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Review

Organoaluminium compounds: classification and analysis of crystallographic and structural data

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Abstract

This review covers the organometallic derivatives of aluminium. There are two associated reviews which cover inorganic and heterometallic aluminium complexes. There are over 350 of organoaluminium X-ray crystallographic studies in which aluminium is found almost exclusively in the +3 oxidation state. The most common geometry around aluminium is tetrahedral, but other arrangements with from three to ten donor sites are also found. Dimeric derivatives are the most common, followed by monomeric derivatives. Higher degrees of oligomerization are also found, but there are only three examples which can be classified as polymers. Several examples exhibit metallic bonding between aluminium atoms. While the most common carbon-bonded ligand is the methyl group, a variety of other organic ligands are observed, including π-bonding moieties. The structures are classified according to structural type, and correlations between bonding parameters are noted. © 1997 Elsevier Science S.A.

1. Introduction

Aluminium is a greyish white metal rapidly obtaining a stable surface oxide layer on exposure to the environment, which serves to protect it to some extent. As an extremely reactive metal it is easily oxidized and complexed, thus although it is the most abundant metal in the lithosphere, it is found only in its oxidized and complexed forms. The most important of these are the aluminosilicates which form the matrix upon which plant life grows and terrestrial animals roam. By contrast, the solubilized aluminium cation is now recognized to be the cause of severe damage to plant and animal life.

Systematic studies of both the coordination and organometallic compounds of aluminium have expanded rapidly over the last three decades. The stereoselective catalytic behaviour of many of these derivatives has proved to be of considerable commercial value for stereospecific industrial synthesis of organic compounds. In some ways, such properties are also related to the stereochemical specificity of biological systems. Knowledge of the structure of these compounds is an important part of understanding this behaviour, and there are well over 1000 published structures to date, almost a third of which are of organoaluminium derivatives. The remainder belong to the group of coordination compounds which have been the subject of a parallel review [1].

Features of interest in aluminium chemistry include the dependence of the Lewis acidities of compounds R_3Al, R_2Al and $RAlX_2$ on both R and X, which affect the behaviour of these derivatives towards potential ligands, and selectivity of donor sites in cases of multidentate ligands. The structural elucidation of such points are of help in understanding the reaction mechanisms of organoaluminium catalysts. To our knowledge there does not yet exist an overall review of such structures. The aim of this review is to provide such a survey for the crystal structures up to the end of 1994, and to draw attention to correlations which can be observed.

The major source of information has been the Cambridge Crystallographic Data Base, with extensions into the first half of 1995 from available major inorganic and organometallic chemistry journals. The structures have been classified according to the coordination number of the aluminium, and subdivided into monomers, oligomers and polymers. Within each division, the compounds are listed in increasing complexity of the coordi-

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nation sphere and increasing covalent radius of the principle coordinating atoms.

2. Monomeric compounds

2.1. Coordination number three

There are 13 colourless organoaluminium compounds, all with oxidation state +3 for the aluminium atom, and these are listed in Table 1. A gas-phase electron diffraction study of $Al(Me)_3$ [2a] shows three equivalent Al–C bond distances (195.7(3) pm) and C–Al–C bond angles of 120°, as expected for a regular trigonal planar environment around the metal atom. The complex $[Al(Me)_3]([12]aneS_4)$ [2b] shows a mean Al–C(Me) distance of 194.9(8) pm and C–Al–C bond angle (119.8°), also essentially that of the trigonal planar environment. The other contact distance, between Al and the thiacrown ether S-donor atoms suggest a weak interaction (Al–S = 271.8(3) and 305.2(3) pm) which has not significantly altered the environment of the Al atom from its planar state. We have therefore included it in this section rather than under coordination number five.

A regular planar geometry has also been observed in a tri-mesityl analogue [3]. Here the ligands are disposed in a propeller-like fashion about the trigonal axis, with a pitch angle of 56° between the aromatic rings and the trigonal plane. Related examples [4–9] which contain dissimilar donor groups exhibit some degree of distortion, as might be expected.

The data in Table 1 indicate that the Al–L bond distance increases with increasing covalent radius of the coordinated donor atom in the sequence: 153 pm-(H, 30 pm) < 170.5 pm (OL, 73 pm) < 184 pm (NL, 75 pm) < 199 pm (CL, 77 pm). These distances are somewhat longer than comparable distances in the three-coordinate Al(III) coordination compounds (165 pm, OL and 178 pm, NL) [1]. The mean value of the sum of all three Al–L bonding distances is almost constant for each chromophore, and also increases with the sum of the covalent radii of the donor atoms in the order: 523 pm (AlO_2C) < 567 pm (AlC_2O) < 585 pm (AlC_2N) < 590 pm (AlC_3).

In the compound $Al(Bu^t)_2(tbp)$ [7] six crystallographically independent molecules are present in the same crystal. These differ mostly by degree of distortion, and represent a unique example in the crystal chemistry of aluminium. Another derivative, $Al(Bu^t)_2\{(Ph_3Si)_2N\}$ [9] has two crystallographically independent molecules coexisting in one crystal, and again differs mainly by degree of distortion.

The 14 derivatives in Table 1 belong to the relatively uncommon three-coordinate state of aluminium(III). This coordinately unsaturated environment for aluminium has only four examples that are outside the organometallic classification [1].

2.2. Coordination number four

The four-coordinate organoaluminium compounds are listed in Table 2 together with their crystallographic and structural data. Although most of the almost 90 examples are colourless, there are some which are white or yellow, with two red and one orange examples. From the three principle geometries possible, only the tetrahedral environment is observed, as might be expected for a non-transition metal. However, none of these has the ideal symmetry of T_d.

Various degrees of distortion about the aluminium are observed as the ligands range from uni- to tridentate. Those with bidentate ligands exhibit distortions which can be monitored via the changes in the L–Al–L bond angles of the respective metallocycles, and both steric and electronic effects can be observed. In the three-membered AlB_2 metallocyclic ring the B–Al–B angle is 46.1(6)° [62]. In the series of four-membered rings the L–Al–L angles are: from 64.7 to 70.4° for RCN_2 ligands; from 74.9 to 78.8° for RPN_2 ligands; 81.7° for the RPNS ligand; 82.1° for the RBCS ligand; from 85.2 to 89.4° for RSiCS ligands. In the series of five-membered rings the L–Al–L angles are: 81.5° for RC_4; from 84.3 to 87.2° for RC_2N_2; 89.3° for RC_3N; 99.4° for RC_3B. For the six-membered metallocyclic rings the values are 94.2 to 95.8° for RC_3O_2 and 99.0° for RPC_2N_2.

The mean Al–L bond distances of the organoaluminium derivatives tend to increase with the covalent radii of the donor atoms, and are somewhat longer than those found in other tetrahedrally coordinated aluminium compounds, with the exception of Al–Se which exhibits the opposite trend.

One example, $[Al(Et)_2Cl_2]^-$ [61], exists in two isomeric forms, orthorhombic and tetragonal. Five examples [10,14a,20,39,46] contain two crystallographically independent molecules within the same crystal, differing only by degree of distortion in the Al–L bond distances and L–Al–L bond angles. In one example [57], two different tetrahedral units are present (AlN_2C_2 and AlC_2Br_2). In another two examples [48] both tetrahedral and octahedral ($AlCl_3C$ and AlO_4C_2) units are present. A similar case is also found in which tetrahedral and pentagonal bipyramidal units coexist ($AlCl_3C$ and AlO_5C_2) [49]. In one example a tetrahedral and a 'sandwich' unit are present in the same crystal ($AlCl_3C$ and $Al(\eta^5\text{-cp}^*)_2$), but in these cases they are all well separated.

These organoaluminium derivatives plus the almost 200 inorganic aluminium complexes [1] with similar geometry illustrate the strong preference of the aluminium(III) atom for a four-coordinate tetrahedral envi-

Table 1
Crystallographic and structural data for three-coordinate organo-aluminium compounds [a,e]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Al-L [pm]		L-Al-L [°]		Ref
$Al(Me)_3$ gas phase				AlC_3	C_{Me} [b]	195.7(3)	C,C [b]	120	2a
by electron diffraction.									
$[Al(Me)_3]([12]\text{-}aneS_4)$	m	979.1(4)		AlC_3	C_{Me}	194.9(8,6)	C,C	119.8(4,3.1)	2b
	$P2_1/n$	844.1(9)	102.36(3)						
(colourless)	4	2141.6(8)							
$Al(PhCH_2)_3$	or	948.0(3)		AlC_3	C	198.9(6,8)	C,C	114.5(2,1.0)	2c
	Pbca	3424.8(11)							
	3	1054.6(5)							
$Al(mes)_3$	trg	1240.9(4)		AlC_3	C	199.5(8,0)	C,C	120.15(5)	3
	$P\bar{3}$	1340.9(4)							
(colourless)	2	1766.4(3)							
$Al(bht)_2Me$	tr	1210.2(2)	102.65(1)	AlO_2C	O	168.6(2,1)	O,O	111.9(1)	4
	$P\bar{1}$	1279.3(2)	110.54(1)		C_{Me}	192.7(3)	O,C	123.8(1,2)	
(colourless) at173K	2	1098.1(2)	68.16(1)						
$Al(dbp)_2(Bu^i)$	m	3159.5(4)		AlO_2C	O	169.2(1,10)	O,O	110.1(1)	5
	C2/c	1074.5(1)	99.99(1)		C_{Bu}	195.2(2)	O,C	125.0(1,4.9)	
(colourless)	8	1794.4(2)							
$Al(tbp)_2H$	m	1002.4(2)		AlC_2H	C	199.2(6,22)	C,C	131.7(3)	6
	$P2_1/c$	2974.5(1)	94.87(1)		H	153(4)	C,H	113.7(14,6)	
(colourless)	4	1145.9(1)							
$Al(Bu^t)_2(tbp)$ [c]	m	1138.6(10)		AlC_2O	C_{Bu}	199.2(11,65)	C,C	125.9(4)	7
	Pn	2911(2)	102.05(6)		O	170.1(5)	C,O	116.2(4,10.9)	
(colourless)	12	2496.9(16)		AlC_2O	C_{Bu}	198.8(12,21)	C,C	127.7(5)	
					O	168.7(7)	C,O	115.9(5,5.2)	
at 130K				AlC_2O	C_{Bu}	195.3(11,11)	C,C	118.9(5)	
					O	172.5(7)	C,O	119.9(4,9.2)	
				AlC_2O	C_{Bu}	200.5(11,19)	C,C	124.1(5)	
					O	171.7(7)	C,O	117.9(5,5.9)	
				AlC_2O	C_{Bu}	199.7(14,66)	C,C	125.3(5)	
					O	172.8(7)	C,O	117.2(5,2.1)	
				AlC_2O	C_{Bu}	201.4(10,30)	C,C	128.7(4)	
					O	169.5(8)	C,O	115.2(4,5.2)	
$Al(Bu^t)_2(dbmp)$	m	820.0(2)		AlC_2O	C_{Bu}	198.0(3,4)	C,C	125.2(1)	8
	$P2_1/c$	1787.6(4)	94.47(2)		O	171.0(2)	C,O	117.3(1,6.6)	
(colourless)	4	1591.0(4)							
$Al(trip)_2(dipp(H)N)$	m	1164.3(5)		AlC_2N	C	196.0(4,1)	C,C	127.8(2)	9
	C2/c	1846.0(6)	95.86(3)		N	178.4(3)	C,N	not given	
	8	3716.5(1)							
$Al(Bu^t)_2(mes_2N)$	or	996.5(3)		AlC_2N	C	198.8(7,9)	C,C	123.0(3)	9
	$Pca2_1$	1374.6(5)			N	182.3(4)	C,N	not given	
(colourless) at 130K	4	1770.0(6)							
$Al(Bu^t)_2((Ph_3Si)_2N)$ [d]	tr	1262.3(4)	93.45(1)	AlC_2N	C	202.1(6,5)	C,C	117.3(2)	9
	$P\bar{1}$	1688.0(3)	100.25(2)		N	188.0(4)	C,N	not given	
(colourless)	4	1860.0(2)	99.46(2)	AlC_2N	C	201.7(5,2)	C,C	117.3(2)	
					N	187.8(4)		not given	
$Al(Bu^t)_2((Ph_3)(dipp)SiN)$	tr	1041.3(4)	97.75(4)	AlC_2N	C	202.0(5,5)	C,C	114.7(2)	9
	$P\bar{1}$	1058.5(6)	96.41(3)		N	183.4(3)	C,N	not given	
(colourless)	2	1828.1(6)	118.97(2)						
$Al(Bu^t)_2((Ph_3)(1\text{-}ad)SiN)$ [d]	tr	1037.2(3)	113.87(3)	AlC_2N	C	201.1(3,11)	C,C	117.0(1)	9
	$P\bar{1}$	1795.7(8)	99.23(3)		N	185.3(2)	C,N	not given	
(colourless)	4	1918.4(8)	96.71(3)	AlC_2N	C	200.9(3,1)	C,C	117.6(1)	
					N	184.5(2)	C,N	not given	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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] Six crystallographically independent molecules.
[d] Two crystallographically independent molecules.
[e] Refs. [2a,2b,2c,3–9] are to be found in the reference list.

