)	
							Al,H 47(2)	
$Al_2O_4(dhat)_4Ca_2$	tr	1300.1(3)	64.08(1)	AlO_3	not given		not given	108
$(dmf)_4(H_2O)_2$	Pß	1382.9(3)	71.93(2)					
	1	1401.4(2)	63.97(2)	CaO_3	not given		not given	
$Al_2O_4(that)_4Ca_2$	tr	1338.70(3)	69.820(2)	AlO_3	not given		not given	109
$(dmf)_4(H_2O)_2$	Pß	1381.20(3)	86.140(2)					
	1	1477.10(3)	65.540(2)	CaO_3	not given		not given	
$[\eta^5$-cp$_2$ZrMe	m	839.74(8)		AlO_2C_3	µO 184.4(2,1)	266.7(1)[f]	µO,µO 87.4(1)	110
$(\mu$-OAlMe$_2)]_2$	$P2_1/c$	865.09(7)	97.36(1)		C_{Me} 195.7(2,5)	92.6(1)	C,C 116.5(1)	
	2	1971.8(1)				133.7(1,4.3)	µO,C 112.4(1,9)	
(colourless)				$ZrC_{11}O$	µO 204.4(2)		µO,C 96.8(1)	
					C_{Me} 227.0(4)			
					C_{cp} 250.8(4,18)			
$[Me_2Al$	tr	907.6(1)	71.03(2)	AlO_2C_2	µO 184.0(3,0)	347.3(1)	µO,µO 84.9(1)	111
	Pß	973.3(2)	74.22(1)		C_{Me} 195.9(8,1)	271.1(2)	C,C 118.6(1)	
$(\mu$-OSnPh$_3)]_2$	1	1308.4(3)	65.05(1)			95.1(2)	µO,C 112.6(2,1.1)	
				SnC_3O	µO 198.4(4)	131.3(2)	µO,C 105.8(1,1.9)	
(colourless)					C_{Ph} 211.7(3,1)		C,C 112.9(1,3.2)	
$(MeAl)_2$[14]	m	819.5(2)		AlN_3C	µN 188.8(3)	-	µN,µN 90.5(1)	112
$aneN_3(GaMe_3)_2$	$P2_1/n$	1378.8(4)	90.70(2)		194.3(3,7)	89.5(1)	97.2(1,4.5)	
	2	1116.2(3)			C_{Me} 193.8(4)	111.3(1)	µN,C 124.7(2,6)	
(colourless)				GaC_3N	µN 213.6(3)		µN,C 104.1(2,1.6)	
					C_{Me} 199.3(8,0)		C,C 114.3(3,3)	
$[(PMe_3)_3Co$	or	1245.7(2)		AlN_2C_2	µN 192.3(5,8)	-	N,N 81.7(2)	113
$(\mu_3$-$N_2)AlMe_2]_2$	Pbca	1949.4(2)			C_{Me} not given	98.3(2)		
	8	1748.3(3)		CoP_3N	N 164.2(4)		not given	
(dark brown)					P 216.9			
$[(PMe_2Ph)_3ClpyW$	tr	1422.6(5)	103.84(4)	AlN_2Cl_2	µN not given		not given	114
$(\mu_3$-$N_1)AlCl_1]_2$	Pß	2514.1(12)	99.78(3)		Cl "			
$.C_6H_6$ (red)	?	1191.1(4)	78.36(4)	WP_3N_2Cl	N 173(3,9)		not given	
$[(\mu$-$NMe_2)(NMe_2)$	tr	937.3(2)	88.98(2)	AlN_3O	µN 195.0(2,16)	281.7(1)[f]	µN,µN 87.5(1)	115
$Al(\mu$-η^2-$OCNMe_2)$	Pß	960.6(2)	78.43(2)		N 176.9(2)	92.5(1)	µN,N 117.5(1,2.2)	
$Fe(CO)_4]_2$	2	1025.7(2)	65.36(1)		O 172.6(2)		µN,O 109.1(1,2.1)	
							N,O 113.2(1)	
(yellow)				FeC_5	OC 178.3(3,17)		C,C 85.6-136.4(1)	
					C 199.8(3)		165.0(1)	

$[(Me_2)_2Al$	tr	899.4(2)	65.85(2)	AlN_4	μN	197.5(5,4)	280.6(2)[f]	μN,μN 85.7(2)	115
$(\mu\text{-}NMe_2)_2Al$	Pß	1423.3(4)	74.81(2)		N	178.8(5,3)	92.2(1,3)	μN,N 113.5(2,2.2)	
$(NMe_2)\{\mu\text{-}\eta^2\text{-}$	2	1490.5(4)	82.08(2)					N,N 114.2(2)	
$OCNMe_2\}Mn(CO)_4$				AlN_3O	μN	192.2(4,6)		μN,μN 88.6(2)	
$Mn(CO)_5]$					N	177.1(5)		μN,N 117.0(2,2.0)	
					O	172.6(3)		μN,O 110.3(2,2.8)	
(orange)								N,O 111.6(2)	
				MnC_5	OC	183.6(5,12)	291.3(1)[d]	C,C 90.0(2,5.2)	
					C	200.0(4)		174.2(2,3.2)	
				MnC_5	OC	183.1(5,32)		C,C 89.8(2,6.1)	
								172.1(2,6.3)	
$[(dmpe)_2Ta$	tr	1089.9(3)	99.12(4)	AlO_3H_3	not given		271.3(9,20)	not given	116
$(\mu\text{-}H)_2Al$	Pß	1119.7(3)	104.69(4)		μH	not given			
$(\text{-}OC_2H_4OMe)_2]_2$	1	1357.9(4)	104.2(4)	TaP_4H_3	P	251.8(9,18)		P,P 76.5(3)[g]	
$[(dmpe)_2MoH$	tr	1278.3(8)	98.34(5)	AlH_3	μH	175(27,1)	256.5(9)	μH,μH 81.7(15)	117
$(AlH_4)]_2$[c]	Pß	2028.3(11)	103.58(5)		H	not given	264.4(14)[f]		
	2	957.2(5)	108.15(5)				98.3(14)		
(yellow)				MoP_4H_3	μH	not given		P,P 80.0(2,3)[g]	
					P	240.9(7,19)		96.0(2,9) 147.0(2)	
								170.0(2)	
				AlH_3	μH	165(26,1)	257.8(9)	μH.μH 75.2(12)	
					H	not given	266.1(15)[f]		
							107.6(13)		
				MoP_4H_3	μH	not given		P,P 79.7(3,4)[g]	
					P	241.0(7,12)		96.2(3,1.2)	
								148.3(2);168.7(2)	
$[(dmpe)_2MnH_2$	m	931.3(2)		AlH_3	μH	164.2(32)	239.3(4)	μH,μH 92.6(12,19.0)	118
$AlH_2]_2$	$P2_1/n$	1351.5(3)	97.01(2)			180.7(28,3)	272.8(6)[f]	164.9(12)	119
	2	1691.2(3)			H	164.2(32)	104.6(11)	μH,H 97.5(14)	
(yellow)							88.4(2,4)	138.4(12)	
				MnP_4H_3	μH	162.1(28,11)		P,P 83.6(2,5)[g]	
					P	221.4(3,8)		96.7(2,3.3)	
								μH.μH 97.9(14)	
								P,μH 87.6(10,9.1)	
								173.9(9,3)	
$[\eta^5\text{-}cp^*_2TiH_2$	m	1119.6(4)		AlH_3	μH	163(1,7)	275.0(3)	μH,μH 83.8(1,7)	87
$AlH_2]_2$	$P2_1/n$	891.5(3)				194(1)	280.0(4)[f]	107.2; 166.9(1)	
	4	2077.7(7)	101.74(3)		H	151(1)	-	μH,H 100.9(1,10.7)	
(green)				$TiC_{10}H_2$	μH	189(1,3)	101.2(1,1)	μH,μH 72.6(1)	
					C	239.2(19)		84.5(1)	
						207.5[e]		cp*,cp* 142.2(2)[e]	
$[(\eta^5\text{-}cp)_2TiH_2$	or	620.8(3)		AlH_3O_2	μO	184.9(27,24)	277.9(14,18)	μO,μO 78.8(11,4)	120
$Al(MeO)H]_2$	$Pc2_1/b$	2774.9(14)				192.3(30)	288.4(18)[f]		
	4	1397.0(6)			μH & H not given		101.2(14,2.1)		
(grey)				$TiC_{10}H_2$	μH	not given		cp,cp 138.0(-,2.1)[e]	
					C	235.4(51,3)			
						202.7(-,12)[e]			

$[(\eta^5\text{-cp}_2)TiH_2$ $Al(EtO)H\}_2$ (violet)	m $P2_1/n$ 2	840.2(2) 1022.8(2) 1586.8(2)	 106.92(2)	AlH_3O_2	μH μO H	176(3,1) 185.2(3,2) 160(4)	278.2(2) 288.7(3)[f] 102.5(1) 103.3(1,1.2)	μH,μH 74.8(1) μO,μO 77.5(1) μH,μO 91.4;142.5(1) μH,H 110.3(2,3.0) μO,H 108.1(1,2.1) μH,μH 75.6(1) cp,cp 138.6[g]	121
				$TiC_{10}H_2$	μH C	175(3,0) 234(1) 203[e]			
$[(\eta^5\text{-cp})_2TiH_2\cdot$ $Al(Et_2N)H]_2$ (dark violet)	m $P2_1/b$ 2	1109.3(2) 1694.7(4) 807.8(1)	 91.99(2)	AlH_3N_2	μH μN H	188(9,3) 200(1,1) 164(9)	282.4(15) 291.1(8)[f] 105.5(45,15) 93.8(4)	μH,μH 69(5) μN,μN 86.2(4) μH,μN 88; 148(3) μH,H 104(4,4) μN,H 110(3,3) μH,μH 79(4) cp,cp 137.5[e]	121
				$TiC_{10}H_2$	μH C	167(9,7) 233(2) 201(-,1)[e]			
[(salpen Al) $Li(thf)_2]_2$	m $P2_1/c$ 4	1189.4(6) 1907.6(6) 2686.2(9)	 101.02(3)	AlN_3O_2	μN μO N	200.3(12,49) 185.6(9,29) 182.0(12,8)	 99.9(9,1.1)	μN,μN 80.7(4,4) μO,μO 81.2 μN,μO 92.2(4,1.1) 117.3(4,9) 166.6(4,2) μN,N 109.6(5,11.7) μO,N 108.5(4,15.1) not given	122
				LiO_4	μO O_{thf}	189.8(26,51) not given			
[(salomphan Al) $Li(thf)_{2-3}$	tr Pß 2	1139.4(4) 1159.3(5) 1390.8(5)	69.05(3) 82.46(2) 77.32(3)	AlN_3O_2	μN μO N	200.0(6,29) 183.4(5,17) 185.6(6)	 97.0(5,3)	μN,μN 85.0(2) μO,μO 85.7(2) μN,μO 94.6(2,7) 124.1; 179.6(3) μN,N 98.8(2,13.2) μO,N 109.2(2,14.6) not given	122
				LiO_4	μO O_{thf}	193.5(14,8) not given			
[(CO)$_4$Cr $\{PPh_2(CH_2)_3O\}$ $Al(CH_2SiMe_3)_2]_2$	m $P2_1/n$ 2	1193.9(3) 1494.0(3) 2101.4(5)	 102.88(2)	AlO_2C_2	μO C	185(1,1) 195(2,1)	 100.3(6)	μO,μO 79.7(5) C,C 121.5(8) μO,C 112.1(7,1.7) C,C 89.5(1.0,2.5) 177.5(1.0,2.5) C,P 91(1,3), 176(1)	123
				CrC_3P	OC P	184(2,5) 238.3(6)			
$[\{(\eta^5\text{-cp})_2Ti$ $AlH_4\}_2(tmeda)]$ $.C_6H_6$	tr Pß 2	840.6(2) 1011.7(2) 1126.9(3)	112.01(2) 109.25(2) 87.04(2)	AlH_4N	μH H N	174(11,6) 155(9,10) 211(1)	278.8 112(5,3)	μH,μH 66(5) μH,H 111(5,13) H,H 118(4) μH,N 89, 155(3) H,N 93(5,1) μH,μH 71(5) cp,cp 139.4[e]	124
				$TiC_{12}H_4$	μH C	162(11,2) 236(1,4) 204[g]			

{[cpFe($C_5H_4CH_2$ $(Me_2)N$]Tl $(2\text{-}C_4H_3S)_2]_2O$}	m $P2_1/n$ 2	1151.8(2) 1312.6(2) 1383.9(3)	96.14(1)	AlC_2ON	μO 169.0(1) N 202.4(4) C 197.8(5,3)	594.4(1) 180	μO,C 115.4(2,2.1) μO,N 103.1(1) C,C 110.9(2) C,N 105.4(2,1.6)	54
(yellow-orange)				FeC_{10}	C_{cp} 164.8(3,1)[e]		cp,cp 178.5(2)[e]	
{[($C_4H_4TiHAlEt_2$] $(C_{10}H_8)$}.Tl	m C2/c 4	2436.7(18) 909.0(4) 1783.2(12)	123.77(6)	AlC_3H	μH not given μ_3C 206 C_{ε} not given	- - H 102 C 77	μH,μC 99	91
(red purple)				$TiC_{11}H$	μH not given μ_3C 235(-,11)	291.0[d]	not given	
$[cp_2YAlH_4(NEt_3)]_2$	m $P2_1/b$ 4	1138.1(4) 1338.8(4) 1415.5(2)	102.01(3)	AlH_4N	μ_xH/H not given N 212.7(26)	330.8(11) 410.8(11) 678.0(9)[f]	Y,Y 58.7(2) Y,N 127.9(5) 172.7(3)	125
(colourless)				$YC_{10}H_3$	μ_xH/H not given C_{cp} 264	370.0(9)[d]	Al,Al 121.3(1) C,C 127.5	
$(cp_2YAlH_4)_2OEt_2$	m $P2_1/b$ 4	1898.4(6) 1698.1(6) 889.6(3)	81.41(3)	AlH_4	μH/H not given	320.2(7,6) 356.5(8,19) 497.2(8)[f]	Y,Y 81.0(2,5.4) Y,O 129.2(6,9)	125
(colourless)				AlH_4O	μ_xH/H not given Et_2O 193.6(18)			
				$YC_{10}H_3$	μ_xH/H not given C 262	437.8(8)[d]	Al,Al 94.3(2,1) C,C 128.7(-,1.3)	
$[LiHAl(CMe_3)_3]_2$	tr Pß 1	880.6(4) 894.6(4) 1091.6(5)	74.83(4) 76.10(4) 62.32(3)	AlC_3H	μH 175(3) μC 208.1(4) C 202.9(4,20)	299(-,19) 116(2,4) 74.8(2)	μH,μC 94(1) μH,C 105(1,1) μC,C 114.7(2,1.4) C,C 118.8(1)	126
at 153(3)K				LiH_3C	μH 180(3,12) μC 235.2(6)	271[d]	μH,μH 83(1) μH,μC 87.0(9) 134.3(8)	
(colourless)								
$K(\mu\text{-}OCH_2CH_2OMe)$ $Al\{(Me_3Si)_2CH\}_2$	m $P2_1/n$ 4	1484.3(3) 1279.0(3) 1725.9(3)	93.82(1)	AlO_2C_2	μO 177.2(3,4) C 201.7(4,2)	- - 102.4(1,2)	μO,μO 95.7(1) C,C 112.0(2) μO,C 112.0(1,1.0)	41
at 173K				KO_3	μO 281.1(3,9) 264.3(3,6) O 269.0(4)	- 104.5(1)	μO,μO 66.4(1,9.1) 127.7(1,6.9) μO,O 64.0(1) 110.7(1,12.6) 172.7(1)	
(colourless)								
$[Me_2Al(\mu\text{-}OBu^t)_2]_2$ $Mg(\mu\text{-}OBu^t)_2]_2$[c]	m $P2_1/c$ 4	1547.7(5) 1457.8(4) 1882.2(6)	110.04(3)	AlO_2C_2	μO 185.5(8,0) C_{Me} 196(2,0)	288.8(5) - 95.9(4,4)	μO,μO 89.2(3) C,C 116.0(7) μO,C 111.7(5)	60
(colourless)				MgO_4	μO 195.4(7,1) 204.3(8,0)	288.6(7) 95.2(3)	μO,μO 81.9(3,1.9) 125.1(3,1.0)	
				AlO_2C_2	μO 187.0(9,0) C_{Me} 195(2,0)	289.5(6) - 96.2(4,6)	μO,μO 88.1(4) C,C 114.9(8) μO,C 113.0(6)	
				MgO_4	μO 196.6(8,14) 203.5(8,0)	290.1(8)[d] 95.2(3)	μO,μO 82.0(3,2.9) 124.5(4,2.0)	

$[Me_2Al(\mu\text{-}NPr^i_2)_2$	m	776.7(2)		AlN_2C_2	μN	196.2(4)	280.0(2)	μN,μN 94.78(2)	60
$Mg(\mu\text{-}I)]_2$	$P2_1/n$	1607.2(3)	97.68(2)			211.4(4)	-	C,C 111.5(3)	
	2	1648.2(5)			C_{Me}	195.1(6)	86.7(2)	μN,C 112.1(2,3.9)	
(colourless)				MgN_2I_2	μN	211.4(4,0)		μN,μN 86.2(2)	
					μI	280.7(2,24)	86.7(2)	μI,μI 88.66(5)	
							91.34(5)		
$[Me_2Al(\mu\text{-}NPr^i_2)$	m	889.3(1)		AlN_2C_2	μN	196.3(9,10)	286.9(4)	μN,μN 96.3(3)	127
$Mg(\mu\text{-}OMe)]_2$	$P2_1/n$	1399.5(2)	96.60(2)		C_{Me}	198(1,1)	-	C,C 108.1(6)	
	2	1638.2(3)					88.2(3,3)	μN,C 113.0(5,2.6)	
(colourless)				MgO_2N_2	μO	196.3(5,6)	295.7(2)[d]	μO,μO 82.2(2)	
					μN	215.5(7,3)	97.8(2)	μN,μN 85.5(3)	
								μO,μN 123.4(3,5.5)	
$[Me_2Al(\mu\text{-}NEt_2)_2$	m	2583.0(6)		AlN_2C_2	μN	195.1(4,3)	286.2(2)	μN,μN 94.3(2)	128
$MgMe]_2$	C2/c	1014.1(5)	123.95(2)		C_{Me}	196.2(6,3)	-	C,C 114.2(3)	
	4	1507.9(3)					89.8(2,2)	μN,C 111.7(2,3.4)	
(colourless)				MgN_2C_2	μN	210.3(4,2)	273.5(3)[d]	μN,μN 85.7(2)	
					μC	227.0(5,26)	89.9(2)	μC,μC 105.6(2)	
							74.1(1)	μN,μC 116.3(2,5.2)	
$\{MeSi(Bu^tNAlMe_2)$	m	2884(2)		AlN_2C_2	μN	199.5(4)	330.7(2)	μN,N 80.1(1)	44
$(Bu^tNH)(Bu^tN$	C2/c	909.0(8)	108.5(2)		N	187.1(4)	-	C,C 111.9(2)	
$MgMe)\}_2$	4	1829(2)			C_{Me}	198.6(7,6)	105.2(2)	μN,C 114.2(2,8.6)	
								N,C 116.3(2,3.2)	
(colourless)				MgN_2C_2	μN	216.8(4)		μN,N 79.0(2)	
					N	219.2(4)	78.6(2)	μC,μC 101.4(2)	
					μC	223.9(6,38)		μN,μC 125.2(2,4.2)	
								N,μC 112.5(2,14.8)	
$\{MeSi(Bu^tNAlMe_2)$	tr	937.0(7)	102.47(7)	AlN_2C_2	μN	195.1(3)	285.1(1)	μN,N 80.1(1)	44
$(Bu^tNH)(Bu^tN$	Pß	1011.8(10)	95.15(7)		N	187.8(3)	-	C,C 111.9(2)	
$MgI)\}_2$	1	1434.8(10)	115.49(6)		C_{Me}	196.2(4,21)	86.9(1)	μN,C 114.2(2,8.6)	
								N,C 116.3(2,3.2)	
(colourless)				MgN_2I_2	μN	218.7(3)		μN,N 78.8(1)	
					N	221.7(3)	89.1(1)	μI,μI 90.9(1)	
					μI	283.6(3,66)		μN,μI 114.2(1)	
								153.4(1)	
								N,μI 108.8(1,12.8)	
$[Me_2Si(Bu^tN)_2$	m	909.5(4)		AlN_2C_2	μN	188.2(6,5)	261.2(4)	μN,μN 80.4(2)	129
$(AlMe_2)(MgI)]_2$	$P2_1/c$	2185(1)	121.6(1)		C_{Me}	198.5(10,25)	-	C,C 108.9(5)	
	2	1228.5(6)					77.1(2,4)	μN,C 116.1(5,9.4)	
(colourless)				MgN_2I_2	μN	227.9(6,20)	410.1(8)	μI,μ1 87.1(1)	
					μ1	283.0(3,19)	92.9(1)	μN,μI 103.6(2,1)	
								165.9(2,4)	
$[(C_{10}H_{14})SnCl$	tr	1040.4(3)	98.63(2)	$AlCl_4$	μCl/Cl not given		-	not given	130
$(AlCl_4)]_2 \cdot C_6H_6$	Pß	1334.3(3)	109.23(2)						
	1	1119.4(2)	105.77(2)	$SnCl_4C_x$	μCl	262.9(1,51)		μCl,μCl 82.1(1)	
(colourless)						293.9(1,139)	97.9(1)		
					C	314(-,24)			

$[\{C_6H_6Zr(\mu\text{-}Br)_3$	m	1980.2(3)		$AlBr_4$	μBr	235(2,5)	-	μBr,μBr	99(1,0)	25
$ZrC_6H_6\}(\mu\text{-}Br)_2$	B2/b	4346.6(7)	96.05(2)		Br	224(2,2)	-	Br,Br	118(1,0)	
$AlBr_2]_2(Al_2Br_7)$	8	1301.2(3)					91.1(6,3)	μBr,Br	107 - 113(1)	
$.2\_C_6H_6$				ZrC_6Br_5	μBr	271.7(11,36)	318.8(10)[d]	μBr,μBr	76.5(3,2.2)	
						282.4(11,42)	71.9(3,7)		106.2(3,2)	
(dark red)					C	269(-,11)				
						230(-,4)[e]				
				$AlBr_4$	μBr	239(3,3)		μBr,Br	102 - 109(1)	
				(dimer)	Br	224(3,5)	110(1)	Br,Br	113(1,2)	
$\{(\eta^5\text{-}C_5H_5)(CO)Fe$	m	1445(2)		AlC_3O	CO	198(2)		C,O	100(1,4)	131
$(\mu\text{-}\eta^2CO)AlEt_3\}_2$	C2/c	1412(2)	100.50(15)		C_{Et}	192.5(30,25)				
	4	1470(3)				207(4)				
(bright red)				FeC_8	OC	188(2)	249.1(8)[d]	not given		
					OC	170(2)				
					C_{cp}	208(3,3)				
$[[Me_3Al(dhmp)]$	m	917.5(3)		AlC_4	C	206.5(10,9)		C,C	109.5(5,7.0)	132
$\{Na(eb)_2\}]_2$	$P2_1/c$	1735.6(6)	97.98(1)		C_{Et}	198.6(12,4)				
	2	1311.2(5)		NaC_8O_2	O	233.9(9,9)		O,O	85.8(3)	
(colourless)					C	257[e]				
					Cπ	281				
$\{Li_4[Me_2SiCH_2)_3$	tg	1566.66(8)		AlC_4	μ_4C	206.0(5)	265(1,1)	$\mu_4C,\mu C$	105.3(3)	133
$Al]_4(\mu_4CH_4)\}$[c]	P4	-			μC	205.1(8,2)	137.5(6)	μ_4C,C	112.1(4)	
	4	1702.9(2)			C	198.5(8)	77.3(4,1)	μC,μC	108.1(3)	
at 193K								μC,C	112.8(3,1.8)	
				LiC_3	μ_4C	213(2)	351(2)[d]	$\mu_4C,\mu C$	96.6(5,2)	
(colourless)					μC	218(1,1)	110.7(8)	μC,μC	140.5(9)	
				AlC_4	μ_4C	207.1(5)	262(1,3)	$\mu_4C,\mu C$	105.7(3,3)	
					μC	206.1(8,11)	135.1(6)	μ_4C,C	113.8(4)	
					C	199.5(8)	75.6(7,1)	μC,μC	107.6(3)	
								μC,C	111.8(3,1.0)	
				LiC_3	μ_4C	210(1)	350(2)[d]	$\mu_4C,\mu C$	99.7(5,1.6)	
					C	220(1,6)	112.7(7)	μC,μC	135.7(7)	
$\{[(C_5H_4Bu^t)_2Sm$	tr	1003.0(1)	109.36(1)	AlH_4O	μ_3H	180	326.2(1,17)	$\mu_3H,\mu H$	82.8(-,1)	134
$(\mu_3\text{-}H)]_2$	Pß	1332.8(2)	115.27(1)		μH	157(-,2)	496.8[f]	μ_3H,H	102.7	
$[(\mu\text{-}H)_2AlH$	2	1034.9(1)	89.45(1)		H	153	-	μH,μH	110.8	
$(thf)]_2\}$					O	200.3(3)	109.5(-,8.3)	μH,H	120.6(-,3.9)	
								(H),O	90.8(-,2.3)	
(yellow green)									164.2	
				$SmC_{10}H_4$	μ_3H	200(-,1)	422.9[d]	$\mu_3H,\mu H$	52.7	
					μH	225(-,4)		$\mu_3H,\mu H$	57.8(-,5)	
					C	248.1(-,4)[e]		μH,μH	139.6	
								cp,cp	125.8[e]	

$([cp_2Sm(\mu_3\text{-}H)]_2$	tr	1101.2(3)	88.76(2)	AlH_4N	μ_3H	115	327.6(5,8)	H,H	118.6(-,4.4)
$[(\mu\text{-}H)_2AlH$	$P\bar{1}$	1191.1(3)	78.65(2)		μH	169	511.3[f]	H,N	85.9
$(NEt_3)]_2)$[c]	4	1431.4(4)	96.17(2)		H	159			101.8(-,6)
					N	211(1)			
				$SmC_{10}H_4$	μ_3H	241		H,H	143.9
					μH	176	409.6(4)[d]		
								cp,cp	123.6[e]
				AlH_4N	C	246.4(-,6)[e]			
					H	not given	328.0(5,3)	H,N	102.4
					N	211(1)	511.4[f]		
				$SmC_{10}H_4$	H	not given			
					C	246.5(-,3)[e]	406.8(4)[d]	cp,cp	124.4[e]
$([cp_2Yb(\mu_3\text{-}H)]_2$	m	1330.7(2)		AlH_4N	μ_3H	231(5)	326.0(2)	$\mu_3H,\mu H$	73(2)
$[(\mu\text{-}H)AlH_2$	$P2_1/a$	1553.8(2)			μH	161(5)	372.8(3)	μ_3H,H	88(2,5)
$(NEt_3)]_2).C_6H_6$	4	1407.592)	134.53(1)		H	154(5,4)	-	μ_3H,N	166(2)
					N	210.8(8)	119(1)	$\mu H,H$	119(2,6)
								$\mu H,N$	93(2)
								H,H	117(2)
								H,N	99(2)
				$YbC_{10}H_3$	μ_3H	207(5,3)	362.3(1)[d]	μ_3H,μ_3F	57(2)
					μH	215(5)		$\mu_3H,\mu H$	70(2)
					C	233(-,1)[e]		cp,cp	127.9[e]
$([cp_2Y(\mu_3\text{-}H)]_2$	m	875.0(2)		AlH_4O	μ_3H	200(10)	324.293)	$\mu_3H,\mu H$	77(3)
$[(\mu\text{-}H)AlH_2$	$P2_1/b$	1104.3(3)			μH	157(6)	398.9(3)	μ_3H,H	93(3,7)
$(thf)]_2)$	2	1645.3(3)	95.57(2)		H	148(7,2)	121(3,21)	μ_3H,O	164(2)
					O	197.2(1)		μ_3H,H	119(3,3)
								$\mu H,O$	88(2)
								H,H	121(4)
								H,O	96(3,3)
				$YC_{10}H_3$	μ_3H	234(60,6)	375.3(1)[d]		
					μH	217(6)	117(3)	cp,cp	127.5[e]
					C	236[e]			
$([cp_2Lu(\mu\text{-}H)]_2$	m	1133.9(2)		AlH_3N	μH	186(9,11)	326(1)	$\mu H,\mu H$	129(4)
$[(\mu\text{-}H)AlH$	$P2_1/b$	1330.0(2)			H	132(9)	409(1)	$\mu H,H$	73, 118(4)
$(NEt_3)]_2).C_6H_6$	4	1406.192)	102.28(1)		N	213(3)	-	$\mu H,N$	77(4)
							110(2,14)	H,N	121(4)
				$LuC_{10}H_4$	μH	173(9)	361.3(1)[d]	$\mu H.\mu H$	54(4,3)
						251.9,16)	123(2)		86(4)
					C	229[e]		cp,cp	128.4[e]
$([cp_2Y(\mu\text{-}Cl)]_2$	m	1232.5(5)		AlH_3N	μH	180(10)	362	$\mu H,H$	116(8,4)
$[(\mu\text{-}H)AlH_2$	$P2_1/a$	1878.0(7)	69.89(2)		H	150(10,0)	-	H,H	113(7)
$(NEt_3)]_2)$	2	884.8(2)			N	204.5(9)	136(7)	$\mu H,N$	106(6)
								H,N	103(5,2)
(colourless)				$YC_{10}HCl$	μH	210(10)	438[d]	$\mu H,\mu Cl$	74(4)
					μCl	274.0(5,30)	106.2(1)	$\mu Cl,\mu Cl$	73.8(1)
					C	238(-,1)[e]			

{[(cp*)(Me)Zr	m	2801.5(4)		AlF_2C_2	μF 178.1(4,5)		not given		138
(μ-F)]$_2$[(μ-F)$_2$Al	$P2_1/c$	2393.4(4)	108.80(1)		C_{Me} 191.9(9,3)	-			
Me_2]$_2$}._tl	16	2302.2(2)				140.2(2)			
(colourless)				ZrC_6F_4	μF 214.3(3,36)		μF,μF 67.48(11)		
					C_{Me} 228.3(6)	111.67(12)			
					C_{cp} not given				
{[(C_6H_6)$_2$Sn	or	1986.9(1)		$AlCl_4$	μCl 216.9(4,8)	-	not given		139
(-Cl)$_2$]$_2$[(μ-Cl)$_2$	Pbca	1594.1(1)			Cl 210.5(4,11)	-			
$AlCl_2$]$_2$]$_2$}	8	2595.4(2)				119.1(1,3.5)			
.C_6H_6				$SnC_{12}Cl_4$	μCl 262.3(2,16)		μCl,μCl 78.5(1,1)		
at 223K					291.2(3,74)	101.5(1,4)	167.8(1,1.3)		
(colourless)					C 320(-,9)[e]		C_5,C_6 100.8(-,1.1)[e]		
[(Me_3Si)$_2$$NAlH_3$	m	2115.7(4)		AlH_3N	μH 152(4,4)	-	H,H 107(2)		6
$Li(Et_2O)_2$]$_2$	$P2_1/c$	938.7(2)	95.71(3)		H 159(4,2)	-			
	4	2498.3(5)			N 185.8(3,3)	157(3)			
(colourless)				LiH_2O_3	μH 178(4,4)		H,H 107(2)		
					O 193(8)				
[(thf)$AlMe_3$	m	1139.6(2)		AlC_3O	μC 196.6(7,3)	-	not given		140
$Ca(cp^*)_2$]$_2$	$P2_1/n$	2011.2(1)	97.20(1)		C_{Me} 194.9(8)	-			
	2	1262.7(2)			O not given	168.2(4,8.5)			
(colourless)				CaC_{12}	μC 297.4(7,26)		not given		
					C_{cp} 270(1)				
[Me_2AlMe_2	m	1216.9(3)		AlC_4	μC 207(3,0)	-	μC,μC 101.5(9)		141
$Y(cp^*)_2$]$_2$	$P2_1/n$	1251.9(2)	99.97(2)		C_{Me} 200(3,2)	-			
		1679.9(2)				177(1,1)			
at 203K				YC_{12}	μC 266(2,1)		μC,μC 84.9(7)		
					C_{cp} 266(3)				
[Me_2AlMe_2	m	1226.7(3)		$AlCl_4$	μC 204.9(17,3)	-	μC,μC 101.7(7)		142
$Sm(cp^*)_2$]$_2$	$P2_1/n$	1257.5(3)	100.44(2)		C_{Me} 201.9(21,16)	-	μC,C 109.5(9,6)		
	2	1713.1(2)				176.5(8,1.3)	C,C 116.3(10)		
(red orange)				SmC_{12}	μC 274.6(16,4)		μC,μC 85.0(5)		
					C_{cp} 267.1(21,37)		μC,cp 105.1(-,1.3)[e]		
					241.7(-,3)[e]		cp,cp 138.6[e]		
[cpW(CO)$_3$$AlMe_2$]$_2$	m	1812.0(4)		AlO_2C_2	μCO 180.8(18,15)		O,O 95.1(8)		143
	C2/c	618.8(2)	93.29(2)		C_{Me} 194(3,1)		O,C 108.7(11,1.1)		
	4	2226.6(5)					C,C 123.4(14)		
				WC_3	μOC 185.2(20,27)		μC,μC 83.8(8)		
					OC 197.0(23)		μC,C 87.9(9,8)		
					C_{cp} 234(2,4)				
					201.6(11)[e]				

C: Al + 3M

{[(C_5H_4Me)Ti F_2]$_3$Al}	rh R3c 6	1654.9(5) - 2091.2(19)		AlF_6	μF	181.2(2,0)	311.3(2) - 105.40(8)	μF,μF	80.91(10)	144
(blue) at 153K				$TiC_{10}F_2$	μF C_{cp}	209.5(2,0) 204.2(1)[e]		μF,μF cp,cp	68.29(9) 134.3[e]	
{[$en_2Cr(OH)_2$]$_3$ Al}(S_2O_3)$_3$.13H_2O	m $P2_1/n$ 4	2489(3) 996.8(5) 2342(3)	116.30(6)	AlO_6	μHO	189.0(8,20)	295.1(4,7) - 101.3(4,5)	μO,μO	79.6(3,2)	145
(cherry red)				CrN_2O_2	μHO N	192.7(-,7) 206.0(-,11)		μO,μO	77.7(3,2)	
{[$en_2Co(OH)_2$]$_3$ Al}(S_2O_3)$_3$.5H_2O	m C2/c 4	1834.2(3) 1727.3(2) 1479.5(2)	108.81(1)	AlO_6	μHO	189.9(3,4)	288.8(1,0) - 98.2(2,2)	μO,μO	82.4(1,0)	145
(orange)				CoN_4O_2	μHO N	192.2(3) 195.3(5)		μO,μO	81.3(1,2)	
{[cpW(CO)$_3$]$_3$ Al(thf)$_3$}	tr Pß ?	1141.9(3) 1126.3(4) 1615.6(6)	98.13(1) 100.55(1) 100.23(1)	AlO_6 WC_8	μCO O_{thf} μOC OC C_{cp}	182.7(9) 194(2) 185(2) 195(2) 204(1)[e]		O,O not given	90(-,3)	146
{[(OC)$_4$Mn (COMe)$_2$]$_3$Al}[c]	m $P2_1/n$ 4	1394.8(5) 1218.2(6) 1954.5(6)	90.51(2)	AlO_6 MnC_6	O C OC	187.3(10) 181.8(10) 183.9(12,21)		O,O C,C	92.5(4) 175.9(3,4) 90.0(6,4.2) 165.4(6)	147
(pale yellow)										

Footnotes: *a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.*

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. There are two crystallographically independent molecules.

d. M-M distance.

e. Centroid of the carbon ring.

f. Al-Al distance.

g. Five member metallocyclic ring.