Table 2
Crystallographic and structural data for four-coordinate organo-aluminium compounds [a,i]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Al-L		L-Al-L [°]		Ref
$NaAlMe_4$ (colourless)	or Cmcm 4	923.4(3) 922.1(3) 830.3(2)		AlC_4	C[b]	200.7(3,17)	C,C[b]	109.5(2,8.2)	10
$NaAlEt_4$[c] (colourless)	m $P2_1/c$ 8	1390.0(2) 1320.7(2) 1444.3(1)	117.43(1)	AlC_4	C	201.6(2,7)	C,C	109.5(1,1.5)	10
				AlC_4	C	201.3(2,4)	C,C	109.5(1,3.1)	
$Na(Hmpa)[AlEt_4].C_6H_6$ (colourless)	or Pnma 4	2135.5(4) 1471.7(5) 1864.9(4)		AlC_4	C	not given			11
$NaAl(Pr^n)_4$ (colourless)	m C2/c 8	980.2(5) 1533.6(4) 2161.1(10)	98.43(1)	AlC_4	C	201.4(6,13)	C,C	109.5(2,2.6)	10
$[Al\{(Me_3Si)_2CH\}_2(dsm)][Li(tmeda)_2]$	m $P2_1/n$ 4	1746.7(4) 1433.1(4) 2011.1(3)	99.51(2)	AlC_4	C	204.8(3,44)	C,C	85.2(1)[d] 113.7(1,5.1)	12
$Na[Al(6,9\text{-}C_2B_8H_{10})_2]$ (colourless) at 173K	m $P2_1/c$ 4	1637.8(3) 1878.1(3) 1480.6(3)	90.197(5)	AlC_4	C	206		not given	13
$[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2][N(PPh_3)_2]$	m $P2_1/c$ 4	1637.8(2) 1878.1(3) 1480.6(3)	90.197(5)	AlC_4	C	206.5(20,15)	C,C	109.5(9,10.8)	14a
$Na[Al(2,7\text{-}C_2B_8H_8)_2]$[c] (colourless) at 128K	m $P2_1$ 4	1003.5(2) 1243.3(3) 1169.0(3)	111.019(7)	AlC_4	C	201.8(5,2)	C,C	82.1(1,3)[d] 124.3(2,12,0)	14a
				AlC_4	C	202.1(5,5)	C,C	82.2(2,1)[d] 123.7(2,12.9)	
$K[Al(Me_3)(CN)]$	m C2/c 8	1990.2(7) 921.1(4) 961.5(4)	107.74(5)	AlC_4	C_{Me}	197.1(8,4)	C,C	109.5(4,7.4)	14b
					NC	204.7(7)			
$K[Al(1,3\text{-}COD)_2]$	m $P2_1/c$ 4	965.8(6) 1222.0(8) 1415.0(9)	113.85(1)	AlC_4	C	203.2(2,18)	C,C	88.0(9) 121.0(1,5.9)	14c
$AlH_3(tpi)$ (white) at 203K	m $P2_1/n$ 4	840.9(4) 1525.1(3) 1645.9(8)	104.11(2)	AlH_3C	H	not given		not given	15
					C	203.4(3)			
$Al(bht)_2(Bu^t(H)CO)Me$ (colourless)	m $P2_1/n$ 4	1007.65(5) 2620.1(2) 1401.06(4)	103.638(3)	AlO_3C	C	172.8(3,2)	O,O	105.3(1,7.8)	16
					CO_{Bu}	192.0(3)	O,C	112.8(2,9.4)	
					C_{Me}	195.5(4)			
$Al(bht)_2(Ph(MeO)CO)Me$ (colourless)	tr P$\bar{1}$ 2	939.4(2) 974.1(3) 2309.1(7)	91.43(2) 91.93(2) 116.41(2)	AlO_3C	O	171.8(9,4)	O,O	107.4(5,8.6)	16
						185.1(7)	O,C	110.8(5,8.6)	
					C_{Me}	196(2)			
$Al(bht)_2(Ph_2CO)Me$	m $P2_1/n$ 4	1200.2(2) 2488.1(2) 1376.7(3)	90.573(9)	AlO_3C	O	172.7(6,6)	O,O	104.1(3)	17
					CO_{Ph}	190.3(6)	O,C	113.7(3,4.5)	
					C_{Me}	194.2(8)			
$Al(dbmp)_2(dk)Me$ (colourless)	m $P2_1$ 2	1054.1(2) 1580.8(4) 1188.5(1)	103.49(1)	AlO_3C	O	not given			18
					O_{dk}	192.3			
					C_{Me}	not given			
$Al(dbmp)(bhmap)Me$ (colourless)	m $P2_1/n$ 4	1569.8(5) 961.3(2) 1942.0(3)	101.70(2)	AlO_3C	O	170.6(4)	O,O	94.2(2)[e]	19
					O	180.0(4,36)		108.4(2,2.8)	
					C_{Me}	193.3(7)	O,C	114.1(3,5.0)	
$Al(bht)(C_{12}H_{23}O_2)Et$[c] (yellow)	m $P2_1$ 2	934.28(6) 1430.79(6) 1133.22(6)	91.971(4)	AlO_3C	O	173.2(3)	O,O	95.8(2)[e]	20
					O	172.0(5)		107.8(3,4.9)	
						191.1(5)	O,C	113.9(4,6.1)	
					C_{Et}	196.2(9)			
$Al(tbtas)Me$ (colourless)	m $P2_1/m$ 2	936.0(7) 1498(1) 984.6(7)	109.76(6)	AlN_3C	N	173.2(5,0)	N,N	98.4(2)[d]	21
						180.5(6)		117.3(2)	
					C_{Me}	not given	N,C	118.8(3,1.9)	
$K[AlMe_3H]$ (colourless)	or Cmca 8	964.7(8) 1733.2(4) 771.1(2)		AlC_3H	C_{Me}	199.3(6,6)	C,C	112.0(2,5.6)	22
					H	173.0(57)	C,H	106.9(2.0,5.5)	
$Al\{(Me_2Si)_2CH\}_2(Me_3C)(H)$ (colourless) at 173K	tr P$\bar{1}$ 2	1089.1(2) 1290.6(2) 1666.2(2)	75.82(1) 78.02(1) 76.16(1)	AlC_3H	C	205.0(5,2)	C,C	112.1(2,10.0)	23
					C_{Me}	204.7(3)		107(1,8)	
					H	171(2)			
$K[AlMe_3(NO_3)].C_6H_6$ (colourless)	or $P2_12_12_1$ 4	771.6(4) 985.5(5) 1837.5(5)		AlC_3O	C_{Me}	196.8(9,20)	C,C	113.9(4,5.9)	24
					O	193.0(6)	C,O	103.9(3,9.6)	
$[AlMe_3(NO_3)][K(db\text{-}[18]\text{-}C\text{-}6)].C_6H_6$ colourless)	m $P2_1/c$ 4	1180.4(3) 2882.8(4) 911.8(3)	96.61(3)	AlC_3O	C_{Me}	196(2,2)	C,C	114.6(8,2.6)	25
					O	192(1)	C,O	103.4(6,7.5)	
$AlMe_3(Me_3NO)$ (colourless)	m $P2_1/n$ 4	783.1(2) 1431.8(3) 887.2(2)	92.48(3)	AlC_3O	C_{Me}	198.1(3,6)	C,C	112.6(1,6)	26
					O	185.7(2)	C,O	106.1(1,6.8)	

Table 2 (continued)

$AlMe_3(Ph_3PO)$	tg	1384.2(2)		AlC_3O	C_{Me} 196.5(3,0)	C,C	113.3(1)	26
	$R\bar{3}$	-						
(colourless)	6	1815.9(4)			O 183.7(2)	C,O	105.3(1)	
$(NMe_4)[Al(Me)_3(ac)]$	m	694.9(5)		AlC_3O	C_{Me} 202(1,3)	C,C	112.5(7,3.2)	27
	$P2_1/c$	2202.2(9)	94.40(5)					
(colourless)	4	957.6(6)			O 183(1)	C,O	106.3(6,4.1)	
$Al(PhCh_2)_3(Et_2O)$	m	810.6(1)		AlC_3O	C 198.6(7,2)	C,C	113.0(3,5.1)	28
	$P2_1$	1509.8(2)	111.02(1)					
(colourless)	2	1003.7(1)			O 190.1(4)	C,O	105.6(3,1.8)	
$Al(mes)_2(thf)$	m	845.7(1)		AlC_3O	C_{mes} 201.7(6,6)	C,C	101.5(3,10.1)	29
	$P2_1/c$	1431.8(2)	98.271(9)					
	4	2223.4(3)			O_{thf} 196.9(5)	C,O	116.2(3,8.4)	
$Al(pfp)_3(thf)$	tr	1044.9(3)	112.57(2)	AlC_3O	C 199.5(3,6)	C,C	113.6(1,3.5)	30
	$P\bar{1}$	1085.3(3)	90.35(1)					
(pale yellow) at 153K	2	1090.1(4)	107.34(1)		O_{thf} 186.0(2)	C,O	105.0(1,2.2)	
$[Al(6,9\text{-}C_2B_8H_{10})$	tr	1396.4(3)	92.227(8)	AlC_3O	C 202.8(3,3)	C,C	99.44(12)[f]	31
	$P\bar{1}$	1596.6(4)	86.689(7)		C_{Et} 196.6(3)			
$(Et)(Et_2O)].\frac{1}{2}C_6H_6$	4	855.0(2)	102.060(8)			C,O	99.87(13)	
					O 190.9(2)			
(pale yellow)								
Al(dha)(Et)(thf)	or	1571.4(4)		AlC_3O	C 205.7(4,2)	C,C	81.5(1)[f]	32a
	Pbca	1862.0(5)			C_{Et} 196.6(4)		124.4(2,2)	
	8	1876.6(4)			O_{thf} 190.3(3)	C,O	108.6(1,5.9)	
$Al(C_4Ph_4)(Ph)(Et_2O)$	m	1055.98(5)		AlC_3O	C_{Ph} 197.9(6)	C,C	91.6(3)[f]	32b
	Cc	2270.89(12)	98.064(3)				124.4(3,2.0)	
	4	1334.17(4)			C 196.7(6,2)	C,O	104.8(2,2.0)	
					O 190.7(5)			
Al(o-tolyl)$_3$(Et_2O)	m	1164.8(2)		AlC_3O	C 199.0(4,5)	C,C	114.4(1,1.8)	32c
	$P2_1/n$	1403.3(2)	106.48(1)					
	4	1429.0(2)			O 192.8(3)	C,O	103.8(1,3.1)	
$Cs[Al(Me)_3NCS]$	m	884.9(4)		AlC_3N	C_{Me} 197(1,1)	C,C	114.4(5,10.9)	33
	$P2_1/c$	1379.8(5)	102.98(3)					
	4	794.3(4)			SCN 194(1)	C,N	103.8(4,5)	
$(TlMe_2)[Al(Me)_3NCS]$	m	1603.1(8)		AlC_3N	C_{Me} 197(4,5)	C,C	114(2,6)	34
	C2/m	1244.7(6)	106.17(5)					
	4	641.0(3)			SCN 208	C,N	102(2,2)	
$Rb[Al(Me)_3N_3]$	m	1000.3(5)		AlC_3N	C_{Me} 198.7(10,6)	C,C	113.8(5,2.0)	35
	$P2_1/n$	749.7(4)	108.70(3)					
	4	1180.6(5)			N_2N 194.4(6)	C,N	104.6(4,3.3)	
$Cs[Al(Me)_3N_3]$	or	802.7(9)		AlC_3N	C_{Me} 198(1,2)	C,C	114(1,1)	36
	Pbcn	1050.7(9)						
	4	1030.7(9)			N_2N 197(1)	C,N	107(1,1)	
$Al(Me)_3(MeCN)$	or	661.7(3)		AlC_3N	C_{Me} 201(1,1)	C,C	116	37
	Pnma	782.1(4)						
	4	1613.5(7)			N 202(1)	C,N	102	
$Al(Me)_3(qn)$	m	894(2)		AlC_3N	C_{Me} 201(1,1)	C,C	113.8(3,5)	38
	$P2_1/m$	1066(2)	106.19(10)					
(colourless)	2	684(2)			N 206(1)	C,N	104.5(3,1)	
$Al(Me)_3(tmor)$[c]	m	845.2(4)		AlC_3N	C_{Me} 197.5(6,4)	C,C	115.0(3,2.3)	39
	$P2_1/c$	2107.5(4)	90.37(2)		N 203.0(4)	C,N	103.1(2,1.7)	
	8	1226.7(2)		AlC_3N	C_{Me} 196.8(6,3)	C,C	114.8(3,2.6)	
					N 203.2(4)	C,N	103.3(2,1.4)	
$Al(Me_3SiCH_2)_3(Me_3N)$	tr	953.5(2)	88.03(1)	AlC_3N	C 198.6(4,3)	C,C	115.6(2,3)	40
	$P\bar{1}$	1091.3(2)	86.03(1)					
(white)	2	1227.3(2)	86.93(1)		N 205.8(3)	C,N	102.3(1,4)	
$Al(Me)_3(PPh_3)$	rh	1434.4(4)		AlC_3P	C_{Me} 198.1(2,0)	C,C	116.6	41
	$R\bar{3}$	-						
	6	1650.3(7)			P 253.5(1)	C,P	100.6(1)	
$Al(Me)_3(P(o\text{-tolyl}))$	rh	1497.8(1)		AlC_3P	C_{Me} 197.4(6,0)	C,C	113.9	41
	R_3C	-						
	4	3419.5(5)			P 258.4(2)	C,P	104.5(1)	
$Al(Me)_3(PMe_3)$				AlC_3P	C_{Me} 197.3(3)	C,C	117.1(8)	42
gas phase by electron diffraction								
					P 253(4)	C,P	100.0(1.3)	
$(NMe_4)[Al(Me)_3I]$	or	1408.7(6)		AlC_3I	C_{Me} 201(4,5)	C,C	115(2,3)	43
	Iba2	1425.1(6)						
	8	1374.2(5)			I 266(1)	C,I	103(2,5)	
$K[AlCl_3(Me)]$	or	1801(1)		$AlCl_3C$	Cl 216.8(11,10)	Cl,Cl	103.6(3,1.4)	44
	Pnma	689(1)						
	4	589(1)			C_{Me} 193.8(16)	Cl,C	114.8(4,2.3)	
$AlCl_3(tmcb)$	or	1566.4(8)		$AlCl_3C$	Cl 213.1(2,10)	Cl,Cl	109.3	45
	Pnma	1088.6(4)						
	4	722.2(2)			C 197.9(5)	Cl,C	109.1(2,9)	
$AlCl_3(C_{15}H_{27}P_3)$[c]	or	1461.9(3)		$AlCl_3C$	Cl not given			46
	$P2_12_12_1$	1702.9(7)						
(yellow)	8	1768.2(13)			C not given			