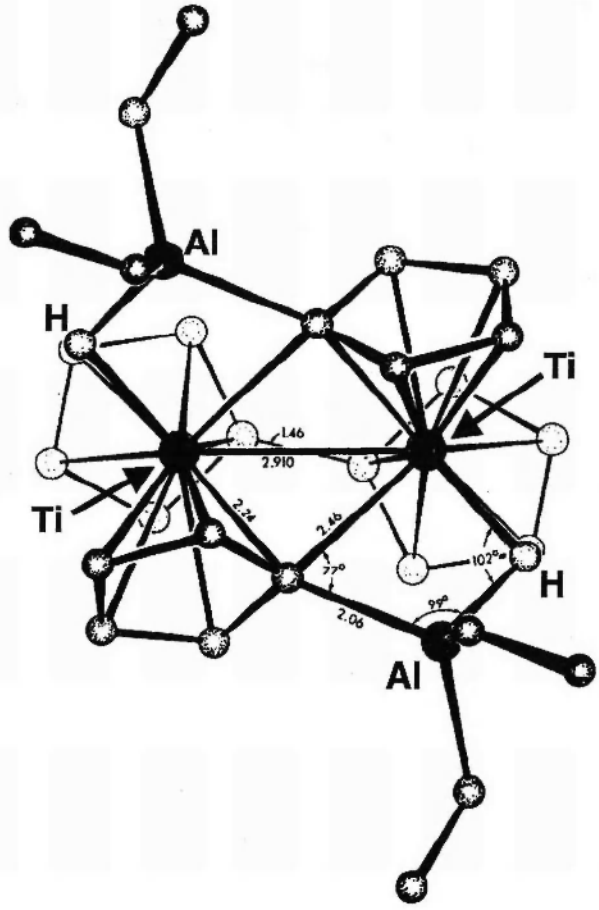

Fig.7. Structure of $[(C_5H_4TiAlEt_2(C_{10}H_8)]_2$ [91]

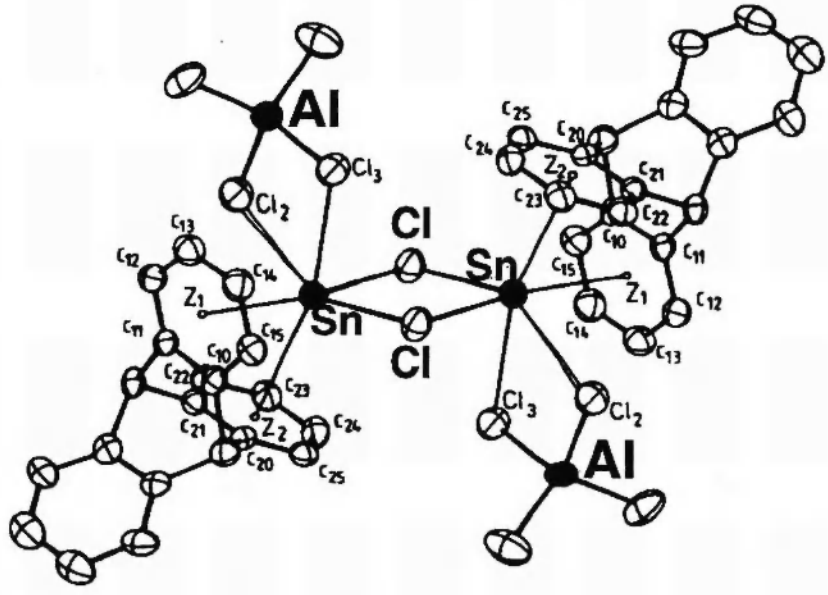

Fig.8. Structure of $[(C_{10}H_{14})SnCl(AlCl_4)]_2$ [130]

The angle between Y-Y axis and the plane passing through the cp ring centres and their respective Y atom is 29.8°. This deflection of the cp ring is no doubt due to the coordination at the yttrium atom of an extra ligand, the H-atom which is found exactly within the bisector plane of the wedge-like sandwich as a result of its bridging to the aluminium atom. The colourless AL/Zr cluster [138] has two cp*ZrMe units of the dimer linked by two direct fluorine bridges and two 1,3-bidentate F_2AlMe_2 groups. A similar structure is found in another complex [139] where two (η^6-C_6H_6Sn) units of the dimer are linked by two direct chlorine bridges and two 1,3-bidentate Cl_2AlCl_2 groups (Table 3B).There are four derivatives [6,140-142] which contain a central heterocyclic eight member ring: $[AlHLiH]_2$ [6], $[AlCCaC]_2$ [140], $[AlCYC]_2$ [141] and $[AlCSmC]_2$ [142]. Each aluminium atom is in a distorted tetrahedral environment. Lithium in the first derivative [6] also has a tetrahedral coordination, while Ca [140], Y [141] and Sm [142] are sandwiched by pentamethylcyclopentadienyl rings. The Al-X-M bridge angle in this series increases in the order: 157(3)° [6] < 168.2(4)° [140] < 176.5(8)° [142] < 177(1)° [141]. The M-C(bridge) as well as the M-C(cp) distances increase with increasing covalent radius of M in the order: 266 and 266 pm (Yb(III), 98.5 pm) < 275 and 267 pm (Sm(III), 102 pm) < 297 and 270 pm (Ca(II), 114 pm) [148], all with coordination number eight. In an Al/W cluster [143] the aluminium and tungsten atoms are bridged by carbonyl groups with oxygen bound to aluminium and carbon to tungsten in slightly puckered twelve member rings (Table 3B).

The third class of heterotetrametallic derivatives (Table 3C) has the aluminium central atom in a six coordinate environment. The octahedral geometry is significantly distorted, and is surrounded by four member rings ($AlTiF_2$) [144], ($AlCrO_2$) and ($AlCoO_2$) [145] in a propeller-like manner. The "pitch angle" of the four member rings of the "blades" is 86.9° [144]. The Al-M distances are 311.3(2) pm (M = Ti) [133], 295.1(4) pm (Cr) [145] and 288.8(1) pm (Co) [145]. The Al-L-M bridge angle closes as the Al-M distance decreases: 105.40(8)° (L = F) [133] < 101.3(4)° (OH) [145] < 98.2(2)° (OH) [145].

In a light yellow Al/W cluster [146] the almost regular octahedral stereochemistry around the central aluminium atom involves three Al-O-C-W linkages through one of the carbonyls of each of three $[W(CO)_3cp]$ moiety. The octahedral aluminium coordination is completed by three tetrahydrofuran ligands in a *mer* configuration. The three tungsten moieties display approximate mirror symmetry and are very nearly isostructural. The molecular structure of an Al/Mn cluster [147] belongs to the D_3 symmetry point group. An octahedral coordination about the central aluminium is created by six OCMe ligands in the manner Al-O-C(Me)-Mn. The four CO groups about each manganese atom completes a slightly distorted octahedral geometry (MnC_6).

The data in Table 3 indicates some examples which contain two crystallographically independent molecules within the same crystal [60,84,102,117,133,147]. These differ mostly by degree of distortion of the M-L distance, L-M-L and M-L-M angles, and represent more examples of distortion isomerism [57]. The aluminium atoms are found mostly in a distorted tetrahedral environment, but there are some trigonal bipyramidal examples. As noted above, all of the derivatives in section C of Table 3 have octahedrally coordinated aluminium atoms. The mean Al-L(terminal) and Al-L(bridge) distances increase with covalent radius of the donor atom in the order: 150 pm (H) < 192.5 pm (LN) < 197 pm (LC) < 209 pm (Cl) < 224 pm (Br) for the former and 176 pm (H) < 178 pm (F) < 182 pm (LO) < 198 pm (LN) < 208 pm (LC) < 218 pm (Cl) < 235 pm (Br) for the latter.

The stereochemistry about the metal partners of the aluminium atom varies from three to ten coordination. There are several examples [25,101-104,107,131,138,143,146] which contain "open sandwich" (η^5- or η^6-) ligands plus other ligands which usually serve as bridges between metal atoms. Another set of examples [54,84,87,104,110,120,121,124,125,130,134-137,140-142,144] contain η^5-sandwiched M, and in one case [139] $\eta^{\pm}$-sandwiched tin(II). In addition, except in two cases [54,104], other donor atoms are present and serve as bridges to aluminium atoms. In the two exceptions [54,104] the η^5-ring serves as the bridge to the aluminium atom.

There are twenty three different metal atoms found with aluminium in over seventy heterotetrameric derivatives. These include the non-transition metals: Mg(8 examples) > Li (5) > Ca (4) > Sn (3) > Na, K, Ga (1 each); the transition metals: Ti (9) > Y (6) > Co (4) > Zr, W, Mn, Fe (3 each) > Cr, Mo (2 each) > Ta, Pd (1 each); the lanthanide metals: Sm (8) > Nd, Yb, Lu (1 each; and there is even one actinide example with uranium [99]. A summary of the Al-M, Al-Al and M-M distances are given in Table 3D and 3E, respectively. The shortest Al-M distance four the heterotetrameric derivatives are: 233.3(1) pm (M = Co, transition metal) < 261.2(4) pm (Mg, main group metal) < 319.6 (7) pm (Y, lanthanide metal) < 376.2(4) (U, actinide metal). The shortest M-M distance increases in the order: 207.9(1) (Mo-Mo) < 271 pm (Li-Li) < 361.3(1) pm (Lu-Lu). Finally, the shortest Al-Al distance in the heterotetramers is 264.4(14) pm [117].

Table 3D. Summary of Al-M Distances [pm] in Heterotetranuciear Aluminium Clusters[a]

Al-M	Distances: M = non transition. [ref]
-Mg	261.2(4) [129]; 280.0(2) [60]; 285.1(1) [44]; 286.2(2) [128]; 286.9(4) [127]; 288.8(5) [60]; 289.5(6) [60]; 330.7(2) [44].
-Li	262(1,3), 265(1,1) [133]; 299(-,19) [126]
-Al	see Table 3E.
-Sn	347.3(1) [111]
	M = transition.
-Co	233.5(1,2) [107]; 259.8(2,7) [107]; 288.8(1) [145].
-Mn	239.3(4) [118,119].
-Mo	256.5(9) [117]; 257.8(9) [117].
-Ta	271.3(9,20) [116].
-Ti	275.0(3) [87]; 277.9(14,18) [120]; 278.2(2) [121]; 278.8 [124]; 279.2(11) [104]; 282.4(5) [121]; 311.3(2) [144].
-Cr	295.1(4,7) [145].
-Fe	594.4(1) [54].
	M = lanthanide and Actinide.
-Y	320.2(7,6) [137]; 324.2(3) [136]; 330.8(11) [125]; 356.5(8,19) [137]; 362 [137]; 398.9(3) [136]; 410.8(11) [125].
-Sm	326.2(1,17) [134]; 327.6(5,8), 328.0(5,3) [84].
-Yb	326.0(2), 372.8(3) [135]
-Lu	326(1), 409(1) [135]
-U	376.2(4) [103]

Footnote: The first number in parenthesis is the e.s.d, the second is the maximum deviation from the mean.

5. HETEROOLIGONUCLEAR COMPOUNDS

The crystallographic and structural data for these derivatives are gathered in Table 4. There are five examples containing five metal atoms, and the structure of $Al_3Mg_2(Pr^iO)_{13}$ [149] is shown in Figure 9 as an example. Each magnesium atom is coordinated to a terminal $Al(Pr^iO)_4$ group via double OPr^i bridges. The two magnesium atoms are joined by another bridging isopropoxy group and another $Al(OPr^i)_4$ group, which is doubly bridged (via isopropoxy) to one magnesium and singly

bridged to the other. The molecule is unsymmetrical, with both a tetrahedral and a five coordinate magnesium. Each aluminium atom is in a pseudo tetrahedral environment (AlO_4).

Table 3E. Summary of M-M Distances [pm] in Heterotetranuciear Aluminium Clusters[a]

M-M	Distances [ref]; M = non transition.
Al-Al	264.4(14), 266.1(15) [117]; 266.3(3) [107]; 266.7(1) [110]; 271.1(2) [111]; 272.6(6) [118.119]; 280.0(4) [87]; 280.6(2), 281.7(1) [115]; 288.4(18) [120]; 288.7(3), 291.1(8) [121]; 497.2(8), 678.0(9) [125].
Li-Li	271 [126]; 350(2), 351(2) [133].
Mg-Mg	273.5(3) [128]; 288.6(7), 290.1(8) [60]; 295.7(2) [127]; 410.1(8) [129]
	M = transition.
Mo-Mo	207.9(1) [106].
Fe-Fe	249.1(8) [131].
Pd-Pd	257.0(13) [105].
Mn-Mn	291.3(1) [115].
Ti-Ti	311.0(7) [104].
Zr-Zr	318.8(10) [25].
Co-Co	333.8 [107].
	M = lanthanide.
Lu-Lu	361.3(1) [135].
Yd-Yd	362.3(1) [135].
Y-Y	370.0(4) [125]; 375.3(1) [136]; 437.8(8) [125]; 438 [137].
Sm-Sm	406.8(4), 409.6(4) [84]; 422.9 [134].

Footnote: (a). The first number in parenthesis is the e.s.d, the second is the maximum deviation from the mean.

The molecular structure of an Al_3Mo_2 cluster [150] indicates three aluminium environments. One is the predictable dimethylaluminium, in a distorted (AlC_2Mo_2) environment bridging the two molybdenum atoms (Al-Mo = 294.4(6) and 300.3(6) pm, Mo-Al-Mo angle of 106.2(2)°). The other two aluminium atoms are involved in a unique structural feature of this system. An AlMe group bridges the two molybdenum atoms (Al-Mo = 265.7(2) and 266.2(6) pm), and at the same time is

involved in a multicentre bonding arrangement with the two unique carbon atoms of the C_5H_4 groups (AlC_3Mo_2). This is also linked to the remaining $AlMe_2$ group giving a tetrahedral (AlC_4) environment. This compound was also studied by another group [151] and published in the same year (1974), both studies yielding comparable results.

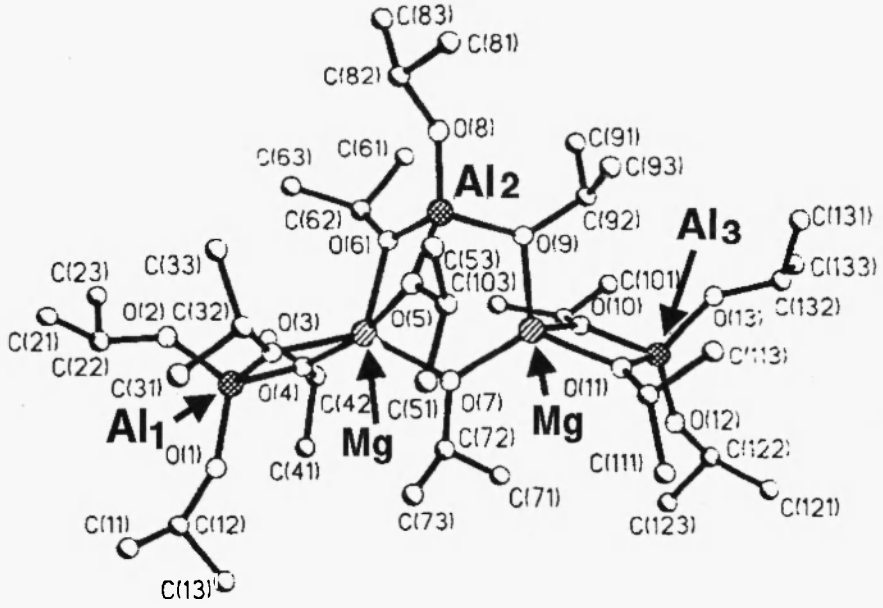

Fig.9. Structure of $Al_3Mg_9(Pr^iO)_{13}$ [149]

The crystal structure of yellow $Hg_3(AlCl_4)_2$ [152] contains discrete molecules having a nearly linear Cl-Hg-Hg-Hg-Cl central skeleton, the chlorine atoms being shared with two nearly tetrahedral terminal $AlCl_4$ units. The mean Hg-Hg bond length is 255.7(1) pm, and both the Hg-Hg-Cl and Hg-Hg-Hg angles are 174.5°. An $AlSn_4$ derivative [153] approaches 3m point symmetry and contains a Sn_4N_3O cage, the atoms of which occupy the corners of a distorted cube formed by two different size, interpenetrating, concentric tetrahedra of tin and nitrogen or oxygen atoms. The nitrogen atoms carry tert-butyl groups and the oxygen atoms are ligated to an $AlMe_3$ unit. The aluminium is in a distorted tetrahedral environment (AlC_3O).

There are eleven examples which contain six metal atoms, and represent the richest variety in the heterooligonuclear series. The number of aluminium atoms varies from Al_4M_2 [105,151,154-156], Al_3U [157] to Al_2M_4 [88,127,158-160].

A colourless (Al_4Sn_2) cluster [154] contains a folded eight member $Al_2Sn_2Cl_4$ ring with the two tin(II) centres linked by two bidentate bridging $AlCl_4$ counter ions. Each tin(II) is η^6-bonded to a hexamethyl benzene ring and is further connected to another $AlCl_4$ group, also acting as a bidentate ligand. A striking feature of the skeleton in an Al_4Mo_2 derivative [151] is the presence of pairs of Al atoms arranged in a way reminiscent of the trialkyl and triaryl aluminium dimers, with bridging C atoms provided by the adjacent cyclopentadienyl rings which are denoted as C_5H_4 in the formula (Table 4).

The molecule of an Al_4Pd_2 cluster [105] is centrosymmetric with the centre of symmetry at the midpoint between the two bonded Pd atoms (Pd-Pd = 257(1) pm). The two benzene rings are π-bonded to both Pd atoms, giving rise to a binuclear sandwich structure. Each Pd atom of the Pd-Pd centre is connected by a single bridging chlorine atom to an $-AlCl_3(\mu\text{-}Cl)AlCl_3$ moiety. A centrosymmetric dimer is found in an Al_4Pr_2 derivative [156a] which is composed of two triangular $[Al_2Pr(\mu\text{-}OPr^i)_4(OPr_i)_4(Pr_iOH)]^+$ units linked by a pair of chloride atoms. The praseodymium(III) atoms are heptacoordinated and the aluminium(III) atoms are in distorted tetrahedral arrangements (AlO_4).