Table 2 (continued)

$[AlCl_3(\eta^1\text{-cp}^*)]$	tr	910.6(3)	99.73(2)	$AlCl_3C$	Cl	216.2(3,20)	not given		47
	$P\bar{1}$	970.5(3)	90.76(2)		C	202.0(6)			
$[Al(\eta^5\text{-cp}^*)_2]$	2	1872.7(5)	92.24(2)	AlC_{10}					
					C	215.5(8,18)[g]			
(colourless)									
$[AlCl_3Et]$	m	749.7(4)		$AlCl_3C$	Cl	211.9(6,4)	Cl,Cl	105.9(3,1.1)	48
	$P2_1/c$	2212.1(8)	94.99(4)						
$[Al(12\text{-}C\text{-}4)Cl_2]$	4	1233.9(5)			C_{Et}	223(3)	Cl,C	112.6(7,8.8)	
(colourless)									
$[AlCl_3Et]$	tr	841.4(3)	73.14(3)	$AlCl_3C$	Cl	216.3(4)	Cl,Cl	106.4(2,1.3)	48
	$P\bar{1}$	1219.3(4)	86.07(3)			251.7(4,1)			
$[Al([18]\text{-}C\text{-}6)Cl_2]$	2	1239.4(4)	81.52(3)		C_{Et}	193(1)	Cl,C	112.4(5,2)	
(colourless)									
$[AlCl_3Et]$	or	2130.6(9)		$AlCl_3C$	Cl	not given			49
	Pbca	1774.7(4)			C_{Et}	not given			
$[Al(b\text{-}[15]\text{-}C\text{-}5)Cl_2]$	8	1326.7(3)		AlO_5Cl_2	O[eq]	215(1,15)	Cl,Cl	169	
					Cl_{ax}	220.0(6,3)			
(colourless)									
$K[Al(PhO)_2(Me)_2]$	or	2048.7(6)		AlO_2C_2	O	180.0(3,0)	O,O	96.8(2)	50
	Pbcn	1012.9(4)					C,C	119.4(3)	
	4	725.9(3)			C_{Me}	196.8(5,0)	O,C	108.7(2)	
$Al(Me_3NO)(pbi)(Me)_2$	tr	851.7(4)	104.67(4)	AlO_2C_2	O	177.0(6)	O,O	106.7(3)	51
	$P\bar{1}$	1009.6(5)	106.97(4)			182.6(6)	C,C	117.3(3)	
(colourless)	2	1225.6(5)	98.10(4)		C_{Me}	196.2(12,0)	O,C	108.1(4,9.2)	
$Al(bht)(Ph_2CO)Me_2$	or	1913.3(3)		AlO_2C_2	O	173.1(8)	O,O	103.1(4)	16
	$Pn2_1a$	1463.8(2)			CO_{Ph}	190.7(8)	C,C	113.1(8)	
(colourless)	4	1002.2(1)			C_{Me}	195(1,1)	O,C	109.3(6,10.1)	
$Al(bht)(mt)Et_2$	m	2455.4(4)		AlO_2C_2	O_{bht}	174.9(5)	O,O	101.7(3)	4
	C2/c	1492.4(2)	91.01(1)		O^{mt}	188.7(6)	C,C	116.4(4)	
(colourless) at 173K	8	1521.6(2)			C_{Et}	196.4(9,6)	O,C	108.8(3,8.1)	
$Al(C_{34}H_{58}N_2P)(Me)_2$	m	1257.6(1)		AlN_2C_2	N	197.8(4,4)	N,N	74.9(1)[d]	52
	$P2_1/c$	1056.3(1)	101.08(1)		C_{Me}	197.0(6)			
	4	3006.1(2)							
$Al((2\text{-}NC_5H_4)_2P)(Me)_2$	m	1060.1(1)		AlN_2C_2	N	192.7(1,3)	N,N	99.0(1)[e]	53
	$P2_1/c$	864.4(1)	104.97(1)		C_{Me}	not given	C,C	119.5(1)	
(red) at 153K	4	1414.9(1)							
$Al((Me_3Si)_2CMe)(Me)_2$	tr	855.8(1)	92.12(1)	AlN_2C_2	N	192.9(2,1)	N,N	70.4(1)[d]	54
	$P\bar{1}$	934.0(1)	103.64(1)		C_{Me}	194.2(4,1)	C,C	120.8(2)	
	2	1128.3(2)	105.56(1)				N,C	113.8(1,8)	
$Al(tipa)(Me)_2$	tr	959.3(2)	104.88(5)	AlN_2C_2	N	186.9(6)	N,N	84.3(3)[i]	55
	$P\bar{1}$	1013.5(1)	109.54(5)			197.9(6)	C,C	115.8(4)	
(red)	2	1127.4(2)	102.69(7)		C_{Me}	196.0(9,9)	N,C	113.0(3,3.8)	
$Al(mpa)(Me)_2$	tr	984.4(1)	74.15(1)	AlN_2C_2	N	186.3(2)	N,N	84.7(1)	55a
	$P\bar{1}$	1026.3(2)	70.14(1)			197.3(2)	C,C	114.8(1)	
(yellow)	2	1131.7(1)	63 70(1)		C_{Me}	195.8(3,2)	N,C	113.2(1,4.7)	
$Al\{PhN(CH_2)_2NH_2\}Me_2$	or	1030.4(3)		AlN_2C_2	N	193.5(10,45)	N,N	86.2(4)	55b
	$P2_12_12_1$	1317.2(5)			C_{Me}	196(1,0)	C,C	118.0(6)	
(colourless)	4	855.2(3)					N,C	111.9(5,4.3)	
$Al(dpta)(Bu)_2$	m	1243.7(7)		AlN_2C_2	N	196.6(3,5)	N,N	64.7(1)[d]	56
	$P2_1/c$	1232.7(3)	98.29(5)		C_{Bu}	195.4(4,2)	C,C	121.2(1)	
(orange)	4	1341.3(9)					N,C	114.5(1,6.4)	
$[Al(tmen)(Me_3C)_2]$	tr	852.6(4)	82.21(3)	AlN_2C_2	N	204.3(4,4)	N,N	87.2(2)[f]	57
	$P\bar{1}$	1286.8(6)	74.45(2)		C	200.6(6,0)	C,C	117.8(2)	
$[Al(Me_3C)_2Br_2]$	2	1455.2(7)	83.99(3)				N,C	112.0(2,2.9)	
				AlC_2Br_2	C	198.2(6,1)	C,C	121.1(2)	
(colourless)					Br	238.6(2,2)	Br,Br	101.73(6)	
							C,Br	108.1(2,9)	
$Al(opn_2)(Ph)_2$	m	1114.2(1)		AlN_2C_2	N	192.7(2,4)	N,N	78.86(8)[d]	58
	$P2_1/n$	1776.3(2)	90.97(1)		C_{Ph}	197.8(2,15)	C,C	113.15(9)	
at 153K	4	1803.0(2)					N,C	115.1(1,2.4)	
$[Al(Me)_2Cl_2][Te(Me)_3]$	m	116.30(3)		AlC_2Cl_2	C_{Me}	198.3(13,10)	C,C	119.2(6)	59
	$P2_1/n$	1259.5(4)	89.97(2)				Cl,Cl	103.4(2)	
(colourless)	4	840.9(2)			Cl	222.1(4,8)	C,Cl	111.0(6,8.2)	
$[Al(Me)_2Cl_2]$	or	1131.3(7)		AlC_2Cl_2	C_{Me}	not given			60
	Pnma	1090.7(5)							
$[Yb([15]\text{-}C\text{-}5)Cl_2]$	4	1771.6(7)			Cl	not given			
$[Al(Et)_2Cl_2]$	or	1270.5(2)		AlC_2Cl_2	C_{Et}	not given			61
	Pnma	1252.2(4)							
$[V_2(PMe_3)_6Cl_3]$	4	2855.4(9)			Cl	not given			
$[Al(Et)_2Cl_2]$	tg	2322.0(5)		AlC_2Cl_2	C_{Et}	not given			61
	$P4_2/nmc$	-							
$[V_2(PMe_3)_6Cl_3]$	8	1864.0(3)			Cl	not given			
$Al(Me)_2(C_2H_{12}B_9)$	tr	746.0(6)	115.37(5)	AlC_2B_2	C_{Me}	195.8(15,2)	C,C	131.9(6)[h]	62
	$P\bar{1}$	646.2(7)	97.02(11)				B,B	46.1(6)[h]	
(colourless) at 173K	1	698.5(4)	87.61(10)		B	231.8(18,20)	C,B	112.0(6,2.1)	
$Cs[Al(Me)_2I_2]$	or	1257.7(4)		AlC_2I_2	C_{Me}	198(2,0)	C,C	115(1)	63
	$C222_1$	931.1(3)					I,I	102.3(2)	
(p-xylene)	4	1425.6(4)			I	264.7(4,0)	C,I	110(1,4)	

Table 2 (continued)

$Cs[Al(Me)_2I_2]$	or			AlC_2I_2	C_{Me} 199(2,0)	C,C 115.4(10)		64
	Ccmm					I,I 102.4(3)		
(p-xylene)	4				I 264.4(5,0)	C,I 109.6(7)		
$Al(mesO)_2$	m	1176.7(2)		AlO_2NC	O 171.8(8,4)	O,O 111.1(3)		65
	$P2_1/n$	1023.2(2)	105.43(2)		N_{py} 196.1(7)	O,N 99.5(3,1.2)		
$(3,5\text{-}Me_2py)(Me)$	4	2156.2(5)				O,C 117.1(4,1.6)		
					C_{Me} 194.6(10)	N,C 109.4(4)		
$Al(Me)_2(bht)(py)$	m	1019.3(7)		AlC_2ON	C_{Me} 196.0(6,4)	C,C 114.3(3)		65
	$P2_1/n$	1798.9(10)	96.44(6)		O 174.0(4)	C,O 116.2(2,7)		
(colourless)	4	1224.9(11)			N_{py} 199.3(5)	C,N 103.0(2,3.0)		
						O,N 101.3(2)		
$Al(Me)_2(bht)(NH_3)$	m	928.7(11)		AlC_2ON	C_{Me} not given	not given		66
	$P2_1/n$	1209.6(5)	96.70(7)		O 174.3(4)			
(colourless) at 193K	4	1683.6(9)			H_3N 201.5(5)			
$Al(Bu^t)_2(Et_2O)$	tr	948.8(3)	92.07(3)	AlC_2OP	C_{Bu} 202.1(6,4)	C,C 116.3(3)		67
	P$\bar{1}$	1141.6(5)	96.80(2)		O 195.0(6)	C,O 106.1(3,3.2)		
$((Ph_3Si)(Pr^i{}_3C_6H_2)P)$	2	2038.3(6)	103.17(2)		P 241.6(3)	C,P 112.7(2,3.7)		
						O,P 101.0(2)		
$Al(Me)_2(bht)(PMe_3)$	m	742.7(2)		AlC_2OP	C_{Me} 197.0(4,0)	C,C 111.7(3)		68
	$P2_1/m$	1573.5(2)	96.37(2)		O 173.6(5)	C,O 117.5(1,5)		
	2	943.0(3)			P 249.9(3)	C,P 101.9(1,0)		
						O,P 104.5(2)		
$Al(Ph)_2(thf)$	tr	962.2(3)	78.75(2)	AlC_2OSi	C_{Ph} 198.6(7,5)	C,C 112.6(3)		69
	P$\bar{1}$	1313.5(3)	82.00(2)		O 192.7(4)	C,O 100.8(2,1.7)		
$((Me_3Si)_3Si)$ (white)	2	1335.4(3)	78.96(2)		Si 247.9(3)	C,Si 116.0(2,1.4)		
						O,Si 108.1(2)		
$Al(Ph)_2(opns)$	m	911.0(5)		AlC_2NS	C 197.2(2,3)	C,C 110.67(9)		58
	$P2_1/c$	2141(2)	106.83(3)		N 189.4(2)	C,N 118.9(1,2.7)		
at 63K	4	1643(1)			S 235.43(8)	C,S 111.5(1,8)[d]		
						N,S 81.72(5)[d]		
$Al(Me)_2(Me_3N)I$	or	1259(1)		AlC_2NI	C_{Me} 195	C,C 120		70
	Pnma	1075(1)			N 202	C,I 110		
(colourless)	4	758(1)			I 258	N,I 102		
$Al(Bu^i)_2Cl\{(Me_3Si)_3P\}$	m	1498.6(3)		AlC_2ClP	C_{Bu} 196(1,1)	C,C 122.5(4)		71
	$P2_1/c$	1148.9(2)	119.57(2)		Cl 217.9(4)	C,Cl 110.1(3,1.1)		
	4	1857.0(4)			P 250.4(3)	C,P 106.1(3,1)		
						Cl,P 99.1(1)		
$Al(Me)_2(PPh_3)(PhSe)$	tr	977.7(2)	82.84(2)	AlC_2PSe	C_{Me} 195.6(1,3)	C,C 118.0(1)		72
	P$\bar{1}$	981.7(3)	77.53(2)		P_{Ph} 251.7(1)	C,P 102.6(1,6)		
	2	1412.5(3)	66.40(2)		Se_{Ph} 239.4(1)	C,Se 112.4(1,6.1)		
						P,Se 107.1(1)		
$[AlCl_2(bht)(Me)]$	or	1525.1(4)		$AlCl_2OC$	Cl 219.5(2,5)	Cl,Cl 101.2(1)		68
	$P2_12_12_1$	1521.8(5)			O 171.3(4)	Cl,O 110.4(1,9)		
$(NHMe_3)$	4	968.0(4)			C_{Me} 199.5(5)	Cl,C 108.2(2,2.9)		
						O,C 117.2(2)		
$AlCl_2(thf)(mes)$	tr	869.7(3)	69.40(2)	$AlCl_2OC$	Cl 214.8(5)	Cl,Cl 110.3(1)		73
	P$\bar{1}$	931.7(2)	74.04(2)		O_{thf} 185.2(1)			
(colourless)	2	980.1(2)	86.32(2)		C_{mes} 196.9(1)	Cl,C 114.4(1,1.1)		
$[AlCl_2(Et)\{(Me_3Si)_3P\}]$	or	1323.4(2)		$AlCl_2CP$	Cl 215.0(4,6)	Cl,Cl 107.8(2)		71
	$Pca2_1$	1314.7(2)			C_{Et} 193(1)	Cl,C 113.1(4,3)		
(colourless)	4	1304.3(2)				Cl,P 104.3(1,6)		
					P 241.5(3)	C,P 113.6(4)		
$[Al(PEt_3)_2(Et)$	m	972.2(3)		AlP_2CB	P 256.1(2,7)	P,P 95.25(5)		14a
	$P2_1/m$	1613.5(4)	90.246(9)		C_{Et} 197.4(4)	P,C 101.6(1,3.9)		
$(7,8\text{-}C_2B_9H_{11})]$	4	1698.4(5)				P,B 101.66(13)		
					B 212.8(5)	C,B 141.23(19)		
(colourless)								
$[AlBr_2(Et_2O)(trip)]$	tr	772.1(7)	8336(2)	$AlBr_2OC$	Br 231.1(6)	Br,Br 103.4(2)		73
	P$\bar{1}$	883.7(5)	8855(2)		O 186.5(11)			
(colourless)	2	1742.7(8)	7250(2)		C 197.6(14)	Br,C 119.1(4,5.1)		
$AlBr_2(dmap)$	m	953.5(3)		$AlBr_2NC$	Br 231.3(2,3)	Br,Br 108.45(8)		74
	$P2_1/c$	1020.9(4)	92.70(2)		N 200.3(5)	Br,N not given		
	4	1262.2(5)			C 196.7(6)	Br,C 119.3(2,1.4)		
						N,C 89.3(3)[f]		

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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] Two crystallographically independent molecules.

[d] Four-member metallocyclic ring.

[e] Six-member metallocyclic ring.

[f] Five-member metallocyclic ring.

[g] Centroids of the carbon ring.

[h] Three-member metallocyclic ring.

[i] Refs. [4,10–13,14a,14b,14c,15–31,32a,32b,32c,33–54,55a,55b,56–74] are to be found in the reference list.

Table 3
Crystallographic and structural data for five-coordinate organo-aluminium compounds [a,g]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore. Al out of plane pm	Al-L [pm]		L-Al-L [°]		Ref
$Al^1(cp^*)$ gas phase by electron diffraction				AlC_5	C^b	238.8(7) {206.3(9)}[c]			75
$[Al\{\sigma\text{-}OC_6H_4(MeO)CO\}_2(CH_3)]$ (colourless)	m C2/c 4	1614.41(24) 770.34(10) 1479.23(21)	 112.756(11) 	AlO_4C	H_3C_{eq} O_{eq} O_{ax}	194.1(5) 177.3(2,0) 196.8(1,0)	C,O_{eq}[b] O_{eq},O_{eq} O_{ax},O_{ax}	120.86(7) 118.2(10) 170.09(9)	76
$Al(oep)(CH_3)$	tr P$\bar{1}$ 2	1043.2(2) 1072.7(3) 1595.9(5)	72.17(3) 72.93(3) 82.40(2)	AlN_4C 46.5(1)	N_{eq} H_3C_{ax}	203.3(3,3) 194.2(3)	N,N N,Cl	87.0(1,4)[d] 103.2(1,6)	77
$[Al(C_{22}H_{22}N_4)(Et)].½C_6H_6$ (orange)	m $P2_1/n$ 4	811.4(1) 2215.9(3) 1359.9(2)	 92.90(2) 	AlN_4C 57	N_{eq} $\underline{Et}C_{ax}$	196.7 197.6(3)	not given		78
$[Al([18]\text{-}C\text{-}6)(Me)_2]$ $[AlMe_2Cl_2]$	m $P2_1/n$ 4	1139.7(4) 1267.0(4) 1707.5(6)	 93.08(4) 	AlO_3C_2 AlC_2Cl_2	O C_{Me} C_{Me} Cl	192.9(5) 218.1(5) 243.5(5) 192.7(7,12) 202.9(7,24) not given	C,C	140.6(3)	79
$Al(tedta)(CH_3)_2$ (colourless)	m $P2_1/c$ 2	815.5(2) 764.2(2) 1415.8(2)	 93.78(2) 	AlN_3C_2	H_3C_{eq} N_{eq} N_{ax}	199(1,0) 184(1) 235.0(8,0)	C,C C,N_{eq} C,N_{ax} N_{eq},N_{ax} N_{ax},N_{ax}	115.9(8) 122.1(4) 96.1(4,4) 78.5(2)[e] 157.0(5)	80
$[Al(dppmp)_3].1¼$toluene	tr P$\bar{1}$ 2	1248.2(2) 1613.7(3) 1714.4(2)	62.61(1) 88.08(1) 67.28(1)	AlC_3P_2	C_{eq} P_{ax}	201.1(6,18) 272.9(3,53)	C,C C,P P,P	119.9(2,5.5) 78.0(2,1.2)[e] 96.6(2,4.6) 164.8(1)	81
$Al(mes)Br_2$ (colourless)	m C2/c 4	1422.7(6) 1237.4(4) 1212.0(3)	 111.47(2) 	AlH_2Br_2C	H Br C	211 228.1(2,0) 195.3(8)	Br,Br Br,C	111.1(1) 124.4(1)	73
$[Al(spiro)].1½C_7H_8$ (colourless)	m $P2_1/n$ 4	767.5(6) 1191.9(8) 3302.5(2)	 94.75(13) 	AlO_2N_2C	O N C	200.6(9,35) 186.5(10,25) 193(1)	O,O N,N O,N O,C N,C	78.7(4)[e] 76.2(4)[f] 89.7(4,1.7)[d] 138.4(4,13.9) 102.0(6,5.3) 119.5(6,8.4)	82
$Al(salen)(Me_3)$ (yellow)	m $P2_1/n$ 4	1175.1(8) 1222.7(9) 1260.9(9)	 98.52(6) 	AlO_2N_2C not given	O N C_{Me}	180.9(7,15) 203.7(8,4) 195(1)	O,O N,N O,N O,C N,C	89.0(3) 77.7(3)[e] 87.9(3,1)[d] 145.0(3,11.9) 110.8(4,6.9) 103.2(4,5.4)	56
$Al(salen)(Et)$ (yellow)	or $P2_12_12_1$ 4	693.0(3) 1018.6(4) 2309.2(8)	 	AlO_2N_2C 54.0	O_{eq} N_{eq} $\underline{Et}C_{ax}$	181.5(5,15) 202.0(6,7) 196.6(7)	O,O N,N O,N O,C N,C	88.4(3) 79.3(3)[e] 87.1(3,1.0)[d] 146.6(3,4.5) 110.1(3,2.8) 102.5(3,2.0)	83
$Al(dmap)_2(CH_3)$	or Pbca 8	1345.8(2) 957.2(1) 2848.2(5)	 	AlC_3N_2	H_3C_{eq} C_{eq} N_{ax}	197.8(3) 201.3(2,6) 226.8(2,23)	C,C C,N N,N	120.0(1,3.4) 79.2(1,3)[e] 93.4(1,6) 173.00(7)	84
$[Al(dmap)(Pr^iNH_2)Cl_2].thf$	m $P2_1/c$ 4	934.7(3) 1851.6(5) 987.5(3)	 117.90(2) 	AlN_2Cl_2C	Cl_{eq} C_{eq} N_{ax}	219.6(1,15) 198.7(1) 217.1(1) 207.0(1)	Cl,Cl Cl,C C,N N,N	115.19(2) 122.1(1,5.9) 81.95(4)[e] 175.50(5)	84

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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 to ring centre distance.
[d] Six-member metallocyclic ring.
[e] Five-member metallocyclic ring.
[f] Four-member metallocyclic ring.
[g] Refs. [56,73,75–84] are to be found in the reference list.

ronment. Although a 'hard' Lewis acid itself, an ability to form stable bonds with softer donor ligands is observed in the organometallic derivatives (methyl predominating) compared to harder donor atoms in the inorganic derivatives (chlorine predominating).

2.3. Coordination number five

Pentacoordinated organoaluminium compounds are mostly colourless with some yellow and orange examples. The crystallographic and structural data for these compounds are given in Table 3. There are 13 examples, comparable to the 15 examples found in the coordination compounds [1].

A gas-phase electron diffraction study of Al(I)cp* showed the molecule to be monomeric [75]. Structural refinements based on C_{5v} symmetry yielded an Al–C distance of 238.8(7) pm, and an Al–cp(centroid) distance of 206.3(9) pm. The other 12 pentacoordinate derivatives are of the more usual geometries, square pyramidal and trigonal bipyramidal.

Four derivatives [56,77,78,83] exhibit square pyramidal geometry about the aluminium(III) atom. The square basal plane is created only by macrocyclic ligands in these derivatives, N_4 donors [77,78] and $N_2 + O_2$ donors [56,83]. In all four examples the apical position is occupied by a C-donor (Me [56,77], Et [78,83]). As the aluminium atom moves away from the square plane towards the apical ligand, the metal–apical ligand distance also increases, for example: 46.5(1) pm and 194.2(3) pm [77]; 54.0 pm and 196.6(7) pm [83]; 57 pm and 197.6 pm [78] respectively.

The L_{eq}–Al–L_{eq} angles in the square plane are in the range 77.7 to 90° and 133 to 157°, indicating a consider-

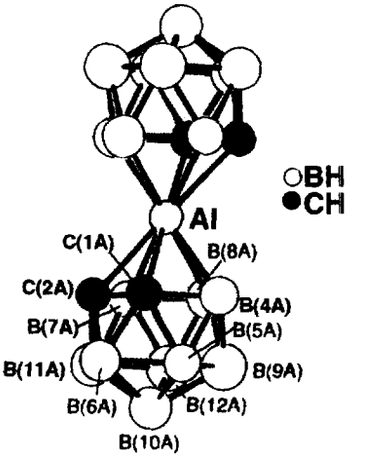

Fig. 1. Structure of the $[Al(\eta^3\text{-}C_2B_9H_{11})_2]^{2-}$ sandwich anion [88].

Table 4
Crystallographic and structural data for six- and higher-coordinate organo-aluminium compounds [a,e]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Al-L [pm]		L-Al-L [°]		Ref
$Al(PhNNNPh)_2(3,5\text{-}Me_2py)Me_3$	m $P2_1/c$ 4	963.1(3) 1723.5(6) 1802.6(8)	 96.16(3) 	AlN_5C	N[b] 200.6 - 205.1(2) 215.5(2) C_{Me} 199.9(3)		N,N[b] 147.3(1) 159.2(1)		85
$(AsPh_4)_2[Al(B_{11}H_{11})(Me_3)]$	m $P2_1/n$ 4	1027.64(46) 2171.10(75) 2194.54(41)	 98.68(2) 	AlB_5C	B 213.1 - 214.0(4) C_{Me} 194.2(4)		B,C 131.5 - 134.7(2)		86
$Al(1,2\text{-}C_2B_9H_{11})(Et)$	or Pnma 4	1630.4(15) 753.3(7) 939.8(6)	 	AlC_3B_3	C_{Et} 193.0(4) C 217.3(7,0) B 213.7(7,1)		C,C 42.1(3)[c] 119.9(4) C,B 46.2(3)[c] 78.9(3,1.4) 148.0(5,10.2) B,B 49.6(3)[c] 83.0(3)		87
$Al([15]\text{-}C\text{-}5)(Me_3)_2$	or Pnma 4	1118.4(3) 1092.8(8) 1771.7(9)	 	AlO_5C_2 (?)	O not given C_{Me} 200(1,1)		C,C 178(1)		79
$Tl[Al(2^5\text{-}C_2B_9H_{11})_2]\cdot$ $(tol)_2$[d] (colourless)	tr $P\bar{1}$?	1134.7(2) 1174.8(2) 1270.8(2)	92.429(6) 90.876(6) 93.343(5)	AlB_6C_4 AlB_6C_4 AlB_6C_4	B 220(2,6) C 230(2,1) B 218(2,4) C 227(2,1) B 220(2,9) C 226(2,3)		not given		88

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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] Three-member metallocyclic ring.
[d] Three crystallographically independent molecules present.
[e] Refs. [79,85–88] are to be found in the reference list.