The Al_4Na_2 cluster [156b] is centrosymmetric with two oxygen atoms of water molecules bridging its two halves. The sodium(I) atom is coordinated to two phenolate oxygen atoms from one [Al(btame)] moiety and one phenolate oxygen atom from the other closest [Al(btame)] moiety. Each aluminium(III) atom is in a pseudo-octahedral environment (AlO_3N_3) created by a hexadentate macrocyclic (btame) ligand, and each sodium(I) atom is pentacoordinate (NaO_5).

In the unique Al_3U_3 cluster [157] the three uranium(III) atoms define an approximately equilateral triangle. Three chlorine atoms bridge the edges of this triangle, and two additional

chlorine atoms cap the U_3 fragment on each side by triple (μ_3-) bridging. The coordination polyhedron of each uranium atom is a distorted pentagonal bipyramid. The equatorial plane is defined by two Cl atoms of the bridges, two Cl atoms of $AlCl_4$ and one μ_3-Cl atom of the caps.

The structure of a colourless Al_2Mg_4 cluster [127] is shown in Figure 10. It contains two $Me_3Al\{\mu\text{-}N(SiMe_3)_2\}Mg\{N(SiMe_3)_2\}$ molecules bound through Mg atoms to the methyl groups of $MeMg\{\mu\text{-}N(SiMe_3)_2\}_2MgMe$. The compound posses a centre of inversion related to the two equivalent fragments.

Colourless $[\{Sn(NBu^t)\}_4\{AlCl\}_2]$ [158] contains a Sn_4N_4 cage, the atoms of which occupy the corners of a distorted cube. The nitrogen atoms are linked to $SiMe_3$ groups, the tin(II) atoms of the cage acts as a donor to the $AlCl_3$ unit. The aluminium atom is in a distorted tetrahedral environment ($AlCl_3Sn$).

The structure of a black Al_2Ti_4 cluster [159] is shown in Figure 11. It is polycyclic with two four member, two six member and one eight member ring. The titanium atom framework represents two almost regular isosceles triangles, and including the aluminium atoms produces a gull-like figure with the wings being linked by bridging hydrogen atoms. All the hydride ligands in the structure are bridging.

There are two heteroheptanuclear derivatives, (Al_6Li) [161] and (Al_3Ti_4) [162]. The molecular structure of the former is a pseudo-hexameric cage consisting of a five member fragment, Al-N-Al-N-Al, crosslinked to a six member, cyclohexane-like, ring, $(AlN)_3$.

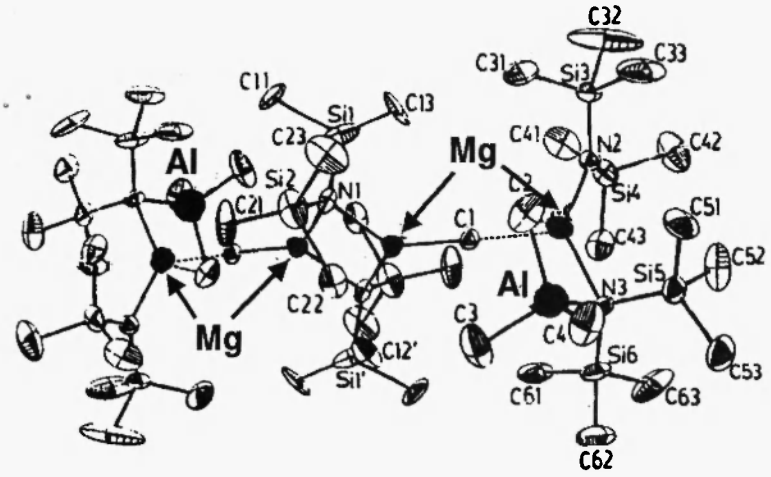

Fig.10. Structure of $[\{(Me_3Si)_2MgMe_2\}_2\{Mg(NSiMe_3)_2\}N(SiMe_3)_2AlMe_3\}_2]$ [127]

The lithium(I) atom is linked to two adjacent molecules through three Li-H-Al bridges, the fourth tetrahedral position being occupied by the oxygen atom of diethyl ether.

The structure of the Al_3Ti_4 cluster [162] is shown in Figure 12. It contains a Ti metallocycle (Ti-Ti = 275 - 279 pm) coupled through three μ-I bridges (Ti-I = 277 pm). The three Al μ-I bridges join three Ti atoms to three Al atoms. The three-membered Ti_3 metallocycle is additionally coordinated by a deformed C_6 ring, which is also one of the caps of a dibenzenetitanium(0) moiety. The aluminium atoms have distorted tetrahedral coordination (AlI_3C).

There are seven heterooctanuclear examples, Al_6Li_2 [163] and Al_4M_4 [128,164-168]. The structure of the former example consists of an open cage $(AlN)_6$ to which two LiH molecules are linked through Li-H-Al hydrogen bridges. The tetrahedral coordination of the lithium(I) atoms is completed by a nitrogen atom of the cage and two nitrogen atoms of the outer -NMe_2 groups. Each aluminium atom has a distorted tetrahedral environment (AlH_2N_2 (x2) and AlN_3H (x4). The structure of a green Al_4Ti_4 cluster [165] consists of four identical cp*$Ti(C_5Me_4CH_2)H_2Al$ moieties bonded by two μ_3-O bridges. The wedge-like cp*$Ti(C_5Me_4CH_2)$ sandwiches have a chess-board conformation. There are two hydrogen bridges in the bisector plane of the wedge-like sandwich, which link the Ti(III) and the Al(III) atoms (see Table 4). The structure of a colourless Al_4Lu_4 cluster [166,167] is shown in Figure 13.

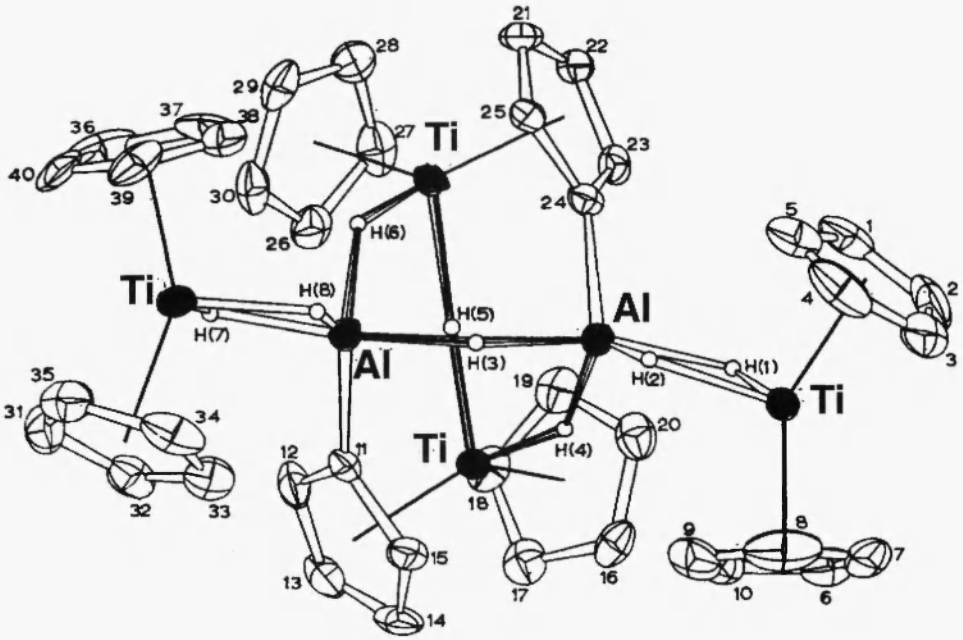

Fig.11. Structure of $[cp_2Ti(\mu\text{-}H)_2Al(\mu\text{-}H)(C_5H_4)Ticp(\mu\text{-}H)]_2$ [159]

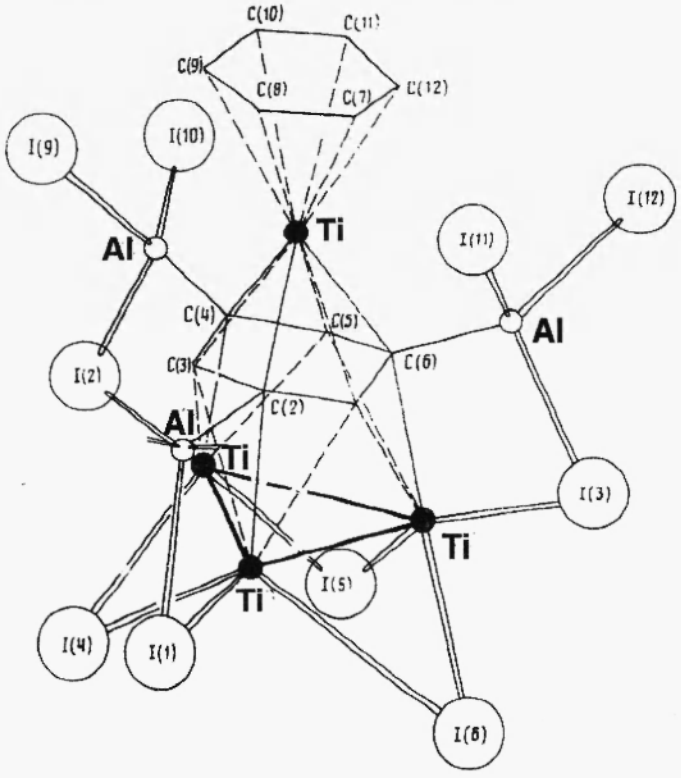

Fig.12. Structure of $Ti_4Al_3I_{18}(C_6H_6)(C_6H_3)$ [162]

Four lutecium(III) atoms are located in the vertices of an elongated tetrahedron. Over each face of the tetrahedron there is one aluminium(III) atom. The heterooctanuclear metal core is a very distorted cube with an approximate point symmetry of D_{2d} formed by the bridging hydrogen bonds. Each Lu(III) atom has the same distorted square pyramidal coordination with the μ^5-ring in the apical position and three aluminium atoms plus the nearest lutecium atom in the square base. There are two aluminium atoms in distorted tetrahedra (AlH_4) and one in trigonal bipyramidal environment (AlH_4O).

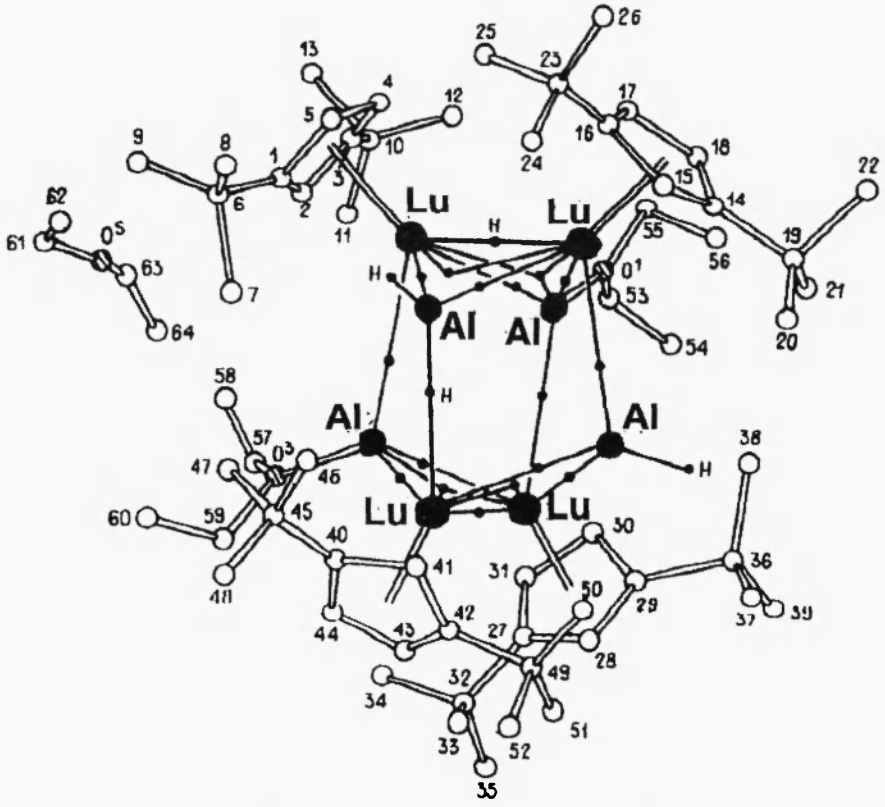

Fig.13. Structure of $\{[(Bu^t_2C_5H_3)LuH]_4[AlH_4(Et_2O)]_2[AlH_4]\}Et_2O$ [167]

Another octanuclear Al_4Sm_4 cluster [168] has a cyclic metal core which resembles a sitting frog. Samarium atoms are located in one plane (deviations of 1 - 2 pm) in the apices of the tetrahedron with mutually equal edges and one acute angle. At the apex of the acute angle a samarium atom is coordinated to two η^5-$C_5H_3Bu^t_2$-ligands. Three other samarium atoms are coordinate to only one η^5-ligand. There are two aluminium environments, one AlH_4 and the other AlH_2N_2.

There is only one heterononanuclear cluster [138] and its structure is shown in Figure 14. Six metal atoms form an open cube, which is shielded by Al and C atoms. The cluster is capped by CH and CH_2 groups, some of the C atoms being hypervalently bound. There are two sets of Al-Zr distances: Al(1)-Zr(1) = 333.0(2) pm; Al(2)-Zr(2) = 333.7(2) pm; and Zr(1)-Al(5) = 288.0(2) pm; Zr(2)-Al(6) = 287.9(2) pm; Zr(3)-Al(4) = 284.6(2) pm. The average Al-Al distance is 268.2(3) pm.

The structure of green $[Eu(C_6Me_6)(AlCl_4)_2]_4$ [169] is shown in Figure 15. The molecule is a cyclotetramer in which four $Eu(C_6Me_6)AlCl_4$ units are connected via four groups of η^2-$AlCl_4$. Each europium(II) atom is coordinated by three groups of $AlCl_4^-$ and one C_6Me_6 group to form a distorted pentagonal bipyramid.

There is one example [170] which contains eighteen metal atoms (Al_6Nd_{12}) and its structure is shown in Figure 16. The crystal is composed of dimers of (Al_3Nd_6). The coordination about each aluminium atom is tetrahedral, and that about neodymium is monocapped prismatic.

TABLE 4. Crystallographic and Structural Data for Hetero-Oligonuclear Aluminium Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromo-phore	M-L [pm]	L-M-L [°]	Ref
PENTANUCLEAR							
$Al_3Mg_2(Pr^iO)_{13}$	m	1592.7(4)		AlO_4	μO^b 177(1)	O,O[b] not given	149
	$P2_1/c$	1823.9(7)	91.34(2)		O 165(1)		
(colourless)	4	1991.4(7)		MgO_4	μO 195.7(9,47)		
				MgO_5	μO 200.5(9,14)		
					210.6(9,30)		
$\{(cp)(C_5H_4)$	or	1939.8(4)		AlC_3Mo_2	Mo 265.9(6,4)	Mo,Mo 126.9(2)	150
	$P2_12_12_1$	1443.8(9)			μ_3C 233(2,3)	μ_3C,Mo 112.8(5,1.4)	
$(MoH)_2Al_3Me_5\}$	4	903.5(2)			C_{Me} 198(2)	μ_3C,C 104.7(7,8)	
						C,Mo 55.6(4,4);131.9(5,1)	
				AlC_4Mo_3	Mo 297.4(6,30)	C,C 87.1(6); 80.5(6,8)[c]	
					C_{Me} 200(2,1)	Mo,Mo 106.2(2)	
				AlC_4	μ_4C 205(2,1)	C,C 103.9(7)	
					C_{Me} 201(3,1)	C,Mo 111.7(6,1.2)	
						μ_3C,μ_4C 102.7(7)	
				MgC_{10}	C_{cp} 228(2,7)	μ_3C,C 109.6(9,3.4)	
					196(-,2)[d]	C,C 114.8(10)	
						cp,cp 144.8[d]	
						147.1[d]	
$\{(cp)(C_5H_4MoH)_2Al_2Me_5\}$	or	1938.3(7)		AlC_3Mo_2	Mp 265.4(4,4)	Mo,Mo 127.3(2)	151
	$P2_12_12_1$	1445.8(6)			μ_3C 232(2,3)	μ_3C,Mo 112.8(6,8)	
	4	900.9(5)			C_{Me} 205(2)	μ_3C,C 103.8(7,4)	
					288.0(7,43)[e]	C,Mo 55.3(3,7);132.7(4,1)	
				AlC_4Mo_3	Mo 297.4(5,23)	C,C 88.1(5);80.4(5,1.1)[c]	
					C_{Me} 200(2,1)	Mo,Mo 106.2(1)	
				AlC_4	μ_4C 208(2,2)	C,C 106.7(9)	
					C_{Me} 203(3,4)	C,Mo not given	
						μ_3C,μ_4C 102.1(6)	
				MoC_{10}	C_{cp} 228(2,6)	μ_3C,C 109.4(9,4.4)	
					475.6(2)[f]	C,C 116.0(11)	
						Mo,Mo 106.2(1)	
						Al,Al 61.9(1)	
$Hg_3(AlCl_4)_2$	m	713.21(2)		$AlCl_4$	μCl 218.3(6,2)	μCl,Cl 106.9(2,2.4)	152
	$P2_1/c$	1504.68(3)			Cl 211.9(6,13)	Cl,Cl 112.0(2,2.6)	
(yellow)	4	1417.71(4)	99.050(3)			105.7(2)[g]	
				Hg_3Cl_2	μCl 254.0(4,23)	Hg,Hg 174.42(4)	
					Hg 255.7(1,6)	Hg,μCl 174.7(1,1.9)	