Table 5
Crystallographic and structural data for dimeric organo-aluminium compounds [a,i]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Al-L [pm]	Al-Al [pm] Al-L-Al [°] μL-Al-μL [°]	L-Al-L [°]	Ref
$[Al_2(trip)_4][Li(tmeda)_2]$. Et_2O[c] (dark green) at 130K	tr P$\bar{1}$ 4	1536.2(14) 1940.1(2) 2801.1(2)	71.873(7) 83.823(7) 79.824(7)	AlC_2	C[b] 202.1(1)	247.0(2)	C,C[b] 107.3(9) 116.8(7)	90
$[Al_2\{(Me_3Si)_2CH\}_4]$ $[Li(tmeda)_2]$ (black-violet)	tr P$\bar{1}$ 2	1210.0(2) 1323.9(2) 2281.7(3)	106.50(1) 98.03(1) 109.07(1)	AlC_2	C 204.0(6,2)	253(1)	C,C 111.9(2) C.Al 124(1,3)	91
$[Al_2\{(Me_3Si)_2CH\}_3\{(Me_2Si)$ $C(H)_2(Me_3Si)CH\}]$ $[Li(tmeda)_2].Et_2O$ at 193K	m $P2_1/n$ 4	1273.5(3) 3378.2(4) 1576.7(3)	93.78(1)	AlC_2 AlC_3	C 201.9(4,16) C 205.4(4,16)	264.1(2)	C,C 115.0(2) C,Al 94.8(1) 149.2(1) C,C 111.6(1,6.8) C,Al 95.4(1,9.8) 149.2(1)	92
$Al_2(trip)_4$ (yellow green) at 130K	or Pban 2	1303.7(4) 1914.6(6) 1262.8(4)		AlC_2	C 199.6(3)	264.7(3)	C,C 113.7(2)	90
$Al_2\{(Me_3Si)_2CH\}_4$ (colourless) at 153(3)K	tr P$\bar{1}$?	975.0(3) 1208.7(3) 2068.4(6)	81.28(2) 85.19(2) 67.22(2)	AlC_2	C 198.2(3,6)	266.0(1)	C,C 116.7(1) C,Al 121.6(1,5.5)	93
$[Al_2\{(Me_3Si)_2CH\}_3\{(Me_2Si)$ $C(H)_2(Me_3Si)CH\}]$ $[Li(tmeda)_2]$ (yellow green) at 173K	m $P2_1/n$ 4	1409.4(3) 3133.4(7) 1427.7(2)	93.21(1)	AlC_2 AlC_2H	C 200.8(6,4) C 206.4(6,0) H 166(6)	266.7(3)	C,C 113.8(3) C,Al 121.8(2,5.9) C,C 111.3(8) C,H 113(2,1) C,Al 113.9(2,10.5) H,Al 91(2)	94
$[Al_2\{(Me_3Si)_2CH\}_4(Me)]$ $[Li(tmeda)_2]$ (yellow green) at163K	or $P2_12_12_1$ 4	1440.4(2) 2039.2(2) 2344.4(3)		AlC_2 AlC_3	C 203.6(8,12) C 206.5(7,2) C_{Me} 201.2(8)	275.2(3)	C,C 107.9(3) C,Al 125.5(3,3) C,C 111.3(3,4.3) C,Al 101.0(3,5.4) 119.9(2)	94
$[Al(\mu\text{-}H)(H)(dmap)]_2$ (colourless)	m $P2_1/n$ 4	900.7(1) 1113.1(1) 1027.9(1)	105.64(1)	AlH_3NC	μH 168.8(3) 192.8(3) H 152.1 N 210.2(4) C 197.4(5)	- not given not given	μH,H 115.6(1) μH,C 118.6(1) μH,N 170.4(2) H,C 124.9(1)	74
$[Al(\mu\text{-}PhMe_2SiO)(Me)_2]_2$ (colourless) at 193(1)K	m $P2_1/n$ 4	797.0(3) 2456.3(10) 1332.2(4)	105.05(3)	AlO_2C_2	μO 185.4(2,4) C_{Me} 194.9(5,9)	276.0(2) 96.3(1,2) 83.7(1,1)	C,C 121.3(1,2) O,C 111.8(1,1.4)	95
$[Al(\mu\text{-}Me_3SiO)(Me)_2]_2$ (colourless)	m C2/m 2	1135.0(5) 1310.1(2) 691.8(4)	111.60(2)	AlO_2C_2	μO 184.3(4,25) C_{Me} 194.0(10,7)	not given	not given	96
$[Al_2(\mu\text{-}HC{\equiv}CSi(H)_2O)_2$ $(Me)_3Cl]$ (colourless) at 199K	tr P$\bar{1}$ 1	688.0(2) 736.1(2) 795.1(2)	102.66(2) 94.20(2) 100.25(2)	AlO_2C C/Cl	μO 185.1(2,1) C 193.1(3) C/Cl 208.5(2)	277.6(2) 97.2(1) 82.8(1)	not given	97
$[Al(\mu\text{-}bo)(Me)_2]_2$ (colourless)	m $P2_1$ 2	726.1(7) 1449.4(8) 1293.8(7)	93.63(7)	AlO_2C_2	μO 184.1(5,20) C_{Me} 195.6(7,11)	277.9(3) 98.0(3,7) 82.0(2,2)	C,C 121.9(3) C,O 111.4(3,2.5)	98
$[Al(\mu\text{-}mto)(Me)_2]_2$ (colourless)	or $P2_12_12_1$ 4	1009.7(1) 1048.5(1) 2692.0(1)		AlO_2C_2	μO 184.1(3,6) C_{Me} 196.3(4,5)	280.7(2) 99.4(1,2) 80.6(1,0)	C,C 118.8(2,9) C,O 112.8(2,2.5)	98
$[Al(\mu\text{-}mto)(Bu^i)_2]_2$[c] (colourless)	tr P$\bar{1}$ 2	1083.8(4) 1279.2(6) 1578.7(7)	81.56(4) 83.04(4) 73.01(3)	AlO_2C_2 AlO_2C_2	μO 184.2(8,10) C 195(1,6) μO 184(1,1) C 195(2,2)	281.5(3) 99.8(4,2) 80.3(4,1) 284.3(6) 101.2(4,0) 78.8(4,6)	C,C 122.8(6,1.1) C,O 111.5(5,4.8) C,C 121.5(6,8) C,O 112.2(5,5.8)	98
$[Al(\mu\text{-}tbbo)(Me)_2]_2$ (colourless)	tr P$\bar{1}$ 1	1004.3(2) 1039.9(2) 1244.6(2)	103.50(1) 98.41(2) 113.63(1)	AlO_2C_2	μO 185.0(3,9) C 184.9(6,10)	284 100.2(1) 79.8(1)	C,C 114.8(2) C,O 114.1(2,4.4)	99
$[Al(\mu\text{-}ampo)(Me)_2]_2$ (colourless)	m $P2_1/n$ 2	986.2(2) 968.2(2) 1341.7(2)	97.98(1)	AlO_2C_2	μO 186.1(3,2) C 194.7(6,4)	286.6(3) 100.8(1,0) 79.2(1,0)	C,C 115.3(2) C,O 114.4(2,7)	100
$[Al(\mu\text{-}dmp)(Bu^i)_2]_2$ (colourless)	tr P$\bar{1}$ 1	919.0(1) 984.3(1) 1027.2(1)	72.67(1) 77.22(1) 72.94(1)	AlO_2C_2	μO 187.3(2,2) C_{Bu} 197.1(3,2)	289.9(1) 100.5(1) 78.5(1)	μO,C 114.4(1,2.1) C,C 115.6(1)	5
$[Me(\mu\text{-}(MeO)(CH_2)_2O)$ $(Me)_2]_2$ (colourless)	m $P2_1/n$ 2	748.57(6) 1431.8(1) 789.40(4)	102.223(5)	AlO_3C_2	μO 186.0(3,33) O 226.9(3) C_{Me} 195.1(5,11)	292.4(2) 103.7(2) 76.3(2)	C,C 120.8(2) C,μO 90.7(2,1.4) C,O 118.8(2,6)	101
$[Al(\mu\text{-}C_6F_5O)(Me)_2]_2$ (colourless)	or Cmcm 4	1105.8(2) 1690.8(2) 1076.4(2)		AlO_2C_2	μO 189.6(5,16) C_{Me} 192.0(7,0)	295.1(5) 102.3(3,1.1) 77.7(2)	C,C 127.5(3) C,O 111.6(2)	106

Table 5 (continued)

[Al(μ-mtp)(Me)$_2$]$_2$[c]	tr	982.8(2)	62.15(2)	AlO_2C_2	μO 186.5(6)	297.7(3)	C,C 127.5(4)	103
	PT	1354.7(2)	87.26(2)		194.6(6)	102.7(3)	C,O not given	
(colourless)	3	1416.4(2)	75.05(2)		C_{Me} 195.2(8,18)	77.3(3)		
				AlO_2C_2	μO 186.1(6,5)	298.5(3)	C,C 131.2(4,4)	
					O 197.2(6,9)	102.3(3,5)	C,O not given	
					C_{Me} 194.9(9,24)	77.6(3,1)		
[Al(μ-eph)(Me)$_2$]$_2$	tg	861.4(1)		AlO_2C_2N	μO 190.5(7,41)	300.0(4)	C,C 109.3(4,9.3)	104
	$P4_12_12$	-			N 219.3(8)	104.0(3)	C,O 99.0(3,1.0)	
(colourless)	4	3534.8(5)			C_{Me} 199.4(9,5)	74,8(3)	120.7(3,7.0)	
							C,N 95.0(3.4.3)	
							O,N 78.5(3)[d]	
[Al(μ-mtp)(Bu^i)$_2$]$_2$	tr	940.8(2)	83.66(4)	AlO_2C_2	μO 187.0(2)	300.5(1)	C,C 124.3(1)	103
	PĪ	979.6(4)	68.69(3)		196.6(2)	103.1(1)		
(colourless)	1	1050.9(4)	66.07(3)		C_{Bu} 197.1(4,5)	76.86(9)		
[Al(μ-mop)(Et)$_2$]$_2$	m	797.33(9)		AlO_2C_2	μO 185.9(3)	301.8(2)	C,C 123.2(12)	103
	$P2_1/n$	939.84(8)	101.06(1)		195.2(3)	104.7(1)		
(colourless)	2	1593.5(1)			C_{Et} 195.5(5,3)	73.3(1)		
[Al(μ-mop)(Bu^i)$_2$]$_2$	m	903.7(2)		AlO_2C_2	μO 186.1(1)	302.3(8)	C,C 123,97(11)	103
	$P2_1/n$	1942.7(3)	100.71(1)		195.0(1)	105.0(6)		
(colourless)	2	933.2(2)			C_{Bu} 196.9(2,3)	75.0(6)		
[Al(μ-pmo)(Bu^i)$_2$]$_2$	tr	994.2(1)	57.28(1)	AlO_2C_2N	μO 189.4(5,41)	302.4(4)	C,C 119.1(3)	105
	PĪ	1009.87(7)	71.77(1)		N 213.0(5)	105.9(2)	C,O 109.7(3,16.1)	
(colourless)	1	1015.0(1)	67.75(1)		C_{Bu} 199.4(7,20)	74.1(2)	C,N 95.2(3,1.0)	
							O,N 77.7(2)[d]	
							151.7(2)	
[Al(μ-pbia)(Me)$_2$]$_2$	or	1583(2)		AlO_3C_2	μO 192.2(6,64)	305.5	C,C 119.4(5)	106
	Pcca	1261(1)			O 204.5(7)	105.3(3)	C,O 103.7(4,19.3)	
(colourless)	4	1766(1)			C_{Me} 196.4(13,2)	73.3(3)	O,O 85.1(3)[d]	
							158.3(3)	
[Al(μ-Me$_2$N(H)CC(MeO)O)	m	809.5(1)		AlO_2C_2N	μO 185.3(3)	-	C,C 122.9(2)	107
	$P2_1/n$	1374.7(1)	104.41(1)		205.5(3)	107.0(1)	C,O 100.0(2,17.1)	
(Me)$_2$]	2	964.1(1)			N 226.0(3)	73.0(1)	C,N 97.1(2,5)	
					C_{Me} 195.1(5,1)		O,N 79.6(1)[d]	
(colourless)							152.6(1)	
[Al(μ-quo)(Et)$_2$]$_2$	m	1813.2(3)		AlO_2C_2N	μO 186.6(9,3)	311.5	C,C 122.5(5,2.5)	108
	$P2_1/c$	978.4(5)	112.06(1)		199.8(9,4)	107.4(4,1)	C,O 108.4(5,12.1)	
(pale yellow)	4	1519.1(2)			N 213.1(9,5)	75.6(4,2)	C,N 95.4(5,2.1)	
					C_{Et} 195.7(14,36)		O,N 79.2(4,2)[d]	
							151.7(4,5)	
[{Me(μ-Ph$_2$N)Al}$_2$	m	1606.9(6)		AlN_3C	μN 199.1(4,1)	268.3	not given	109
	$P2_1/c$	1305.3(5)	97.57(2)		N 184.2(3)	84.6(1,1)		
{NPh(μ-C_6H_4)}]	4	1642.4(1)			C_{Me} 194.7(4)	85.5(1,2)		
				AlN_2C_2	μN 199.7(4,5)			
(colourless)					C 195.5(4)			
					C_{Me} 195.4(4)			
[(CF$_3$CH$_2$NH$_2$)$_2$Si(NCH$_2$CH$_3$)$_2$	tr	920.39(9)	68.8(7)	AlN_3C	μN 197.0(3,37)		μN,μN 81.6(1)	110a
	PĪ	943.32(2)	86.9(4)		N 183.1(3)		μN,C 116.8(1)	
Al(Me)]$_2$ (colourless)	1	1235.4(1)	62.6(4)		C_{Me} 194.4(4)		N,C 122.3(1)	
[Al(μ-tmor)(Et)$_2$]$_2$	m	716.7(1)		AlN_2C_2	μN 197.6(5,20)	277.7(3)	N,C 113.4(2,4.4)	39
	$P2_1/c$	1354.7(2)	96.74(1)		C_{Et} 197.7(6,9)	89.3(2,1)	113.0(3,6)	
(colourless)	4	1622.7(2)				87.8(2,2)		
[Al(μ-Pr^{i}NH)(Me)$_2$]$_2$[e]	tr	858.6(3)	107.48(3)	AlN_2C_2	μN 195.9(5,7)	278.9	C,C 120.6(3)	110b
	PĪ	1136.6(5)	90.52(2)	(trans)	C_{Me} 196.4(9,2)	90.0(2,8)	C,N 110.7(3,2.6)	
(colourless)	3	1344.0(5)	99.21(3)			90.0		
				AlN_2C_2	μN 194.9(5,13)	280.0	C,C not given	
				(cis)	C_{Me} 195.6(8,16)	91.9(2,4)	C,N 110.8(2,1.6)	
						87.2(2,3)		
[Al(μ-$C_6H_{16}NSi_2$)(Me)$_2$]$_2$	or	1539.3(3)		AlN_2C_2	μN 200.5(3,0)	279.0(1)	C,C 104.9(2)	111
	Pbca	1298.7(2)			C_{Me} 195.9(4,10)	not given	C,N 116.6(2,1.3)	
(colourless)	4	1318.9(4)				not given		
[Al{μ-(CH$_2$O)$_2$C(CH$_2$CH$_2$)N)	m	897.0(2)		AlN_2C_2	μN 196.8(3,13)	280.1	C,C 118.7(2)	112
	$P2_1/c$	968.3(2)	103.18(2)		C_{Me} 194.9(4,0)	not given	C,N 111.3(2,1.2)	
(Me)$_2$]$_2$ (colourless)	2	1283.3(3)				not given		
[Al(μ-Et$_3$Si(H)N)(Me)$_2$]$_2$	m	709.5(3)		AlN_2C_2	μN 196.7(3,2)	280.2(3)	C,C 118.8(2)	113
	$P2_1/n$	1145.2(5)	96.83(3)		C_{Me} 195.8(5,1)	90.8(1)	C,N 111.7(2,4.3)	
(colourless)	2	1546.7(5)				89.2(1)		
[Al$_2$(μ-bamen)(Bu)$_2$Cl$_2$]	m	1072.2(2)		AlN_2C_2	μN 194.1(3,6)	280.8(2)	C,C 121.9(2)	114
	$P2_1/c$	2229.2(4)	101.26(2)		C_{Bu} 198.3(5,2)	92.3(1,2)	C,N 110.4(2,2.4)	
(colourless)	4	981.0(3)				87.7(1,4)		
				AlN_4Cl_2	μN 195.4(3,1)		N,N 84.9(1)[d]	
					N 202.5(3,7)		93.9(1,4)[f]	
					Cl 238.0(1,29)		N,Cl 90.0(1,6.0)	
							Cl,Cl 175.4(1)	
[Al(μ-Me$_2$N)(Me)$_2$]$_2$	m	1277.0(12)		AlN_2C_2	μN 195.8(7,10)	280.9(4)	C,C 115.7(5)	115
(colourless)	$P2_1/a$	810.4(7)	117.39(3)		C_{Me} 195.1(12,6)	91.7(2)	C,N 112.5(4,6)	
	2	765.5(9)				88.3(3)		
[Al(μ-(Me$_2$Si)$_2$N)(Me)$_2$]$_2$	tr	935.4(2)	91.24(2)	AlN_2C_2	μN 199.4(2,5)	281.3(1)	C,C 109.8(2,2)	111
	PĪ	1467.0(3)	90.63(2)		C_{Me} 195.9(4,5)	89.7(1,1)	C,N 114.0(1,9)	
(colourless)	4	1753.6(4)	99.46(2)			90.3(1,1)		

Table 5 (continued)

$[Al(\mu\text{-}Me_2N)(Me)_2]_2$	m	1285(3)		AlN_2C_2	μN 196.4(-,9)	281.5	C,C 115.9(4)	116
	$P2_1/a$	815(2)	117.7(2)		C_{Me} 196.3(-,16)	91.6(3)	C,N 112.4(3,8)	
(colourless)	2	765(2)				88.4(3)		
$[Al_2(\mu\text{-bamen})(Et)_2Cl_2]$	m	1705.6(4)		AlN_2C_2	μN 194.5(4,0)	281.9(2)	C,C 114.3(3)	117
	C2/c	1085.5(3)	116.77(2)		C_{Et} 197.1(5,0)	95.5(2)	C,N 113.1(2,2.3)	
(colourless)	4	1105.0(4)				87.5(2,0)		
				AlN_4Cl_2	μN 195.7(4,0)		N,N 85.5(3)[d]	
					N 201.2(5,0)		93.8(2)[f]	
					Cl 239.4(1,0)		N,Cl 91.5(1,4.2)	
							Cl,Cl 175.1(1)	
$[Al_2(\mu\text{-}Ph_3Si(H)N)(Me)_2]_2$	tr	882.1(2)	70.97(2)	AlN_2C_2	μN 197.1(3,0)	283.2(2)	C,C 118.3(2)	113
	$P\bar{1}$	943.5(2)	74.23(2)		C_{Me} 195.2(5,1)	91.8(1)	C,N 111.9(1,2.4)	
(colourless)	1	1334.2(4)	66.02(2)			88.2(1)		
$[Al(\mu\text{-}Bu^t(H)N)(cp')Cl]$	tr	848.9(3)	102.65(3)	AlN_2CCl	μN 196.3(2,8)	285.5(2)	C,Cl 111.4(8)	118
	$P\bar{1}$	886.4(3)	99.61(3)		C 203.1(3)	93.3(1)	C,N 122.5(1,5.5)	
(colourless)	1	1222.5(5)	107.59(2)		C^{cp} 215.4(2)	86.7(1)	N,Cl 105.3(8,4.0)	
$[Al(\mu\text{-NH(1-ad)})(Me)_2]_2$				AlN_2C_2	μN 196.3(2,5)	285.9	C,C 116.2(1)	119
					C_{Me} 195.8(3,1)	93.5(1)	C,N 112.7(1,5.0)	
						86.5(1)		
$[Al(\mu\text{-}N(H)Bu^t)(neo)_2]_2$	or	1936.1(6)		AlN_2C_2	μN 197.7(7,7)	287.0(5)	C,C 114.7(5)	120
	Aba2	974.5(3)			C_{neo} 195.5(12,0)	93.1(3)	C,N 113.4(4,5.3)	
(colourless)	4	1797.2(5)				83.5(3)		
$[Al(\mu\text{-NH(1-ad)})(neo)_2]_2$	rh	1865.5(7)		AlN_2C_2	μN 196.4(16,8)	287.7(9)	C,C 118.5(7)	120
	R3c	-			C_{neo} 201.9(16,3)	94.2(6)	C,N 112.8(6,4.1)	
(colourless)	18	6150.7(4)				81.6(6)		
$[Al(\mu\text{-}N(H)Ph(Pr^i)_2)$	m	1288.3(4)		AlN_2C_2	μN 198.9(3,10)	288.1(2)	C,C 123.2(2,5)	120
	$P2_1/n$	2082.5(7)	94.41(2)		C_{neo} 198.0(4,19)	92.8(1,1)	C,N 110.1(1,8.1)	
$(neo)_2]_2$ (colourless)	4	1594.7(5)				87.1(1,0)		
$[Al(\mu\text{-NHdipp})(Me)_2]_2$	m	1002.9(5)		AlN_2C_2	μN 198.7(2,6)	289.4	C,C 115.7(7)	119
	$Pbn2_1$	1860.5(7)	90.35(4)		C_{Me} 196.0(16,9)	94.7(5)	C,N 113.5(6,6.0)	
(colourless)	4	1554.6(7)				82.6(4)		
$[(AlEt)_2(\mu\text{-diazo-[18]-C-6})]$	m	1229.3(4)		AlO_2N_2C	μN 196.8(4,5)	290.2(3)	O,O 76.9(2)[d]	121
	$P2_1/c$	1111.5(4)	115.88(2)		O 195.5(5,5)	95.0	O,N 83.1(2,2)[d]	
$[EtAlCl_3]_3$	2	1415.4(5)			C_{Et} 194.4(5)	85.0(2)[d]	O,C 107.6(2,1.3)	
							N,C 115.8(2,1.3)	
$[Al\{2,6\text{-}Me_2C_6H_3\}CH{=}N)$	m	2155.6(5)		AlN_2C_2	μN 194.6(5,9)	290.5(3)	C,C 121.8(3)	122
	C2/c	930.20(9)	108.09(1)		C_{Bu} 196.8(6,19)	96.5(2)	C,N 111.8(2,7.1)	
$(Bu^i)_2]_2$ (colourless)	4	1870.5(1)				80.6(2)		
$[Al(\mu\text{-}NHBu^t)(neo)_2]_2$	m	1053.7(5)		AlN_2C_2	μN 201.5(5,15)	295.4(3)	C,C 123.0(3,3.6)	120
	$P2_1/c$	4013.4(14)	110.51(3)		C_{neo} 197.9(8,15)	94.3(2,2)	C,N 110.3(3,10.0)	
(colourless)	4	1157.0(4)				85.7(2,3)		
$[Al(\mu\text{-idb})(Bu^i)]_2$	tr	1076.7(2)	75.57(2)	AlN_2C_2	μN 199.5(7,48)	not given	C,C 130.7(8)	123
	$P\bar{1}$	1226.4(3)	71.14(2)		C 195.4(8)	89.4(2)	C,N 71.5(3)[g]	
(colourless)	2	1323.0(4)	73.58(2)		C_{Bu} 198.0(2)	90.6(2)	117.8(7,15.3)	
$[Al(\mu\text{-nea})(Me)_2]_2$	m	1092.5(4)		AlN_2C_2	μN 195.6(4,14)	not given	C,C 121.4(2,3)	124
	$P2_1$	1112.9(4)	94.18(3)		C_{Me} 195.1(5,7)	92.1(2,4)	C,N 110.8(2,2.1)	
(colourless)	2	1121.2(4)				87.0(1,1)		
$[Al(\mu\text{-bbp})(Me)]_2$[c]	tr	930.9(2)	81.03(2)	AlN_2C_2	μN 196.5(6,8)	-	C,C 115.5(4)	125
	$P\bar{1}$	986.0(1)	81.43(2)		C 193.3(8)	91.9(2)	C,N 99.8(3)[f]	
(colourless)	2	2213.2(4)	73.84(1)		C_{Me} 196.6(11)	88.1(3)	116.6(3,4.3)	
				AlN_2C_2	μN 196.5(7,9)	-	C,C 116.2(3)	
					C 194.5(8)	92.2(3)	C,N 98.6(3)[f]	
					C_{Me} 194.4(9)	87.8(3)	116.9(3,4.4)	
$[Al(\mu\text{-}(Ph)CH(Me)NH)$	or	840.6(3)		AlN_2C_2	μN 195.0(5,6)	not given	C,C not given	126
	$P2_12_12_1$	1550.5(4)			C_{Me} 193.0(8,20)	92.2(2,1)	C,N not given	
$(Me)_2]_2$ (colourless)	4	1754.7(5)				86.2(2,0)		
$[Al(\mu\text{-naa})(Me)_2]_2$	m	688.6(1)		AlN_2C_2	μN 197.4(2,8)	not given	C,C not given	127
	$P2_1/n$	911.8(1)	95.800(1)		C_{Me} 195.4(3)	92.5(1)	C,N not given	
(colourless) at 150K	2	1780.4(2)				87.5(1)		
$[Al(\mu\text{-bp(H)N})(Me)_2]_2$	tr	9046(1)	78.30(1)	AlN_2C_2	μN 197.9(4,2)	not given	C,C 119.6(2,4)	128
	$P\bar{1}$	976.7(1)	75.44(1)		C_{Me} 194.6(4,6)	92.8(2,5)	C,N 111.5(2,6.1)	
(colourless)	2	1771.3(2)	63.01(1)			86.2(1,1)		
$[Al(\mu\text{-bp(H)N})(Bu^i)_2]_2$	m	1283.5(3)		AlN_2C_2	μN 197.5(9,5)	not given	C,C 120.9(5,5)	128
	$P2_1/n$	2230.6(11)	93.00(2)		C_{Bu} 194.4(13,23)	94.1(4,1)	C,N 112.5(5,6.0)	
(colourless)	4	1354.5(3)				85.8(4,1)		
$[Al(\mu\text{-}o\text{-}MeC_6H_4(H)N)$	m	936.5(1)		AlN_2C_2	μN 195.7(7,8)	not given	C,C 118.8(4)	129
	$P2_1/n$	694.8(14)	94.93(8)		C_{Me} 196.4(9,10)	93.2(3)	C,N 111.8(4,3.6)	
$(Me)_2]_2$ (colourless)	2	1489.3(11)				86.8(3)		
$[Al(\mu\text{-}Me_2CN)(Me)_2]_2$	tr	702.7(4)	115.70(5)	AlN_2C_2	μN 192.8(2,3)	not given	C,C 120.1(2)	130
	$P\bar{1}$	776.0(4)	105.72(5)		C_{Me} 197.4(4,5)	96.3(1)	C,N 114.1(2,7.3)	
(colourless)	1	858.3(4)	92.38(5)			83.7(1)		
$[Al_2(\mu\text{-p-}BrC_6H_4PhCN)$	tr	988	107.5	AlN_2C_2	μN 191.7(10,1)	-	C,C not given	131
	$P\bar{1}$	1456	95.1		C_{Ph} 196.8(13,12)	97.1	C,N not given	
$(Ph)_2]_2$ (colourless)	1	985	99.0			82.9		
$Al_2(\mu\text{-}C_8H_{19}N_4)(Me)_3$	tr	819.3(6)	96.05(6)	AlN_2C_2	μN not given		not given	132
	$P\bar{1}$	923.5(7)	111.15(5)		C_{Me} not given			
(colourless)	2	1209.4(8)	107.18(6)	AlN_4C	μN^{eq} 198.7(3)			
					N^{eq} 182.6(2)			
					μN^{ax} 205.5(2)			
					N^{ax} 213.5(2)			
					C_{Me} not given			