$(Me_3CN)_3(Me_3AlO)Sn_4$	m	1017.4(5)		AlC_3O	μ_4O	189.5(5)	μ_4O,C	103.6(3,1.3)	153
	$P2_1/c$	1488.5(7)	91.5(1)		C_{Me}	199.6(9,29)	C,C	114.6(3,1.3)
(colourless)	4	1748(1)						117.9(2,8)[g]
				SnN_3O	μ_4O	220.3(4,9)	μ_4O,μ_3N	79.0(2,7)
				(x3)	μ_3N	218.9(6,17)	μ_3N,μ_3N	81.9(2,4)
						334.8(1,28)[f]		100.2(2,9)[h]
				SnN_3	μ_1N	222.0(6,4)	μ_1N,μ_1N	80.7(2,1.1)
				(x9)				98.8(2,2.4)[i]
HEXANUCLEAR								
$[(\eta^6\text{-}C_6H_6)Sn$	tr	1185.2(1)	85.94(1)	$AlCl_4$	μCl	216.0(2,18)	$\mu Cl,\mu Cl$	103.6(1,2.5)	154
$(AlCl^4)_2]_2.3C_6H_5$	Pß	1183.9(1)	115.59(1)		Cl	210.9(1,34)	$\mu Cl,Cl$	110.1(1,2.5)
	1	1203.1(1)	98.30(1)				Cl,Cl	112.4(1,9)
(colourless)				SnC_5Cl_4	μCl	302.6(1,106)	$\mu Cl,\mu Cl$	69.9(1,1.6)
					C	282.6(3,76)		131.5(1,2.9)
						245[i]		
$[Mo(C_5H_4)_2Al_2Me_3]_2$	tr	902.9(5)	64.86(2)	AlC_3Mo_2	Mo	267.1(3,15)	Mo,Mo	116.9(1)	151
	Pß	912.5(5)	70.34(2)	(x2)	μC	227(1,8)	μC,Mo	
	1	974.8(5)	86.88(2)		C_{Me}	198(1)	54.6(3,1;127.1(3,4.4)	
						279.6(5,1)[e]	C,Mo	117.5(5,5)
							$\mu C,\mu C$	88.3(4)
				AlC_4	μC	210(1,2)	μC,C	108.8(6,4.4)
				(x2)	C_{Me}	197(2,2)		79.3(4,1.4)[c]
							$\mu C,\mu C$	97.8(4)
				MoC_5Al_2	Al	267.1(3,15)	μC,C	110.5(6,5.8)
					μC	230(1,2)	C,C	115.4(8)
					C	228(1,3)	Al,Al	63.1(1)
$[cpFe(C_5H_3)Al_2Me_3Cl$	tr	844(1)	78.61(1)	AlC_3Cl	μC	212(3)		77(1)[c]	155
$]_2$	Pß	907(1)	68.92(6)	(x2)	μCl	231(1)		92(2)[c]
	1	1138(1)	62.44(6)		C_{Me}	not given		
				AlC_3Cl	μC	201(3)	not given	
				(x2)	μCl	248(1)		
					C_{Me}	not given		
						315(1)[i]		
				FeC_{10}	μC	204(2,10)	not given	
					C	204(2,10)		
$[(c_6H_6PdAl_2Cl_7]_2$	tr	942(3)	77.9(5)	$AlCl_4$	μCl	220(2,5)	$\mu Cl,\mu Cl$	96.5(5)	105
	Pß	924(3)	96.2(5)	(x2)	Cl	207(2,0)	$\mu Cl,Cl$	111.1(5,1.8)
(deep brown)	1	956(3)	108.1(3)				Cl,Cl	114.6(5)
								113.8(5)[g]
				$AlCl_4$	μCl	228(2)	$\mu Cl,Cl$	103.3(5,3.5)
				(x2)	Cl	210(2,2)	Cl,Cl	114.7(5,1.4)
								115.6(6)[c]
				PdC_2Cl	Pd	257(1)	Pb,μCl	175.9(5)
				(x2)	μCl	245(1)		
					C	277 - 351		

$\{Pr[Al(OPr^i)_4]_2(Pr^iOH)(\mu\text{-}Cl)\}_2$	m C2/c 4	2518.1(6) 1693.7(3) 1937.6(3)	91.60(2)	AlO_4	μO O	172.4 "	not given	156a
				PrO_5Cl_2	μCl μO O	284.9(2) 239.7 "	μCl,μCl 72.3(1) μCl,μO 83.8(2) μO,μO 62.7(2) 91.5; 110.1(2) μO,O 75.0(2,2.1)	
$\{[Al(tbome)]_4[Na(H_2O)]_2\}.(ClO_4)_2$ 6.2(H_2O)	or Pbcn 4	2722.6(2) 1568.7(4) 3001.3(3)		AlO_3N_3	μO O N	184.0(5,2) 182.0(4) 208.3(5,8)	μO,O 93.4(2,1.3) N,N 85.6(2,3) μO,N 90.9(2.2.6);174.6(2,5) O,N 89.5(2,2.4);172.3(2)	156b
				AlO_3N_3	μO O N	185.0(5) 182.7(5,0) 209.3(6,25)	μO,O 92.9(2,0) O,O 96.4(2) N,N 84.8(2,1.1) μO,N 90.7(2,8);174.4(2) O,N 91.5(2,4.9);172.3(2,2.3) μO,μO 64.9(1) 106.6; 157.9(2) μO,O 96.4(2,18.0);167.0(2) O,O 80.4(2)	
				NaO_5	μO μH_2O	233.5(5,1) 258.5(5) 236.8(5,21)		
$[V_2(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(\eta^2\text{-}AlCl_4)_3(\eta^6\text{-}C_6H_5)](AlCl_4)$	m $P2_1/n$	1256.6(3) 2322.4(7) 2714.1(7)	102.47(3)	$AlCl_4$	μCl Cl	not given "	not given	157
				VC_5Cl_6	μ_3Cl μCl η^6C	286(2,3) 303(2,4) 277(2,3) 294(2,7) 292 422.8(3,42)[f]	V,V 60.0(-,1.0) μ_3Cl,μ_3Cl 68.2(-,6) μ_3Cl,μCl 72.6 - 84.3 C,μCl 100.1 - 106.5	
$[\{(Me_3Si)_2MgMe_2\}_2\{Mg(N(SiMe_3)_2)(N(SiMe_3)_2AlMe_3)_2\}$ (colourless)	tr Pß 1	1228.8(5) 1269.8(6) 1428.5(7)	101.79(4) 90.07(3) 111.57(3)	AlC_3N	μN μC C_{Me}	200(1) 205(2) 196(2,0) 283.8(6)[I]	μN,μC 102.2(5) μN,C 114.9(9,1.8) μC,C 107.1(9,1.7) C,C 109.9(8) C 79.0[g]; N 85.6(4)[g]	127
				MgN_2C_2 (x2)	μN N μC	216.9(9) 198(1) 242(2,2)	μN,N 132.8(4) μN,μC 87.2; 117.1(4) N,μC 109.2(5,5.8) μC,μC 93.0(5)	
				MgN_3C (x2)	μN μC	208(1,0) 216(1) 285.6(8)[I]	μN,μN 93.3(4) μN,μC 133.3(5,3.6) 86.7(4)[h]	
$[\{Sn(B_4{}^tN)\}_4(AlCl_3)_2]$ (colourless)	m $P2_1/c$ 4	1032.5(5) 2311.2(9) 1981.4(8)	124.3(1)	$AlCl_3Sn$	Sn Cl	278(1) 212.4(8)	Cl,Cl 113.9	158
				SnN_3Al	μ_3N	219(2) 323.6(2)[I]	μ_3N,μ_3N 84	

[$cp_2Ti(\mu\text{-}H)_2Al(\mu\text{-}H)(\eta^1{:}\eta^5\text{-}C_5H_4)Ticp(\mu\text{-}H)]_2.tl$ (black)	m $P2_1/c$ 4	1175.3(5) 1570.1(7) 2395(1)	99.24(4)	AlH_3C	μH μC	170(8,14) 195(1) 322.2(2)[e] 278.2(2,1)[i]	μH,μH	72 - 124(4) 161(3,1)	159 160
				$TiC_{10}H_2$ (x2)	μH μC C	322.4(2,7)[i] 184(7,11) 233(1,1) 236(1,4)	μH,μC	94 - 130(2) 138(4)[c]	
				$TiC_{10}H_2$ (x2)	μH C	371.7[f] 178(7,5) 233(1,4)	μH,μH	86(3,2) 171(3)[h] 140(6,4)[g] 74(3,2) 105(3,3)[g]	
$cp_2Ti(\mu\text{-}H)_2Al(\mu\text{-}H)(\eta^1{:}\eta^5\text{-}C_5H_4)Ticp(\mu\text{-}H)]_2.C_6H_6$ (black)	m $P2_1/n$ 4	1135.4(2) 2336.0(3) 1606.2(3)	94.07(3)	AlH_3C	μH μC	175(9,16) 194(1,1) 279(1,1)[e]	μH,μH	69 - 121(4) 152(4,2)	88 160
				$TiC_{10}H_2$	μH C	179(9) 233	μH,μH	67, 84(4) 173(4)[h]	
HEPTANUCLEAR									
$\{[H(HAlNPr^i)_5AlH_2]LiH(Et_2O)\}$ (colourless)	or $Pna2_1$ 4	1976(2) 1038(1) 1660(2)		AlN_3H (x3)	μ_3N H	192.2(7,36) 155(9,10)	μ_3N,μ_3N	89.9(1,3.7) 109.1(1,7.6) 85.4(1,3)[c];109.6(1,3.9)[c]	161
				AlH_2N_2 (x3)	μH μ_3N	154(9,7) 191.5(7,15)	μ_2N,μ_3N	87.6(1,6) 105.9(1) 88.2(1,1)[c];112.0(1,10.5)[c]	
				LiH_3O	μH O	192(9,7) 192.2(17)	μH,μH μH,O	104.3(27,15.3) 119.3(22,4.2) 135.8(14,1.3)[g];151.0(14)[g]	
$\{(\mu\text{-}I)_3Ti_3(1,3,5\text{-}[\mu\text{-}I(I_2)Al]_3C_6H_3\text{-}\mu_3,\eta^6;\eta^6\text{-}Ti(\eta^6\text{-}C_5H_5)\}.\_C_6H_6$	m $P2_1/n$ 4	1138.3(4) 1972.9(4) 1807.7(4)	95.68(2)	AlI_3C	μ_3C μI I	202(2,4) 262.2(8,10) 249.4(8,15)	$\mu_3C,\mu I$ μI,I I,I I,μ_3C	100.6(-,6) 108.3(-,2.0) 118.1(-,1.5) 110.1(-,1.0)	162
				TiC_3I_3 (x3)	μ_3C μC μI	214(2,1) 240(2,4) 277.7(4,20) 285.5(4,15) 276.6(6,16)[f]	Ti,Ti $\mu_3C,\mu I$ μI,μI	60.0(-,5) 90.7(-,1.0) 119.2(-,2.0) 95.6(-,2.0) 120.1(-,1.5) 60.0(5)[h], 70.0(5)[g]	
				TiC_{12}	μC C	204 - 229(2) 247(3,2)			

{[HAl{N(CH$_2$)$_3$NMe$_2$}]$_6$ 2LiH}	tr Pß 1	1016.2(5) 1298.9(4) 1203.0(5)	101.58(4) 118.46(3) 109.18(3)	AlH_2N_2 (x2)	μH μ_3N	153(9,1) 189.5(7,4)	H,H N,N H,N N,N N,H N, μ_3N,N N,N N,μH H, 122(3)[g]; N,105.2(4,9.3)[g]	110(2) 108.0(2) 110(3,6) 122(3)[g] 91.3(2,5) 110.8(2,5.3) 114(3,9) 88.7(1,5)[c];115.2(1,5.2)[c] 113.6(4,10.5) 114.6(4) 98(3)	163
				AlN_3H (x4)	μH μ_3N	148(8,1) 184.8(7,3) 193.1(7,16)			
				LiN_3H	μH μ_3N N	192(8) 209(2) 216(2,4)			
{$Me_2Al(\mu$-$NPr^i_2)_2$ MgMe}$_4$ (colourless)	m C2/c 8	2692.2(3) 1077.5(3) 2728.1(3)	94.02(1)	AlN_2C_2	μN C_{Me}	195.9(6,2) 197.6(8,8) 283.2(3)[i]	μN,μN C,C μN,C	95.2(3) 111.2(3) 112.4(3,3.6) 87.4(2,4)[g]	128
				MgN_2C_2	μN μC	214.6(6,4) 215.1(6) 249.3(6)	μN,μN μN,μC	84.7(2) 130.0(3,3.5) 167.9(3)[h]	
[(η^6-C_6H_6)SnCl($AlCl_4$)]$_4$.1_PhCl (colourless) at 238K	tr Pß i	1248.1(2) 1474.9(2) 1289.9(2)	100.77(1) 93.62(1) 100.98(1)	$AlCl_4$ (x2) $AlCl_4$ (x2) SnC_5Cl_5 (x2) SnC_6Cl_6 (x2)	μ_3Cl μCl μCl Cl μ_3Cl μCl μ_3Cl μCl	216.6(3) 212.8(2,8) 217.0(2,22) 210.9(2,5) 312.5(1) 261.5(1,29) 349.5(2,130) 338.0(1) 274.0(1,68) 389.3(3)[f] 336.8(1,129) 703.5(3)[f]	not given	73.4(1)[h] 94.2(1,9)[h]	164
{[(cp*)($C_5H_4CH_2$)Ti(μ-H)$_2$Al]$_2$(μ_3-O)$_2$ .2C_6H_6 (dark green)	or Pnma 8	2464.7(8) 2657.5(9) 1351.9(4)		AlH_2O_2C	μH μ_3O C	177(7,7) 175.2(6) 185.0(7,7) 203(2,2) 280.9[e]	μH,μH μ_3O,μ_3O μH,μ_3O μH,C μ_3O,C	66(3,6) 81.1(-,4) 96 - 146 100(2,6) 119(1,6) 98.8(3)[c]; 130.6(4,1.7)[c]	165
				$TiC_{10}H_2$	μH C	167(6,5) 184(5) 236(4)	μH,μH	70(3,7) 275.8(2,96)	

$[[(Bu^t_2C_5H_3)LuH]_4$ $[AlH_4(Et_2O)]_2.[AlH_4]$ (colourless)	tr Pß 2	1161.6(2) 1482.2(2) 2423.6(5)	87.51(1) 100.59(2) 75.83(1)	AlH_4O (x2)	μ_3H 165(-,5) μH 200(-,30) O 195(2,3) 292.5(8,10)[i]	$\mu_3H,\mu H$ 74(-,7), 110 $\mu H,\mu H$ 101 μ_3H,O 138, 177 $\mu H,O$ 102(-,10) $\mu_3H,\mu H$ 45(-,1), 62, 133 $\mu H,\mu H$ 111(-,5) μ_3H,H 128 $\mu H,H$ 96, 120 H,H 40 - 87 108 H,cp 112(-,6)[d] 134 - 168[d] Al,Lu 57.0(2,2.1) 98.0(2,5)	166
				AlH_4 (x2)	μ_3H 235(-,5) μH 185(-,35) H 140 324.0(8,15)[i]		
				$LuH_{5/6}C_5$ (x2)	μ_3H 200(-,40) μH 170(-,40) C 258(4) 228.5(-,24)[d] 335.2(1,6)[f] 523 - 549[j]		
$\{(Bu^t_2C_5H_3)LuH\}_4$ $[AlH_4(Et_2O)]_4[AlH_4]$ $.Et_2O$ (colourless)	tr Pß 2	1168.0(4) 1473.4(4) 2424.7(5)	92.25(2) 99.91(2) 105.40(3)	AlH_4O	μ_3H μH not given O 192(2,8) 293.8(9,45)[i]	O,Lu 122.9(7,5.0) Lu,Lu 65.9(2,4.3) 102.6(2,3.2) Al,Lu 57.0(2,2.4) 100.6(2,6) Al,Al 75.0(2,1.8) 98.2(2,6)	167
				AlH_4 $LuH_{5/6}C_5$	322.2(11,53)[i] C 258(3,18) 334.1(2,2)[f] 520.6(2,106)[f]		
$[Bu^t_2C_5H_3)_5Sm_2H_3$ $(AlH_4)_4(tmeda)_2]$ (yellow-green)	m $P2_1/a$ 4	2980.1(6) 1664.9(3) 2146.9(4)	 96.12(2)	AlH_4	μH 170(10,20) 230(20) 256(1)[e] 309(1,3)[I]	H,H 75.2(-,4.7) 105.2(-,9.2) 140.6(-,1)	168
				AlH_2N_2	μ_3H 160(10,12) 210(10) N 212(3,6) 305(1,9)[I]	H,H 70.1, 93.1 N,N 86.3(12,8) H,N 98.4(-,4.9) 169.3(-,4)	
				SmH_3C_5	μ_3H 220(10,0) μH 200(-,10) C 249(-,40)	H,H 67.6 - 140.6 cp,H 83.3 - 122.1[d]	
				SmH_3C_{10}	μH 200(-,30) C 249(-,1)	H,H 103.4 cp,cp 115.6[d]	

NONANUCLEAR								
$\{(cp^*Zr)_3Al_6Me_3(CH_2)_2\}$ 2tl at 153K	m $P2_1/n$ 4	1275.6(10) 3343(4) 1553(2)	96.90(10)	AlC_4 (x4)	μ_4C 209.7(7,94) μ_3C 208.9(7,65) C not given 268.3(3,5)[e] 333.3(2,4)[I]		133.6(3)[c] 81.8(3,1.8)[g]	138
				AlC_4 (x2)	μ_4C 212.8(6) μ_3C not given C not given 286.8(2,18)[I]			
				ZrC_8	μ_4C 225.4(6,57) μ_3C 216.7(6,24) C_{cp} not given	C,C Al,Al	89.8(2) 70.34(10)	
DODECANUCLEAR								
$[Eu(\eta^6\text{-}C_6Me_5)(AlCl_4)_2]_4$	m $P2_1/c$ 2	1765.2(4) 1591.8(4) 1875.2(4)	97.61(5)	$AlCl_4$ (x4) $AlCl_4$ (x4) EuC_6Cl_4	μCl not given μCl not given Cl " μCl not given C 299.9(18,82)	not given not given		169
OCTADECANUCLEAR								
$[Al_3Nd_3(\mu\text{-}Cl)_6(\mu_1\text{-}Cl)_6(\mu\text{-}Et)_9(Et_5)(OPr^i)]_2$	tr Pß 1	1519.6(6) 1526.3(5) 1374.9(4)	90.01(2) 95.12(3) 82.65(3)	AlC_3 (x6)	μC 202.2(-,26) C "		71.5(-,2)[g]	170
				$NdCl_4C_3$ (x10)	$\mu_3/\mu Cl$ 283.5(-,17) μC 202.8(-,10) 272.4(-,18)	Cl,Cl C,C Cl,C	82.6(-,2.2) 72.9(-,7) 92.9(-,1)	
				$NdCl_4C_2O$ (x2)	$\mu_3/\mu Cl$ 282.7(-,4) μC 201.6(-,20) 282.0(-,7) O 289.3(-,7)	Cl,Cl C,C Cl,C	80.1 71.8(-,1.6) 92.3(-,5) 95.0[h]	

Footnotes: *a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.*

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Al-X-Al angle.

d. Centroids of the carbon ring.

e. Al-Al distance. *f. M-M distance.*

g. Al-X-M angle. *h. M-X-M angle.*

i. Al-M distance.

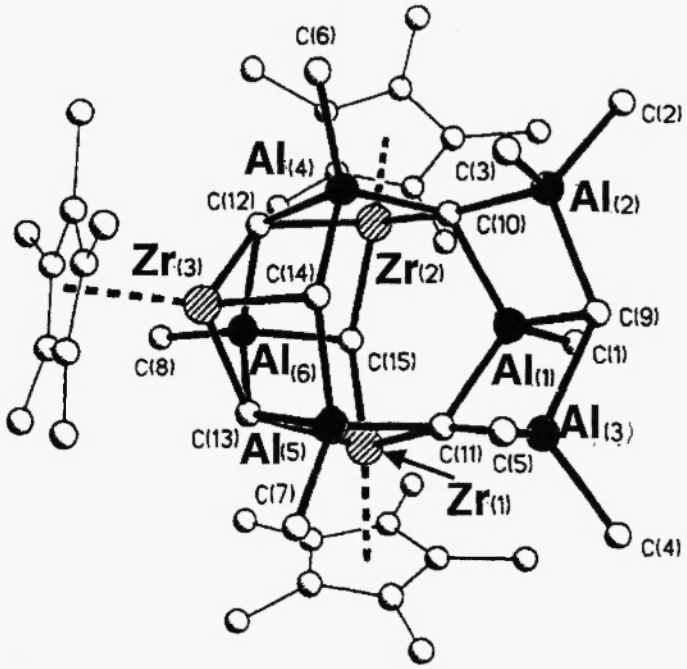

Fig.14. Structure of $(cp^*Zr)_3Al_6Me_8(CH_2)_2$ [138]
(H-atoms not shown)

In the almost thirty heterooligonuclear clusters, aluminium is found mostly in a distorted tetrahedral environment, but there are some trigonal bipyramidal examples. The mean Al-L bond distances in the four coordinate situations increase in the order: 148 pm (H) < 165 pm (LO) < 198 pm (LN) < 198.5 (LC) < 210.5 pm (Cl) < 249 pm (I). The mean Al-L(bridge) distances are: 166 pm (H) < 175 pm (LO) < 204 pm (LN) < 206 pm (LC) < 224 pm (Cl) < 262 pm (I). Both sets of distances increase with the covalent radius of the donor atom, and the terminal bond distances are shorter than the bridging ones. These clusters can be found with main group metal, transition metals and lanthanide metals. While the former prefer lower coordination numbers, mostly four and five, transition metals are often found as sandwich or "open" sandwich moieties, often with other ligands serving as bridges between the metal atoms. The metal-metal distances found in these clusters are summarised in Table 4A. The shortest Al-M, Al-Al and M-M distances are: 265.0(4) pm (M = Mo) [151]; 256(1) pm [168]; 255.7(6) pm [152].

6. HETEROPOLYNUCLEAR COMPOUNDS

Crystallographic and structural data for almost eighty derivatives of this class are summarised in Table 5. Aluminium(III) atoms are found in either a distorted tetrahedral or a pseudo-octahedral stereochemistry. In two colourless $MAlH_4$ derivatives (M = Li [171] or Na [172]) each aluminium atom is surrounded by four hydrogen atoms at the vertices of an almost regular tetrahedron.

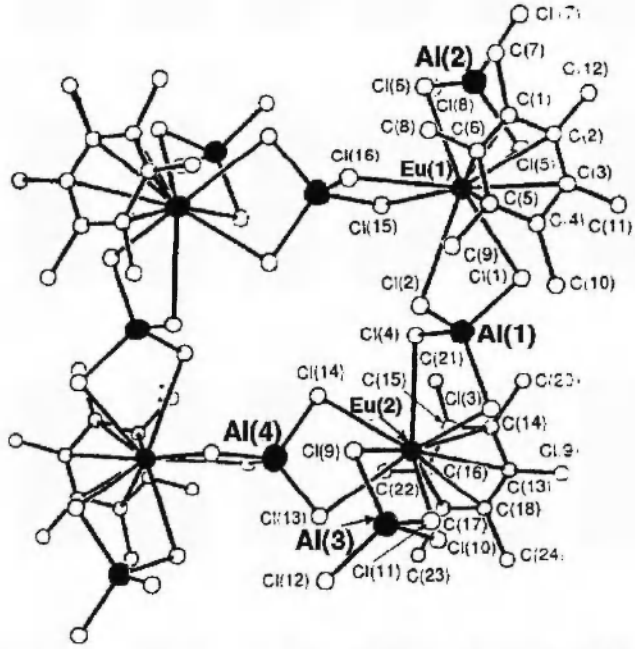

Fig.15. Structure of $[Eu(C_6Me_6)(AlCl_4)_2]_4$ [169]

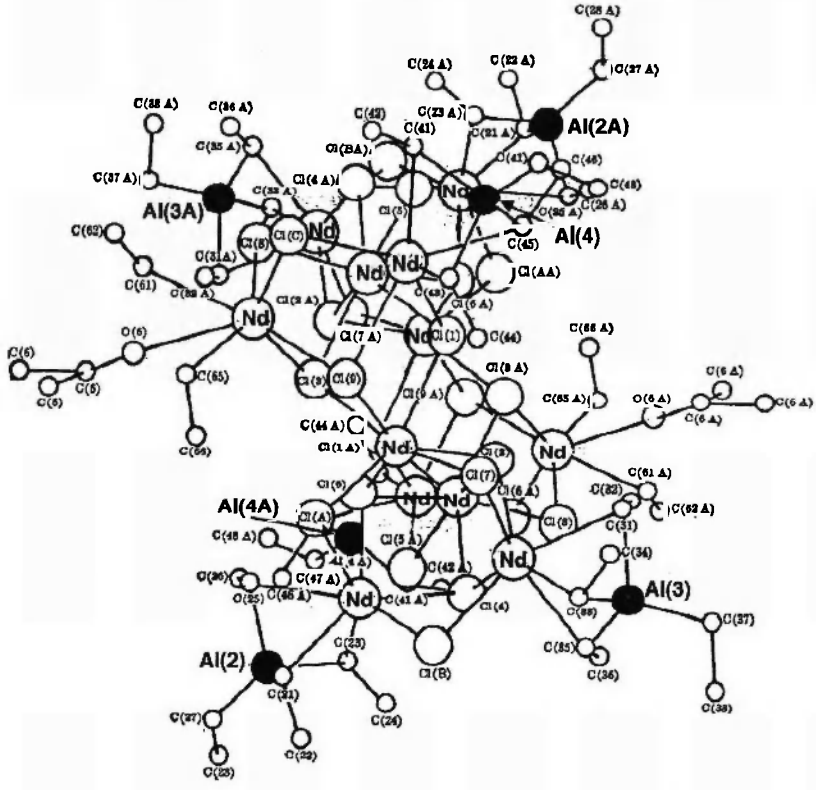

Fig.16. Structure of $[Al_3Nd_6Cl_2(Et)_{14}(Pr^iO)]_2$ [170]

TABLE 5. Crystallographic and Structural Data for Heteropolynuclear Aluminium Compounds[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromo-phore	M-L [pm]		L-M-L [°]	Ref
$LiAlH_4$	m	484.5(4)		AlH_4	μH[b]	154.7(26,31)	μH,μH[b] 109.5(1.4,4.7)	171
	$P2_1/c$	782.6(4)	112.5(2)	LiH_5	μH	194.3(27,60)	not given	
(colourless)	4	791.7(4)			H	215.8(28)		
$NaAlH_4$	tg	502.0(2)		AlH_4	μH	153.2(7)	μH,μH 109.5(5,4.4)	172
	$I4_1/a$	-						
	4	1133.0(3)		NaH_8	μH	249.0(7) x4	not given	
						250.4(7) x4		
$[(Pr^iOH)_2K(\mu\text{-}OPr^i)_2$	or	1193.5(4)		AlO_4	μO	174.3(6,33)	μO,μO 109.5(3,7.9)	173
$Al(\mu\text{-}OPr^i)_2]_n$	$P2_12_12_1$	1651.3(6)						
	4	1368.1(4)		KO_6	μO	270.6(6,11)	93.6(2,9)[c];109.0(3,4)[c]	
(colourless)						309.1(6,45)	μO,μO 55.0(2,3)	
					O	269.7(8,29)	116.5(2,1.6);140.4(2)	
							163.2(2)	
							μO,O 54.8(2,1.2)	
							98.0(2,15.4)	
							141.5; 160.5(2)	
							O,O 111.9(3)	
$KAl_4O(OH)_6$	or	1023		AlO_4	μO	176(-,6)	not given	174
(colourless)	Aba2	758					132[d]	
	4	1004		KO_5	μO	285(-,10)	not given	
$Al_5Mg_2(P_8O_{32})(Pr_2N)_2$	m	1021.92(2)		AlN_4	μO	177.0(3,5)	μO,μO 109.5(1,1.5)	175
(colourless)	I112/b	1021.98(3)						
	1	1001.26(3)	90.987(2)	MgO_4		not given		
$LiAl(NH_2)_4$	m	947.8(1)		AlN_4	μN	185.1(3,13)	μN,μN 109.5(1,9.4)	176
(colourless)	$P2_1/n$	735.1(1)	90.26(1)					
	4	739.8(1)		LiN_4	μN	212.1(7,65)	μN,μN	
							83.8(3);114.0(3,6.4)	
$NaAl(NH_2)_4$	m	732.8(2)		AlN_4	μN	184.8(2,6)	μN,μN 109.5(1,10.1)	177
(colourless)	$P2_1/c$	604.7(2)	94.04(1)					
	4	1315.1(3)		NaN_4	μN	246.1(2,18)	μN,μN 109.5(1,6.9)	
$NaAl(NH_2)_4$	m	732.4(6)		AlN_4	μN	184.5(20,35)	μN,μN 109(2,6)	178
	$P2_1/c$	605.0(5)	94.00(15)					
	4	1318(1)		NaN_4	μN	247(-,2)		
α-$KAl(NH_2)_4$	or	1000(1)		AlN_4	μN	184.5(20,45)	μN,μN 109(2,9)	178
(colourless)	$C222_1$	580(1)						
	4	1014(1)		KN_8	μN	314		

$CsAl(NH_2)_4$ (colourless)	tg P4/m 2	757.9(7) - 537.5(5)		AlN_1	μN	183.7(7)	μN,μN	109(2,8)	178
				CsN_{12}	μN	362			
$LiAlEt_4$ (colourless)	tg $P4_2/nm$ c 2	999(1) - 541.1(5)		AlC_1	μC	202.3(6) 270.6[e]	μC,μC	109.5(6,2.6) 77.2(3)[c]	179
				LiC_1	μC	230.2	μC,μC	93.6(3)	
$LiAlCl_4$ at 293K (colourless)	m $P2_1/c$ 2	700.4(8) 650.3(6) 1299.6(9)	93.3(1)	$AlCl_4$ $LiCl_6$	Cl	213.5(2,16) 252.1(7,73) 278.0(7,61)	not given		180
at 326K		701.1(7) 652.6(6) 1303.0(9)	93.3(1)	$AlCl_4$ $LiCl_6$	Cl	213.5(2,17) 253.4(5,50) 277.8(5,78)	not given		
at 364K		702.3(7) 655.4(6) 1307.5(9)	93.3(1)	$AlCl_4$ LiC_6	μCl	213.4(1,16) 253.3(6,80) 280.1(6,66)	not given		
$NaAlCl_4$ at 293K (colourless)	or $P2_12_12_1$?	1031.4(8) 988.7(8) 616.5(6)		$AlCl_4$ $NaCl_6$	μCl	213.3(2,6) 286.7(3,88) 308.5(3,76)	not given		180
at 363K		1038.2(9) 993.3(8) 618.3(6)		$AlCl_4$ $NaCl_6$	μCl	213.2(2,8) 287.7(3,94) 310.6(3,89)	not given		
at393K		1040.8(9) 996.4(8) 619.6(6)		$AlCl_4$ $NaCl_6$	μCl	212.9(2,9) 288.0(4,97) 311.9(4,95)	not given		
$NaAlCl_4.1\_SO_2$ (colourless)	m $P2_1/n$ 4	3159.8(33) 1004.6(11) 637.0(8)	93.39(9)	$AlCl_4$	μCl	212.8(3,18)	μCl,μCl	109.5(1,1.9)	181
at 248K				$AlCl_4$	μCl	212.2(4,5)	μCl,μCl	109.5(1,2.1)	
				$NaCl_4O_2$	μCl	286.1(5,55) 308.7(4)	μCl,μCl	83.2(1,4.6) 111.0; 154.2(1)	
					O	235.5(9,38)	μCl,O	86.1(2,5.4) 111.0; 165.8(2,8)	
							O,O	90.1(3)	
				NaO_3Cl_3	O μCl	239.1(7,19) 292.8(4,55)	O,O μCl,μCl O,μCl	92.6(3,23.5) 80.6(1,6.4) 86.2(2,4.9) 113.7(2,6.4) 156.8(2,5.3)	
$GaAlCl_4$	m $P2_1/n$ 4	716.4(1) 1017.9(2) 926.7(1)	93.21(1)	$AlCl_4$ $GaCl_6$	μCl μCl	212.9(-,9) 320.6(-,105)	μCl,μCl not given	109.5(-,2.8)	182
$Cd(AlCl_4)_2$ (colourless)	m P1a1 2	1288.7(2) 660.2(1) 705.1(1)	92.89(1)	$AlCl_4$ Cl $AlCl_4$ Cl $CdCl_5$	μCl μCl μCl	217.0(-,21) 206.3 216.4(-,10) 205.6 264.2(-,40)	Cl,Cl Cl,Cl Cl,Cl	109.5(-,4.6) 109.5(-,5.1) 90.0(-,12.4) 167.9(-,3.9)	183

$Cd_2(AlCl_4)_2$ (colourless)	tr Cß 2	655.47(3) 1135.26(1) 935.23(6)	89.70(2) 103.61(1) 90.455(1)	$AlCl_4$ $CdCl_3Cd$	µCl Cl µCl Cl Cd	216.1(-,1) 211.5(-,32) 271.1(-,19) 270.0 256.2	Cl,Cl Cl,Cl	109.5(-,2.4) 86.3 - 131.9(8)	183
$Cd_2(AlCl_4)_2$ (colourless)	tr Cß 2	654.3(1) 1134.3(3) 935.4(2)	89.47(2) 103.71(2) 90.46(2)	$AlCl_4$ $CdCl_3Cd$	µCl Cl µCl Cl Cd	215.0(4,3) 210.5(4) 270.2(3,12) 269.5(3) 257.6(1)	Cl,Cl not given	109.5(1,1.7)	184
$Ti(AlCl_4)_2$ (green)	m I2/c 4	1298.7(3) 770.8(2) 1177.2(3)	 92.58(1) 	$AlCl_4$ $TiCl_5$	µCl Cl µCl	216.3(1,3) 208.0(1) 256.6(1,4)	Cl,Cl Cl,Cl	109.5(1,9.7) 88.7(4,1)[c]; 124.1[c] 90.0(1,2.9) 170.9(1,5)	185
$Co(AlCl_4)_2$ (bright blue)	m I2/c 4	1281(2) 775(1) 1150(2)	 92.2(1) 	$AlCl_4$ $CoCl_6$	µCl Cl µCl	217.4(16,23) 210.5(19) 246.7(13,14)	not given		186
$CuAlCl_4$ (colourless)	tg P42c 2	543.0(1) - 1009.6(1)	 	$AlCl_4$ $CuCl_4$	µCl µCl	213.6(3) 235.9(3)	Cl,Cl Cl,Cl	108.9(2,1.7) 111.0(2) 110.3(2,2.4)	187
$Cu(AlCl_4)_2$ (red)	m $P2_1/c$ 2	661.4(8) 737.6(4) 1231.9(1)	 94.11(9) 	$AlCl_4$ $CuCl_6$	µCl Cl µCl	217(-,6) 206 230(-,1) 296	Cl,Cl Cl,Cl	93.2 112.3(-,3.1) 89.0(2)[c]; 126.8[c] 90.0(-,3.4) 180.0	188
$C_6H_5CuAlCl_4$ (colourless)	m $P2_1/n$ 4	859(1) 2159(3) 607(1)	 93.00(15) 	$AlCl_4$ $CuCl_3C_2$	µCl Cl µCl C [f]	214.3(7,7) 207.8(8) 238.2(6,17) 255.5(6) 223(3,8) 213(3)	Cl,Cl C,C Cl,Cl C,C	109.5(3,2.9) 113.5(2,4)[c]; 125.8(2)[c] 95.8(2,5.9) 33(1)	189
$C_6H_6AgAlCl_4$	m $P2_1/n$ 4	909(3) 1022(3) 1273(3)	 95.05(15) 	$AlCl_4$ $AgCl_4C_2$	µCl µCl C [e]	213.5(20,15) 280(2,24) 270(7,23) 257(6)	Cl,Cl Cl,Cl C,C	109(2,3) 90.8(6,3.1)[c];129.1(6)[c] 70.3 - 144.0(6) 30.0(4)	190
$C_6H_5SnAlCl_4.C_6H_6$ (colourless)	m $P2_1/n$ 4	1128.2(3) 1731.7(8) 1264.6(6)	 110.08(1) 	$AlCl_4$ $AlCl_4$ $SnCl_6C_6$	µCl µCl Cl µCl C	212.6(4,15) 218.2(3,17) 207.5(3,7) 300.0(2,280) 306(1,3)	Cl,Cl Cl,Cl Cl,Cl	109.5(1,3.4) 93.4(1,1.5)[c] 109.5(2,5.2) 74.6(1,6.7)	191