Table 5 (continued)

$[Al(\mu\text{-Me})(Me)_2]_2$	m	1274(2)		AlC_4	μC 214.4(11,10)	260.0(4)	μC,C 106.8(5,1.9)	133
	C2/c	696(1)	123.40(15)		C 197.1(14,13)	74.7(4)	C,C 123.1(4)	
(colourless) at 223K	?	146.3(2)				105.3(4)		
$[Al(\mu\text{-Me})(Me)_2]_2$				AlC_4	μC 214.3(13)	not given		134
					C 196.5(14,7)	76.5		
$[Al(\mu\text{-Me})(Me)_2]_2$	m	1243.3(6)		AlC_4	μC 212.4(2,1)	260.6(2)	μC,C 107.0(1,5)	135
	C2/c	691.9(2)	123.21(1)		C 195.3(2,4)	75.7(1)	C,C 123.2(1)	
at 103K	?	1444.2(6)				104.3(1)		
$[Al(\mu\text{-Me})(Me)_2]_2$ gas phase				AlC_4	μC 214.0(4)	261.9(5)	C,C 117.3(1.5)	2a
					C 195.7(3)	75.5		
(by electron diffraction)						104.5(1)		
$[Al(\mu\text{-c-Pr})(c\text{-Pr})_2]_2$	m	1457.3(3)		AlC_4	μC 208.7(7,14)	261.8(3)	μC,C 110.3(3,4.9)	136
	$P2_1/c$	942.2(2)	98.12(2)		C 193(1,3)	78.2(3)	C,C 116.7(3,1.5)	
(colourless) at 295K	4	1371.9(6)				97.1(3,4)		
	m	1447.0(2)		AlC_4	μC 208.0(7,21)	260.7(3)	μC,C 109.9(3,5.1)	136
at 211K	$P2_1/c$	931.9(2)	99.06(1)		C 194.4(7,16)	77.9(2)	C,C 117.7(3,2.2)	
	4	1343.1(2)				97.4(3,3)		
$[Al(\mu\text{-}\sigma\text{-}C_6H_4CH(Me)CH_2)$	m	1462.1(2)		AlC_4	μC 213.6(1,32)	266.39(7)	μC,C 89.3(1)[d]	137
	$P2_1/c$	839.67(3)	107.998(4)		C 197.4(2)	77.2(1)	112.6(1,2.6)	
$(Et)]_2$ (colourless)	2	875.16(5)			C_{Et} 196.4(2)	102.8(1)	C,C 122.0(1)	
$[Al(\mu\text{-dmb})(Bu_i)_2]_2$	tr	951.4(6)	90.56(4)	AlC_4	μC 211	268	not given	138
	$P\bar{1}$	1083.7(6)	105.46(4)		C_{Bu} not given	79		
(colourless)	1	980.3(3)	120.20(4)			101		
$[Al(\mu\text{-Ph})(Ph)_2]_2$	tr	956.5(50)	106.2(3)	AlC_4	μC 218.2(5,2)	270.2(2)	μC,C 109.3(2,2.2)	139
	$P\bar{1}$	1081.3(50)	111.8(3)		C 195.8(5,2)	76.5(2)	C,C 115.4(2)	
(colourless)	1	832.8(40)	102.3(3)			103.5(2)		
$[Al(\mu\text{-tol})(tol)_2]_2$	m	1031.9(3)		AlC_4	μC 212.8(3,0)	281.7(2)	C,C 108.7(1)	32c
	$P2_1/c$	1020.1(5)	105.84(3)		C 199.8(3,2)	81.9(1)		
(colourless)	2	1654.4(5)				98.1(1)		
$[Al(\mu\text{-PhCC})(Ph)_2]_2$	or	1907(2)		AlC_4	μC 199.2	not given	not given	140
	Pbca	2323(2)			218.4	91.73		
(colourless)	4	721.1(6)			C_{Ph} 194.0	88.3		
$[Al(\mu\text{-}Me_3SiCC)(Me)_2]_2$	m	1399.0(1)		AlC_4	μC 201.3(5)	not given	μC,C 110.6(1)	141
	C2/m	1162.4(1)	109.62(1)		222.9(6)	"		
(colourless)	2	708.4(1)			C_{Ph} 191.6(6,0)	"		
$[Al(\mu\text{-Cl})(Me)(bht)]_2$	m	1041.0(6)		$AlCl_2OC$	μCl 228.4(3,7)	not given	μCl,O 107.8(1,1.3)	142
	$P2_1/n$	986.5(3)	97.20(5)		O 167.2(4)	90.9(1)	μCl,C 109.0(2,9)	
(pale yellow)	2	1642(1)			C_{Me} 192.0(8)	89.1(1)	O,C 127.7(3)	
$[Al(\mu\text{-Cl})(Me)Cl]_2$	m	1192(5)		$AlCl_3C$	μCl 225.5(10,10)	322	μCl,Cl 106.7(5,1.1)	143
	C2/c	692(2)	109.55(1.0)		Cl 205(1)	91.1(5)	μCl,C 111.6(5,1.2)	
(colourless)	4	1253(5)			C_{Me} 193(3)	88.9(5)	Cl,C 124.5(1.5)	
$[Al(\mu\text{-Cl})(Me_3Si)CH)Cl]$	tr	679.1(2)	92.58(1)	$AlCl_3C$	μCl 228.6(2,8)	not given	μCl,Cl 109.1(1,5.2)	144
	$P\bar{1}$	918.3(3)	94.35(1)		Cl 206.8(2)	91.01(7)	μCl,C 112.1(2)	
(colourless) at 208K	1	1238.2(2)	111.22(1)		C 191.2(5)	88.99(7)	Cl,C 123.1(2)	
$Al_2(\mu\text{-Cl})_2(Ph)(cp')$	tr	915.0(3)	103.51(3)	AlC_xCl_2	μCl 237.8(2,29)	-	μCl,C 99.1(1,8)	118
	$P\bar{1}$	1300.6(4)	97.35(1)		C 212.3-241.8(3)	94.2(1,1)	μCl,cp' 119.4(1,2.5)	
	2	1435.0(3)	103.06(1)		C_{Ph} 196.6(3,1)	85.9(1,1)	Cl,cp' 117.2(1)	
$[Al(\mu\text{-Cl})(Me)(cp^*)]_2$	m	855.0(2)		AlC_4Cl_2	μCl 238.1(1,12)	354.8(1)	μCl,C 101.9(1)	145
	$P2_1/c$	891.7(3)	104.65(2)		C 221.1(3,110)	96.34(4)	C,C 148.6(1)	
(colourless) at 208K	2	1601.2(7)			C_{Me} 193.1(3)	83.66(4)		
$[Al(\mu\text{-Cl})(Me)(cp^*)]_2$	m	865.7(2)		AlC_4Cl_2	μCl 238.8(3,10)	356.1	μCl,C 101.2(2)	146
	$P2_1/c$	891.4(2)	104.95(1)		C 220.9(8,114)	96.44(9)		
(colourless)	2	1620.8(2)			C_{Me} 191.6(7)	83.56(8)		
$[Al(\mu\text{-Cl})(Bu^i)(cp^*)]_2$	m	1304.0(6)		AlC_4Cl_2	μCl 239.6(4,56)	356.5(4)	μCl,C 101.2(3,5.7)	145
	$P2_1/n$	892.8(2)	98.06(3)		C 209.6-235.9(8)	96.1(1)	C,C 143.7(4)	
(colourless)	2	1308.3(3)			C_{Bu} 195.1(8)	83.9(1)		
$[Al(\mu\text{-Cl})(cp^*)Cl]_2$	m	1124.0(2)		AlC_5Cl_2	μCl 234.3(1,3)	not given	μCl,Cl 97.4(1,3)	147
	$P2_1/c$	1262.8(3)	112.27(2)		C 222.7(3,57)	"		
(colourless)	2	857.5(2)			Cl 214.9(1)	"		
$[Al(\mu\text{-Cl})(cp')Cl]_2$	m	780.4(1)		AlC_5Cl_3	μCl 234.1(1,6)	not given	μCl,μCl 96.1(1,0)	147
	$P2_1/a$	1526.3(2)	108.64(1)		C 222.6(3,20)			
(colourless)	2	1126.0(1)			Cl 214,8(1)			
$[Al(\mu\text{-}C_6H_5S)(Me)_2]_2$	m	1413.3(2)		AlC_2S_2	μS 240.7(2,10)	-	C,C 126.3(3,1)	148
	$P2_1/a$	1114.6(2)	116.72(1)		C_{Me} 194.2(6,11)	87.1(1,2)	C,S 108.6(2,8.7)	
(colourless)	4	1528.7(2)				89.5(1,1)		
$[Al(\mu\text{-BzS})(mes)_2]_2$	m	1066.0(4)		AlC_2S_2	μS 238.2(3,24)	-	C,C 119.6(3)	148
	$P2_1/n$	1226.8(2)	106.94(2)		C 197.7(7,11)	90.89(8)		
	4	1779.3(3)				89.11(8)		
$[Al(\mu\text{-PhS})(mes)_2]_2$[c]	tr	1106.8(5)	90.97(2)	AlC_2S_2	μS 239.4(2,23)	-	C,C 118.7(2)	148
	$P\bar{1}$	1247.0(3)	107.77(3)		C 197.0(6,12)	94.4(1)		
	4	1765.4(5)	112.23(3)			85.6(1)	C,C 121.7(3)	
				AlC_2S_2	μS 239.7(2,2)	-		
					C 196.7(2,3)	92.8(1)		
						87.2(1)		
$[Al(\mu\text{-}Ph_3SiS)(Me)_2]_2$	tr	907.2(2)	101.08(2)	AlC_2S_2	μS 236.3(2,9)	-	C,C 121.1(3,4)	148
	$P\bar{1}$	1384.7(3)	95.34(2)		C 192.9(6,8)	92.2(1,4)		
	2	1672.4(4)	103.38(2)			87.6(1,0)		

Table 5 (continued)