$(C_6H_5)ClSnAlCl_4$ (colourless)	m $P2_1/n$ 4	1962.4(6) 953.1(1) 709.9(1)	93.65(1)	$AlCl_4$ $SnCl_5C_5$	μCl Cl μCl C	214.6(6,42) 207.7(6) 292.1(4,403) 320(2,19)	Cl,Cl Cl,Cl	109.4(3,6.5) 78.7(1,10.3) 99.7(1)[g]	192
(p-$Me_3C_5H_4$)$ClSnAlCl_4$ (colourless)	m I2/c 8	1897.0(7) 1090.3(4) 1547.0(4)	107.33(1)	$AlCl_4$ $SnCl_5C_6$	μCl Cl μCl C	215.0(5,30) 209.1(5) 292.9(3,313) 311(1,19)	Cl,Cl Cl,Cl	109.4(2,6.0) 78.8(1,11.9) 149.0(1,4.3)	192
(mes)$ClSnAlCl_4$ (colourless)	m $P2_1/n$ 4	929.3(1) 1265.4(1) 1377.0(1)	95.76(1)	$AlCl_4$ $SnCl_5C_5$	μCl Cl μCl C	214.5(1,28) 210.6(1) 293.8(1,292) 271[h]	Cl,Cl Cl,Cl	109.5(1,9) 78.2(1,10.6) 112.1(1,8.6) 147.0(1,1.0) 100.7(1)[g]	193
(mes)$ClSnAlCl_4$ (colourless)	m $P2_1/n$ 4	929.7(4) 1277.5(6) 1397.5(4)	95.57(3)	$AlCl_4$ $SnCl_5C_6$	μCl Cl μCl C	213.2(3,31) 209.0(3) 294.5(2,301) 305.8(6,162) 273.1(6)[h]	Cl,Cl Cl,Cl	109.5(1,3.6) 78.1(1,11.3) 120.84(6) 146.7(1,1.1)	194
α-(tl)$ClSnAlCl_4$ (colourless)	tr Pß 2	720.13(7) 866.25(7) 1132.9(1)	96.51(1) 93.23(1) 100.218(7)	$AlCl_4$ $SnCl_5C_5$	μCl Cl μCl C	215.1(1,42) 210.06(9) 293.9(1,380) 316.6(2,192) 285.1(2)[h]	Cl,Cl Cl,Cl	109.5(1,6.2) 77.5(1,9.8) 121.96(2) 145.0(1,1.4)	194
β-(tl)$ClSnAlCl_4$ (colourless)	tr Pß 2	711.0(9) 942(1) 1156(1)	113.3(1) 99.5(1) 91.9(1)	$AlCl_4$ $SnCl_5C_6$	μCl Cl μCl C	214.3(2,35) 209.5(2) 293.4(1,480) 315.4(4,172) 283.7(4)[h]	Cl,Cl Cl,Cl	109.5(1,6.4) 76.7(1,8.2) 112.9(3) 146.8(1,1.8)	194
$(C_6H_5)Pb(AlCl_4)_2.C_5H_6$ (colourless)	m $P2_1/n$ 4	1136.5(1) 1730.7(2) 1270.7(2)	110.14(1)	$AlCl_4$ $AlCl_4$ $PbCl_5C_6$	μCl μCl Cl μCl C	212(1,3) 219.5(10,15) 206.5(10,15) 304.0(8,186) 310(4,3) 277(4)[h]	Cl,Cl Cl,Cl Cl,Cl	109.5(5,4.9) 92.6(4,1.8)[c] 109.5(5,8.5) 74.4(2,10.2)	195
$Dy(AlCl_4)_3$	trg $P3_112$ 3	1049.2(1) - 1563.6(2)		$AlCl_4$ $AlCl_4$ $DyCl_3$	μCl μCl Cl μCl	213.2(4,1) 219.0(4,14) 205.9(5,4) 278.7(3,96)	Cl,Cl Cl,Cl Cl,Cl	109.5(1,5.4) 95.4(1) 111.9(1,5.3) 73.7(1,4.1) 115.3(1,11.5)	196

$Ti(AlBr_4)_2$	or	627.4(1)	$AlBr_4$	μBr	232(2,9)	Br,Br	109.4(8,8.3)	197
(emerald green)	Pnn2	1280.1(4)		Br	225.5(10)		86.5(5,3.7)[c]	
	2	867.6(3)	$TiBr_3$	μBr	270.9(4,96)			
						124.7(3)[c]		
						Br,Br	90.0(2,6.8)	
							177.0(5)	
$[cp_2Y(Li_2AlH_5(Et_2O)$	or	1352.1(5)	AlH_3O	μH	150(10,10)	H,H	117(8,1)	198
(colourless)	Pcab	1287.7(5)		H	150(10)	H,O	99(6,4)	
	8	3073(1)		Et_2O	189.0(9)		154(9,2)[c]	
			$YC_{10}Cl_2H$	μH	235(10,5)	H,Cl	68(-,4)	
				μCl	274.4(5,58)	Cl,Cl	74.8(1,4)	
				C_{cp}	264(2,5)	H,cp	96(-,4)	
					236.4(-,2)	Cl,cp	108.1(-,10.5)	
							104.6(2,7)[g]	
$LiAlH(NEt_2)_3$	or	980.0(3)	AlN_3H	μN	186.6(2,12)	N,N	101.5(1);	199
(colourless)	Pbca	3302.2(9)		μH	151.8(20)	121.0(1,1)		
	8	1041.1(3)			267.6(4,33)[e]	N,H	103.8(7,3.0)	
at 193K						Li,Li	132.6(1)	
						N	80.9(1,5)[c]	
			LiN_3H	μN	223.5(4,64)	H	102.0(10)[c]	
				μH	195.1(20)	N,N	81.7(1)	
							132.9(2,3.5)	
						N,H	76.2; 119.0(6,4)	
$[(Cs_2(18\text{-crown-6}))_3$	m	1355.2(2)	AlC_3O	μO	185(1,4)	not given		200
$(Al_3Me_9SO_4)_n]_n$	$P2_1/n$	1673.1(4)		C_{Me}	200.1(3)			
	4	1702.9(4)	CsO_3	μO	312(-,4)			
(colourless)				O	322(-,2)			
					392[i]			
$K(\mu\text{-}Cl_2Al$	tr	908.1(1)	AlC_2Cl_2	μ_3Cl	224.6(1,7)	Cl,Cl	97.73(5)	201
$[CH(SiMe_3)_2]_2]_2$	P$\bar{1}$	1122.6(2)		C	197.0(3,5)	C,C	121.5(1)	
	2	1354.8(3)			88.81(1)	Cl,C	108.8(1,4.7)	
					74.64(1)		97.6(1,5)[c]	
(colourless)				μ_3Cl	209.1(1,18)		141.1(1,1.7)[c]	
						Cl,Cl	70.2(1.5.8)	
							132.3(1,16.1)	
							107.9(1,3.9)[g]	
$KAlF_4$	tg	504.3(2)	AlF_6	F_{eq}	181.7(1)	not given		202
(colourless)	P4/mbm	-		F_{ax}	175.2(1)			
by neutron	2	616.4(6)	KF_x	F	284.8(1)			
diffraction								
$KAlF_4$	m	734.0	AlF_6	F_{eq}	187(-,3)	F,F	90.0(-,2.0)	203
(colourless)	$P2_1/m$	723.7	106.8	F_{ax}	176			
at 4K	4	640.7	AlF_6	F_{eq}	182(2)	F,F	90.0(-,1.7)	
				F_{av}	176			
			KF_x	F	not given			

β-RbAlF$_4$ (colourless)	tg I4c2 20	1166.6(5) - 1255.1(6)		AlF$_6$ AlF$_6$ RbF$_x$	F$_{eq}$ 181.4(2) F$_{ax}$ 173.1(3) F$_{eq}$ 183.8(2,32) F$_{ax}$ 174.8(14,1) F 269.9 - 364.5	not given		204
CsAlF$_4$ (colourless)	hx P62m 3	950.0 - 371.3		AlF$_6$ CsF$_x$	F 187.0(-,13) F 175.5 F 323.7(-,303)	F,F	90.0(-,4.2) 176.4(-,1.4)	205
TlAlF$_4$ (colourless)	tg P4/mmm 1	361 - 637		AlF$_6$ TlF$_8$	F 180 F 288	not given		206
TlAlF$_4$ (colourless)	tg P4/mmm 1			AlF$_6$ TlF$_8$	F$_{eq}$ 180.8(2) F$_{ax}$ 184.6(10) F 288.5(10)			207
K$_3$AlF$_6$.H$_2$O (colourless)	or Cmcm 4	920.0(3) 811.9(4) 748.6(3)		AlF$_6$ KF$_5$O KF$_6$O	F 187.2(1,0) 177.3(1,5) F 273.2(1,42) O 282.2(2) F 299.6 - 322.8(1) O 332.8(2)			208
Rb$_3$AlF$_6$.H$_2$O (colourless)	or Cmcm 4	960.4(4) 837.9(4) 754.2(2)		AlF$_6$ RbF$_x$O	F 188.7(1,0) 178.3(4,10) F 280.0 - 333.0(3) O 202.8(6)	not given		209
Tl$_3$AlF$_6$.H$_2$O (colourless)	or Cmcm 4	1007.5(1) 825.7(1) 748.2(1)		AlF$_6$ TlF$_x$O	F 187.11(5,0) 177.4(8,1) F 276.3 - 352.8(6) O 295(1)	F,F	90.0(6,4) 177.1(10)[d]	210
Mg$_2$AlF$_6$.2H$_2$O (colourless)	tg I4cm 4	935.3(5) - 724.1(6)		AlF$_6$ HgF$_4$O	F$_{eq}$ 179.6(6) F$_{ax}$ 172.4(42) 189.6(42) F 286.1(9,34) O 214.4(9) 251.1(1)[i]	not given not given		211
SrAlF$_5$ (colourless)	tg P4 32	1491.9(20) - 1521.8(20)		AlF$_6$ SrF$_x$	F 178(-,14) 226 F 221 - 378	not given		212
α-BaAlF$_5$ (colourless)	or P2$_1$2$_1$2$_1$ 4	1371$_0$ 560$_4$ 493$_0$		AlF$_6$ BaF$_x$	F 178.5(6,24) 185.8(6,10) F 262.4 - 381.5(6)	F,F	90.0(2,3.1) 177.4(2,1.7)	213
β-BaAlF$_5$	m P2$_1$/m 8	514$_8$ 1955$_6$ 755$_3$	92.4$_3$	AlF$_6$	not given			213

γ-$BaAlF_5$	m $P2_1/m$ 4	525[8] 972[4] 736[6]	90.8[9]	AlF_3	not given			213
$MnAlF_5$	or Ama2 4	954 985 358		AlF_6 MnF_6	F 175(-,4) 192 (x2) F 206 - 209	not given		214
$MnAlF_5$	or Cmcm 4	358.37(4) 985.4(1) 953.7(1)		AlF_6 MnF_6	F 177.6(1,21) 183.2(1) x2 F 201.9(1) x2 222.4(1) x4	F,F 90.0(1,3.1) 171.4(1)[d] 125.3(1); 167.7(1)[c] F,F 90.0(1,17.4) 107.4(1)[g]		215
α-Li_3AlF_6 (colourless)	or $Pna2_1$ 4	951.0(1) 822.95(3) 487.62(1)		AlF_6 LiF_6	F 180.7(1,23) F 186.5 - 242.4(3)	not given		216
Na_3AlF_6 (colourless)	m $P2_1/n$?	540.24(2) 559.59(2) 775.64(3)	90.278(1)	AlF_6 NaF_6 NaF_6	F 180.8(1,5) F 225.7(1,30) F 249.8(2,318)	F,F 90.0(1,9) F,F 90.0(1,4.3) F,F 56.1 - 106.92(6)		217
Na_3AlF_6[j] (colourless)	or $P2_1/n$ 2	541.39(7) 560.12(5) 777.69(8)	90.183(3)	AlF_6 NaF_3 NaF_3	F 180.4(2,4) F 226.5(2,31) F 250.6(3,305)	F,F 90.0(1,6) 145.0(1)[c] F,F 90.0(1,4.2)		218
Na_3AlF_6 (colourless)	m $P2_1/n$ 2	546 561 780	90	AlF_6 NaF_6	F 181(-,2) F 221 - 268	not given		219
Ca_2AlF_7 (colourless)	or Pnma 4	768.5(1) 699.8(1) 954.9(1)		AlF_6 CaF_7 CaF_8	F 180.1(3,27) F 231.6(4,88) F 226.3 - 301.4(4)	F,F 90.0(-,4.8) 98.9 - 152.7[c] F,F 76.0(-,14.2); 107.5 149.3(-,2.9); 174.4 F,F 75.1 - 161.6 104.8 - 137.1[g]		220
$Na_5Al_3F_{14}$ (colourless)	tg P4/mnc 2	701.38(8) - 1040.2(2)		AlF_6 NaF_x	F 180.0(-,26) not given	F,F 90.0(-,1.7)		221
$Sr_{10}Al_2F_{25}Cl$	c Fd3m 8	1642.09(3)		AlF_6 SrF_{12} SrF_8Cl	F 178.1(1,0) F 257.0(1,141) F 260.9(2,57) Cl 319.5	F,F 90.0(2,1.0) F,F 55.2 - 75.5(1) 135.0(1) F,Cl 55.3 - 126.8(1) 72.1(1) x4		222

K_2LiAlF_6 (colourless)	rh R3m 6	562(1) - 2762(1)		AlF_6 AlF_6 LiF_6 KF_{12} KF_{12}	F F F F F	181.3(4,0) 377.7(8)[e] 179.7(4,0) 267.1(8)[e] 205.7(9,83) 284.2(4,53) 288.3(4,182)		171.7[c] 85.0[c]	223
$LiCaAlF_6$ (white)	trg P31c 2	499.6 - 963.6		AlF_5 LiF_5 CaF_6	F F F	180.0(3,0) 200.9(3,0) 227.3(3,0)	F,F F,F F,F	90.0(1,2.8)[k] 90.0(1,13.7) 90.0(1,3.3)	224a
$LiCaAlF_6$	trg P31c 2	500.7(1) - 964.2(1)		AlF_5 LiF_5 CaF_6	F F F	180.5 200.9 228.1	not given		224b
$LiSrAlF_6$ (colourless)	trg P31c 2	507.1(6) - 1018.9(1)		AlF_5 LiF_5 SrF_6	F F F	179.9(1) 202.0(2) 242.4(2)	F,F F,F F,F	90.0(1,4.4) 90.0(1,15.5) 90.0(1,4.9)	225
$LiPdAlF_6$ (blue)	trg P31c 2	497.21(9) - 914.0(9)		AlF_6 LiF_6 PdF_6	F F F	180.8(1) 198.5(1) 218.8(1)	not given		226
$KCuAlF_5$ (colourless)	or Pnma 4	673.1(1) 704.0(1) 979.3(1)		AlF_5 CuF_5 KF_{10}	F F F	179.9(-,14) 187.7(-,4) 212.3(-,1) 285.4 - 319.9	not given		227
Na_2ZnAlF_7	or Pmnb 4	709.2 1009.2 733.7		AlF_6 ZnF_6 NaF_5 NaF_8	F F F F	180.1(3,16) 198.8(2,8) 260.6(3,141) 250.8(3,299)	F,F F,F 	90.0(2,3.0) 142.8(2)[c] 90.0(2,5.1) 127.2(3)[g]	228
Na_3MgAlF_7 (colourless)	or Imm2 4			AlF_5 MgF_6	F F	180.4(-,31) 195.1(-,8)			229
Na_2CoAlF_7 (pink)	m C2/c 16	1237.77(4) 721.00(3) 2401.92(9)	99.670(2)	AlF_5 CoF_5 NaF_8	F F F	180.1(2,19) 201.1(2,10) 214.9-283.45(2)		126.1(1,1.1)[g]	230
Ba_2ZnAlF_9 (colourless)	or Pnma 4	1784.1(1) 554.16(2) 736.16(2)		AlF_6 (ZnF_6) BaF_7	F 	178.5-217.2 not given		149.22[c]	231
$Cs_2NaAl_3F_{12}$ (colourless)	rh R3m 1	731.0(5)	57.45(10)	AlF_6 NaF_6 CsF_9	F F F	174.8(6) 182.8(1) 230.2(3) 302.7-405.7(5)	F,F F,F	90.0(1,1.4) 128.43(22)[c] 90.0(1,1.4)	232

$Li_3Na_3Al_2F_{12}$	c Ia3d 8	1212.2(2)		AlF_6 LiF_4 NaF_8	F 180.7(3) F 184.6(1) F 235.1(1) 254.4(1)	F,F F,F F,F	90.0(1,1.8)[1] 109.5(1,7.8) 72.5(1,10.8)	233
$Li_3Na_3Al_2F_{12}$	c Ia3d 8	1209.7(4)		AlF_6 LiF_4 NaF_8	F 181 F 180 F 240; 258		not given	234
$Na_3Sr_4Al_5F_{26}$	tg $P4_2/n$ 4	1026.79(5) - 1837.3(2)		AlF_6 SrF_9 NaF_8	F 180.0(6,56) F 259.8(6,246) F 252.0(8,328)	F,F F,F	90.0(4,2.6) 153.0(3,2)[d] 70.5(5,12.7)	235
$Ba_2CaMgAl_2F_{14}$	m C2/c 4	1356.7(1) 520.0(4) 1457.7(10)	91.50(4)	AlF_6 MgF_5 CaF_8 BaF_{12}	F 179.9(10,52) F 198.8(9,53) F 237.0(9,162) F 287.5(9,278)		not given	236
$Na_3H_3[Al(gly)_3]_2$ (colourless)	c $P4_132$ 4	1287.2(2)		AlO_5 NaO_5	O 188.9(3,1) O 228.4(3) 239.2(3) 258.1(3)	O,O	not given 52.4 - 138.8(1) 174.1(1)	237
$KAl_3(SO_4)_2(OH)_6$	hx R3m ?	697.0(1) - 1727(1)		AlO_6 KO_6 KO_6	HO 186.4(5) x4 O 196.3(9) x2 HO 287.1(15) x6 O 282.1(13) x6	O,O	90.0(1,1.2)	238
$KAl_3(SO_4)_2(OH)_6$	h R3m ?	702.0(2) - 1722.3(8)		AlO_5 KO_6 KO_5	HO 187.9(1) x4 O 194.7(1) x2 HO 283.6(1) x6 O 286.6(1) x6	O,O	90.0(1,1.0) 137[d]	239

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Al-X-M bridge angle. *d. Al-X-Al bridge angle.*
e. Al-M distance. *f. Midpoint of C-C.*
g. M-X-M bridge angle. *h. Centroid of carbon ring.*
i. M-M distance.
j. Derivative was studied at another eleven temperatures from 373 to 900K.
k. Al-F-Ca, 134.33(23)°; Al-F-Li, 98.27(16)°; Ca-F-Li, 122.59(12)°.
l. Al-F-Li, 136.10(7)°; Al-F-Na, 104.7(1,3.8)°; Li-F-Na, 91.64(4), 114.56(6)°; Na-F-Na, 98.54(4)°.

The M(I) cations act as bridges between the tetrahydridoaluminates. While the lithium(I) atom is surrounded by five hydrogen atoms, the sodium(I) atom has eight nearest neighbour H atoms which define the vertices of a distorted triangular dodecahedron. The shortest Al-Al and Al-Li distances [171] are 375.3(1) and 318.6(4) pm, respectively. The corresponding data for the sodium derivative [172] are not given.

There are three colourless derivatives [173-175] in which four O-donor ligands form a distorted tetrahedral environment about each aluminium atom. One has chains of alternating potassium(I) and aluminium(III) atoms joined by double OPr^i bridges [173], as shown in Figure 17.The polymer extends along the 21 axis in the c direction. Isopropyl groups sheath the metal-oxygen backbone and produce a non-polar exterior (Figure 17B). Potassium(I) is found in distorted octahedral environments.

The structure of $K_2Al_2O(OH)_6$ [174] contains $[(OH)_3AlOAl(OH)_3]^{-2}$ groups built up from two AlO_4 tetrahedra sharing an oxygen atom. These groups are held together by the potassium(I) atoms which are themselves in a distorted environment (KO_6).

The polymers $MAl(NH_2)_4$ (M = Li [176], Na [177,178], K or Cs [178]) have structure built up from $[Al(NH_2)_4]^-$ tetrahedra and the heterometal atom M. It is noted that the coordination number about M, as well as the mean M-N distance increase with the ionic radius of M in the order: 212 pm (Li, 4-coord, 73 pm) < 247 pm (Na, 4-coord, 113 pm) < 314 pm (K, 8-coord, 165) < 362 pm (Cs, 12-coord, 202 pm).

The structure of $LiAlEt_4$ [179] is found to consist of linear chains of alternating lithium and aluminium atoms double bridged by ethyl groups, with Al-Li distance of 270.6 pm and Al-C-Al angle of 77.2°.

There are several examples of the general formula: M^IAlCl_4 (M = Li or Na [180,181], Ga [182], Cd [183,184] or Cu [187]); $M^{II}(AlCl_4)_2$ (M = Cd [182], Ti [185], Co [186], Cu [188]; $C_6H_6M^IAlCl_4$ (M = Cu [189], Ag [190]; $C_6H_6M^{II}(AlCl_4)_2$ (M = Sn [191], Pb [195]; $LSnClAlCl_4$ (L = C_6H_6 and its derivatives [192-194] and $Dy(AlCl_4)_3$ [196]. Each aluminium(III) atom is in a distorted tetrahedral environment with four chlorine atoms. As expected, the stereochemistry about the M atoms is variable. Some are tetrahedrally coordinated ($Cd^ICl_3Cd^I$ [183,184] and Cu^ICl_4 [187]); five coordinated ($Cu^ICl_3C_2$ [189] and $Ag^ICl_3C_2$ [190]; six coordinated (M^ICl_6, M = Li, Na [180], Ga [182]), $M^{II}Cl_6$ (M = Cd [183], Ti [185], Co [186], Cu [188]); "open" sandwich plus six chlorine ligands, $M^{II}C_6H_6$ (M = Sn [191-194] and Pb [195]); finally eight coordinated $D^{III}{}_4Cl_8$ [196].

The structure of $Cd_2(AlCl_4)_2$ [184] is shown in Figure 18. Three of the $AlCl_4^-$ chlorine atoms form bridges to cadmium atoms to give the distorted tetrahedral environment about the cadmium indicated above. The resulting Cd-Cd bond distance is 257.6(1) pm. This structure was also published in another paper [183] with comparable results.

The polymers $LiAlCl_4$ and $NaAlCl_4$ [180] were studied at three different temperatures and it was found that the unit cell dimensions increase smoothly with temperature. The M^I -Cl distances also increase but the Al-Cl distances are almost unchanged. The isomers α- and β-(tl)ClSnAlCl$_4$ [194] differ mostly by degree of distortion.

In emerald green $Ti(AlBr_4)_2$ [197] each titanium(II) atom is in a distorted octahedral environment of six bromide atoms. Two edges (4Br) and one two vertices (2Br) come from four crystallographically equivalent $AlBr_4$ tetrahedra. Each of these is connected through one edge (2Br) and one vertex (Br) to two crystallographically equivalent Ti atoms. The fourth vertex of the tetrahedron (Br) is not coordinated to a titanium atom.

The infinite chains of $AlBr_4$ tetrahedra are connected through titanium atoms and extend along the a axis.

Dimeric $cp_2Y(\mu\text{-}Cl)_2Ycp_2$ fragments make up a polymeric chain in a colourless derivative [198] by linkage through $AlH_3(Et_2O)$ units via Y-H-Al bridges.

Monoclinic $LiAlH(NEt_2)_3$ [199] contain chains of $AlHN_3$ and $LiHN_3$ tetrahedra linked through common edges. The Al-Li bond distances are 264.3(4) and 270.9(4) pm. The Al-H-Li and Al-N-Li bridge angles are 102.0(10)° and 80.9(1)°, respectively, and the Li-Al-Li angle is 132.6(1)°.

Another colourless derivative [200] crystallizes in infinite chains of -(sulphate)AlCs(18-crown)Cs(sulphate)Al-. Each cesium atom interacts with the six crown oxygen atoms plus two sulphate oxygen atoms. The Cs-Cs distance is 392 pm, which is slightly longer than the sum of two eight coordinate cesium(I) radii (376 pm). In an Al/K polymer [201], each metal atom is in a distorted tetrahedral environment. The $Al\{CH(SiMe_3)_2\}_2$ moieties form a chain with K(I) atoms via double bridges of chlorine (AlC_2Cl_2 and KCl_4).

In this series of tetrahedrally coordinated Al(III) [171-201] the mean Al-L(terminal) and Al-L(bridge) distances increase with covalent radius of the donor atom in the order: 150 pm < 189 pm (LO) < 208 pm (Cl) < 225.5 pm (Br); and 152 pm (H) < 176 pm (LO) < 185 pm (LN) < 202 pm (LC) < 215 pm (Cl) < 232 pm (Br), respectively. The structure of the derivatives of the general formula M^IAlF_4 (M = K [202,203], Rb [204], Cs [205], Tl [206,207]) may be described as a sequence of

$[AlF_{4/2}F_2]_\infty^-$ layers of AlF_6 octahedra sharing four corners in the (001) plane with M^I ions between the layers.

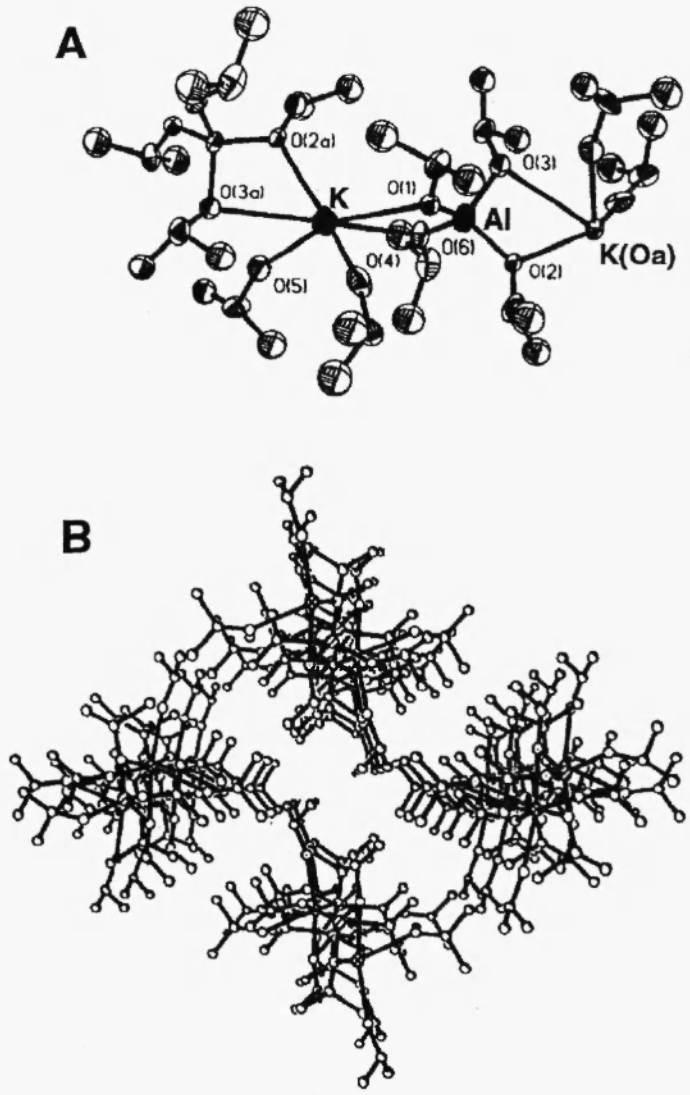

Fig.17.
A. A portion of $[(Pr^iOH)_2KAl(OPr^i)_4]_n$.
B. Packing diagram viewed down the crystallographic c axis [173]

The structure of $M^I_2AlF_5.H_2O$ (M = K [208], Rb [209], Tl [210], Hg [211]) is built up from endless and slightly kinked chains of AlF_6c octahedra (Al in OOO plane) running along the direction of the c axis. The octahedra share two fluorine atoms in *trans* positions, and the M^I atoms and water molecules are located between the chains. In the mercury derivative [211] the structure contains the quasi-linear $\{H_2O\text{-}Hg\text{-}Hg\text{-}OH_2\}^{+2}$ cations between the chains. The Hg-Hg bond distance is 251.1(1) pm and the equal Hg-O bond distances are 214.4(9) pm.

In the polymers of formula $M^{II}AlF_5$ (M = Sr [212], Ba [213]) aluminium and fluorine atoms are grouped in two different kinds of chains, both with the formula $(AlF_5)^{-2}$, linear and bent. The latter exists in three isomeric forms, but only data for the a-form has been made available (Table 5).

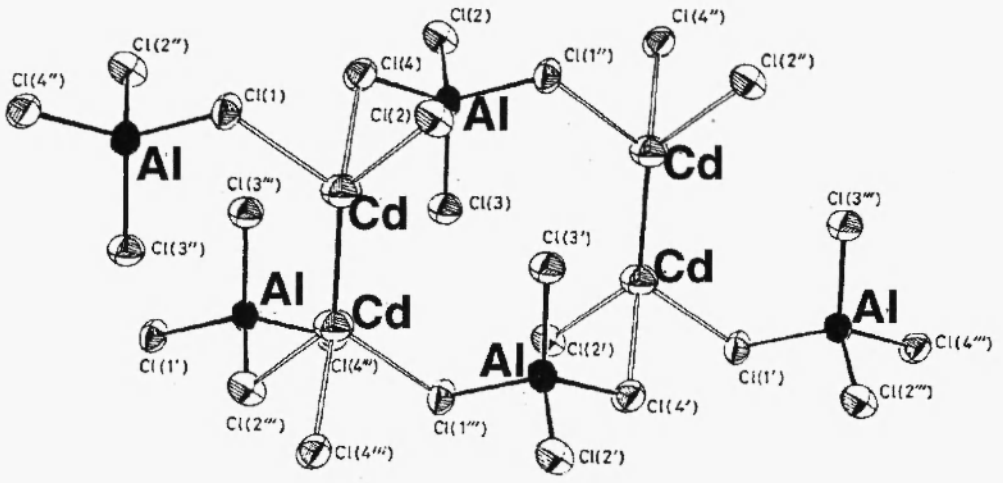

Fig.18. A portion of $[Cd_2(AlCl_4)_2]_n$ [184]
(*in projection down the a axis*)

The polymer Na_3AlF_6 [218] has been studied at twelve different temperature from 295K to 900K. It was found that the unit cell dimensions increase with temperature, and there is a space group change from $P2_1/n$ to Immm at 890K. The mean Al-F bond distance increases from 180.4 pm at 295K to 180.8 pm at 373K and then remains unchanged to 673K. At a temperature of 800K it reduces back to 180.4 pm, then as the temperature increases to 900K it smoothly decreases to 177.4 pm. On the other hand, the mean Na-F bond distance (for NaF_6) smoothly decreases with temperature from 225.5 pm at 295K to 220.9 pm at 900K. The mean Na-F distance for NaF_8 smoothly increases with temperature from 250.6 pm at 295K to 282.4 pm at 900K.

There are several derivatives which contain two different heterometal atoms. One set has the general formula $M^{I}M^{II}AlF_6$ [224-227]. and the other $M^{I}_2M^{II}AlF_7$ [228-230]. In the former each of the cations occupies a distorted octahedral site, except for potassium [227] which is ten coordinate. In the latter set the Al(III) and M(II) atoms are six coordinate, except for sodium which is eight coordinate (Table 5). The structure of the latter derivatives contain $[M^{II}_2AlF_{10}]_n^{-3n}$ layers of octahedra parallel to the (001) plane in which the M(II) atoms form chains of corner-shared octahedra. The sodium(I) atoms exhibit similar eightfold coordination.

A distorted octahedral aluminium atom occupies a position on the threefold axis in another polymeric complex [237], and is coordinated to six O atoms from three facial glycolate ligands. Half of the hydroxy sites are deprotonated, leading to a very short symmetrical hydrogen bond between two-fold related hydroxy sites (O...O = 242.5(4) pm) with the H atom lying on the twofold axis. Three such hydrogen bonds connect two *fac* Al(III)-glycolate moieties to give binuclear units along a common threefold axis. The binuclear units are stacked into three dimensions by O-Na links.

The structure of alunite, $KAl_3(SO_4)_2(OH)_6$ [238,239] is also included in this review as an example of a typical "inorganic" complex. There are many mixed oxide, carbonates, phosphates and sulphates, etcetera, which will be the subject of an later review. The structure of alunite shows aluminium to be coordinated by four OH groups and two oxygen atoms from two separate SO_4 groups, giving an octahedral environment. Six oxygen neighbours from six sulphate groups afford a flattened octahedron about potassium (Al-O = 282.1 pm), while the six OH neighbours form an elongated octahedral arrangement about potassium (Al-O = 287.1 pm) [238].

In the series of heteropolymeric aluminium compounds the heterometal atoms include main group, transition and lanthanide metals. There is no example with an Al-Al distance less than 300 pm, but there are several with Al-Li distances below 300 pm, for example: 264.3(4) and 270.9(4) pm [199], 267.1(8) pm [223] and 270.6 pm [179]. For M-M distances the values are: 251.1(1) pm (Hg^{I} [211]), 256.2, 257.6(1) pm (Cd^{II} [183,184]). It must, however, be noted that for several examples in Table 5 the relevant data are not given in the original manuscript.

7. CONCLUSIONS

This review classifies almost three hundred heterometallic compounds of aluminium. In addition, there are almost five hundred coordination compounds [1] and three hundred organometallic compounds [2] of aluminium whose structures have been reviewed. The data

presented here show aluminium present, with other metal atoms, in molecules with from two to eighteen metal atoms per unit. These exist in a various degrees of condensation from dimers to polymers with a wide range of ligand donor-atoms.

In general, in all derivatives of aluminium [1,2] the aluminium(III) atom favours a tetrahedral environment, and this is also the case in this series. The mean Al-L bond distances for such derivatives, for the most common donor atoms, are given in Table 6. In general, the mean Al-L bond distance increases with the covalent radius of the coordinated atom in the order: heterometallics < coordination complexes < organometallics. Also, the Al-L(terminal) distances are shorter than the corresponding Al-L(bridge) distances. One example [213] exists in three isomeric forms, and another [202,203] exists in two isomeric forms. Some examples [7,12,27,50,60,63,66,75,84,102,117,133, 147] contain two crystallographically independent molecules differing by degree of distortion (Al-L and L-Al-L parameters), and these are typical examples of distortion isomersim [57].

TABLE 6. Summary of the Mean$_a$ Al^{III}-L(atom) Bond Distances (pm) for Four Coordinate Derivatives

COORD. ATOM	Cov. Rad. [pm]	Heterometallic Compounds this paper	Coordination Compounds [ref. 1]	Organometallic Compounds [ref 2]
H	30	150(15,15)	154(26,46)	172(1,1)
μH		168(24,42)	167(0,1)	175(10,12)
LO	73	176(11,22)	180(13,11)	184(14,16)
μLO		180(11,9)	181(5,2)	186(4,10)
LN	75	192(15,21)	193(14,24)	192(8,9)
μLN		192(11,15)	194(15,4)	197(14,24)
LC	77	198(18,13)		197(14,8)
μLC		221(10.19)		196
Cl	99	210(5,8)	212(7,9)	216(14,6)
μCl		221(7,27)	226(4,2)	232(7,13)
Br	113	223(9,3)	227(7,30)	234(3,5)
μBr		234(3,14)	244(7,6)	249(1,1)

Footnotes: a. The first number in parenthesis is the difference between the shortest and the mean, the second is between the highest and the mean.

Summaries of the metal-metal distances are given in each section (Tables 1B, 3D and 4A) where it can be seen that aluminium bonds to a variety of other metal atoms of both the "hard" and "soft" variety. The metal atoms cover the range from main group to actinide. This illustrates the rich diversity of the chemistry of aluminium in its nearly twelve hundred structurally determined compounds.

During the collection and organisation of the data it became clear that, despite the increasing availability of data retrieval systems, finding relevant material can be a difficult and expensive proposition. Some published papers do not provide relevant data, or refer it to supplemental material, such as names of ligands, atomic coordinates and molecular distances. This can lead to the overlooking of important structural features, which may only become apparent when comparisons are attempted. It is therefore hoped that this review, and its coordination and organometallic partners will draw attention to such comparisons, and provide a cross linking of different areas of interest in aluminium chemistry.

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