$[Al(\mu\text{-MeS})(Me)_2]_2$ gas phase				AlC_2S_2	μS 237.0(3) C_{Me} 194.5(5)	- 94.5 85.5	C,C 128.6(2,5)	149
$[Al(\mu\text{-}C_6F_5S)(Me)_2]_2$ (colourless)	m $P2_1/a$ 4	1413.3(2) 1114.6(2) 1528.7(2)	116.72(1)	AlC_2S_2	μS 240.7(2,10) C_{Me} 194.2(7,10)	- 87.1(1,2) 89.5(1,1)	C,C 126.3(3,1) C,S 108.6(2,8.7)	150
$[Al(\mu\text{-}(Me_3Si)_3P)(Et)_2]_2$	m C2/c 4	1808.5(2) 945.2(1) 2023.3(2)	100.30(1)	AlC_2P_2	μP 245.7(1,3) C_{Et} 197.2(4,2)	- 90.17(4) 89.83(4)	C,C 114.2(2) C,P 112.6(2,2.0)	71
$[Al(\mu\text{-}(Me_3Si)_3P)(Me)_2]_2$	tr $P\bar{1}$ 1	917.9(9) 970.1(5) 989.2(3)	76.42(3) 80.34(7) 63.89(8)	AlC_2P_2	μP 245.7(2,4) C_{Me} 195.9(4,8)	- 90.60(5) 89.4(3)	C,C 113.4(2) C,P 113.6(1)	151
$[Al(\mu\text{-PhP})(Bu^i)_2]_2$	m C2/c 4	1120.1(9) 1505.9(6) 1766.5(5)	105.4(2)	AlC_2P_2	μP 247.6(1,1) C_{Bu} 182.6(2,5)	361.5(1) 93.8(1) 86.2(1)	C,C 126.0(1) C,P 109.4(1,1.5)	152
$[Al(\mu\text{-Br})(trip)_2]_2$ (colourless)	tr $P\bar{1}$ 2	1255.7(3) 1357.9(3) 1918.3(4)	100.49(2) 108.02(2) 97.21(2)	AlC_2Br_2	μBr 248.8(4,13) C 197.3(10,0)	- 86.7 93.3(6)	C,C 130.0(4)	73
$[Al(\mu\text{-MeSe})(mes)_2]_2.C_6D_6$ (colourless)	or Cmca 4	2341,9(3) 1483.0(2) 1202.0(2)		AlC_2Se_2	μSe 251.9(2,0) C 198.1(7,0)	- 89.4(1) 90.6(1)	C,C 118.4(4) C,Se 118.7(2)	72
$[Al(\mu\text{-}(Me_3Si)_2As)(Et)_2]_2$ (colourless)	m C2/c 4	1821.4(2) 954.2(1) 2045.3(2)	99.89(1)	AlC_2As_2	μAs 253.5(1,4) C_{Et} 197.6(6,11)	- 91.01(5) 88.99(5)	C,C 115.0(3) C,As 112.5(3,2.2)	153
$[Al(\mu\text{-}Bu^t_2As)(Et)_2]_2$ (colourless)	m $P2_1/n$ 4	890.7(1) 1169(1) 1473.5(3)	90.25(1)	AlC_2As_2	μAs 256.7(2,5) C_{Et} 201.7(5,32)	- 94.54(4) 85.46(4)	C,C 111.5(3) C,As 114.5(2,2.8)	154
$[Al(\mu\text{-}Bu^tTe)(Bu^t)_2]_2$ (yellow)	m C2/m 2	1736(1) 1197(1) 852(1)	113.84(7)	AlC_2Te_2	μTe 273.2(3,0) C_{Bu} 211(1,11)	- 93.9(4) 86.1(1)	C,C 120.8(2) C,Te 111.5(2,9.6)	155
$[Al_2(\mu\text{-H})(\mu\text{-}CH_2)\{(Me_3Si)CH\}_4][Li(tmeda)_2]$[c] at 173K	tr $P\bar{1}$ 4	1470.6(4) 2168.3(7) 2200.5(6)	80.09(2) 84.39(2) 77.37(2)	AlC_3H AlC_3H	μH 187(2,1) μH_2C 197.1(4,5) C [e] 202.2(4,10) μH 185(2,4) μH_2C 196.8(4,5) C [e] 202.5(4,11)	274,4(1) 92(1,4) 86.6(7,1) 274.8(2) 92.2(8,3.6) 87.8(8,9)	C,C 119.0(2,5.4) C,H 106.2(7,5.4) C,C 117.4(2,2.7) C,H 106.7(6,3.8)	156
$[Al_2(\mu\text{-}CH_3)(\mu\text{-}Me_3CO)(Me)_4]_4$ gas phase by electron diffraction				AlC_3O	μC 210.3(10) μO 184.2(12) C_{Me} 194.8(7,0)	271.8(12) 87.8(6,7.6) 92.2(7)	C,C 112.4(10,5.0) C,O 114.6(7)	157
$[Al_2(\mu\text{-Ph})(\mu\text{-}Me_2SiNBu^t)_2(Ph)_3]$	m C2/c 8	2333(4) 1868(2) 1912(2)	128.4(1)	AlC_3N AlN_2C_2	μC 220.7(5) C_{Ph} 202.6(4,2) μN 199.8(9) μN 197.5(6) N 182.4(6) μC 214.5(8) C_{Ph} 200.4(5)	272.6(4) 86.7(3) 95.4(2,1.3)	$\mu C,C$ 105.7(2,3.5) $\mu N,C$ 121.9(3,1.8) $\mu N,N$ 82.9(3)[g] $\mu N,C$ 127.2(2) N,μC 118.1(3) N,C 120.3(3)	158
$[Al_2(\mu\text{-}Ph_2N)(\mu\text{-Me})(Me)_4]$ (colourless)	m $P2_1/c$ 4	785.0 1061 2185.5	91.74	AlC_3N	μN 200.5(3,0) μC 214.2(5,3) C 194.8(5,8)	- 82.2(1,3.3) 94.58(16)	C,C 111.1(1,6.2) C,N 109.4(1,14.7)	159
$[Al_2(\mu\text{-Cl})_2\{\mu\text{-}(Ph_2P)_2CH\}_2(Et)_4]$ at 233K (colourless)	m $P2_1/c$ 4	1434.8(3) 1131.1(3) 1990.3(4)	90.18(2)	AlC_3Cl AlC_2ClP	μCl 239.2(2) C 204.7(4) C_{Et} 196.7(4,8) μCl 227.3(2) P 243.1(2) C_{Et} 195.7(4,8)	- 106.8(1)	C,C 117.3(2,4.5) C,Cl 99.9(1,1.2) C,C 113.4(2,9.7) C,P 111.5(1,6) C,Cl 107.3(2,8) Cl,P 91.3(1)	160
$[Al_2\{\mu\text{-}C_4H_3(Me)N(Me)_2\}]_2$ (colourless)	tr $P\bar{1}$ 2	700.5(1) 725.9(1) 886.8(1)	67.69(1) 70.99(1) 88.48(1)	AlC_4	C 201.2(1) 228.6 C_{Me} 196.6(2,4)		C,C 115.1(1,4.0)	161
$[Al(\mu\text{-PhCCPh})(Et)(thf)]$ (colourless)	m $P2_1/n$ 2	1006.92(7) 1645.99(9) 1200.16(3)	68.708(3)	AlC_3O	C 198.5(3,1) C_{Et} 197.0(3) O_{thf} 190.7(3)	347.2(2)	C,C 103.7(4) C,O 114.5(8)	162
$[Al\{(Ph_2P)_2N\}(Me)_2]_2$ (colourless)	tr $P\bar{1}$ 2	1026.8(5) 1595.6(7) 1687.0(8)	95.01(4) 96.91(4) 114.45(3)	AlC_2NP	N 189.4(6,1) P 253.5(3,9) C_{Me} 194.8(9,6)		C,C 110.9(3,4) C,N 116.2(3,3.3) C,P 107.2(3,8.4) N,P 97.7(2,1)	163
$[Al(\mu\text{-}Me_2PCH_2)(Me)_2]_2$ (colourless)	tr $P\bar{1}$ 1	688.50(4) 783.63(4) 954.16(4)	76.039(3) 68.191(4) 65.599(4)	AlC_3P	C 200.6(6) P 245.1(2) C_{Me} 197.9(7,10)		C,C 114.5(3,3.0) C,P 103.8(2,1.6)	164
$[Al(\mu\text{-}Me_3Si)_2(Me_2P)C)Me_2]_2$ (colourless) at 223K	m $P2_1/n$ 4	1671.8(2) 1536.2(1) 1328.7(1)	96.58(1)	AlC_3P	C 207.8(2,1) P 251.9(1,2) C_{Me} 198.4(3,9)		C,C 108.5(1,2) C,P 97.9(1,2)	165
$[Al(\mu\text{-}Me_2PCH_2)(Me_2PCH_2)Cl]_2$ (colourless)	tr $P\bar{1}$ 1	651.1(2) 995.6(3) 1003.4(3)	104.98(2) 104.48(2) 103.06(2)	AlC_2ClP	C 197.7(2,13) P 242.5(1) Cl 217.6(1)		C,C 113.4(1) C,Cl 113.5(1,1.3) C,P 104.6(1,5.6) Cl,P 106.0(1)	164
$[Al\{(MeC(Me_2N)_2)(Me)_2]_2$ (colourless) at 173K	m $P2_1/c$ 2	818.7(5) 726.6(3) 1477.8(4)	103.58(3)	AlN_2C_2	N 192.6(1,3) C_{Me} 197.4(1,5)		N,N 111.6(1) C,C 112.5(1) N,C 108.2(1,2.7)	166

Table 5 (continued)

$[Al\{\mu\text{-}PhN(Ph)CO\}(Me)_2]_2$ (colourless)	m $P2_1/c$ 2	664(3) 1205(1) 1828(1)	94.9(2)	AlC_2ON	O 180.5(6) N 194.7(7) C_{Me} 194.0(11,0)		C,C 117.6(5) C,O 109.3(4,1.0) C,N 108.5(4,1.2) O,N 102.6(3)	167
$[Al\{\mu\text{-}N(CF_3)_2C_6H_3(Bu^t)O\}(Me)_2]_2$ (colourless)	tr $P\bar{1}$ 1	941.4(1) 963.7(1) 1147.7(2)	66.86(1) 83.29(1) 80.48(1)	AlC_2ON	O 183.6(2) N 193.2(2) C_{Me} 195.0(4,0)		C,C 118.7(1) C,O 107.9(1,1.5) C,N 109.6(1,1.3) O,N 101.9(1)	168
$[Al\{\mu\text{-}N(SO_2CF_3)(Ph)CC(Ph)N(SO_2CF_3)(Me)\}]_2$ (colourless)	m $P2_1$ 2	1079.8(5) 1626.4(9) 1240.6(7)	92.87(4)	AlC_2ON	O not given N not given C_{Me} not given		not given	169
$[Al(\mu\text{-}2\text{-}SC_6H_4N)(Me)_2]_2$ (colourless)	m C2/c 8	3165.1(3) 836.4(1) 1412.8(1)	103.84(1)	AlN_2C_2	N 199.3(4,1) C_{Me} 198.1(6)		N,N 129.5(2) C,C 117.0(2) N,C 102.9(2,1.6)	170
				AlC_2S_2	S 233.8(3,3) C_{Me} 196.5(5)		C,C 122.3(2) S,S 97.34(9) C,S 108.6(2,3.7)	
$Na[Al_2(\mu\text{-}H)(Me)_6]$ (colourless)	c $Pa\bar{3}$ 4	1123.9(4)		AlC_3H	μH 165 C_{Me} not given	330 180	not given	171
$K[Al_2(\mu\text{-}F)(Me)_6].C_6H_6$ (colourless)	or Pnma 4	1407.1(5) 1440.4(5) 886.2(3)		AlC_3F	μF 178.2(2) C_{Me} 195.1(5,14)	- 180	C,C 114.2(2,1.8) C,F 104.2(1,1.0)	172
$K[Al_2(\mu\text{-}F)(Et)_6]$ (colourless)	rh $R\bar{3}$ 1	895(3)	55.2(3)	AlC_3F	μF 182.0(3) C_{Et} 200.1(16)	- 180	C,C 115.13 C,F 102.5(4)	173
$[K(dbz\text{-}[18]\text{-}C\text{-}6)][Al_2(\mu\text{-}O_2)(Me)_6].1\frac{1}{2}C_6H_6$ (colourless)	tr $P\bar{1}$ 2	1321.0(8) 1367.1(8) 1409.0(8)	68.11(4) 65.46(4) 87.42(4)	AlC_3O	μO_2 186.0(9,8) C_{Me} (colourless)	- 128.3(7)	not given	175
$Al_2(\mu\text{-}O)\{(Me_3Si)_2CH\}_4$ at 213K	m C2/c 4	2297.9(2) 959.3(1) 2078.1(1)	98.99(1)	AlC_2O	μO 168.77(4) C 195.4(1,3)	- 180	C,C 122.63(6) C,O 118.7(5,1.2)	176
$Al_2(\mu\text{-}O)(py)_2(Bu^t)_4$ (colourless)	tr $P\bar{1}$ 1	907.4(2) 948.6(3) 972.8(3)	104.28(2) 99.48(2) 112.92(2)	AlC_2ON	μO 171.0(1) N 202.9(2) C_{Bu} 201.9(3,2)	- 180.0(1)	C,C 117.0(1) C,O 114.0(1,5) C,N 104.0(1,7) O,N 101.7(1)	176
$[K(dbz\text{-}18\text{-}C\text{-}6)][Al_2(\mu\text{-}PhO)(Me)_6]$ (colourless)	m $P2_1/n$ 4	1976.3(6) 983.0(3) 2066.1(6)	116.00(2)	AlC_3O	μO 189(1) C_{Me} 201(2,3)	- 127.5(6)	C,C 112.7(7,2.5) C,O 106.0(6,2.1)	50
$[Al_2(\mu\text{-}OCH(Me)N(Ph)(Ph)CO\}(Me)_5]$ (colourless)	m $P2_1/n$ 4	1360(3) 1374(2) 1240(2)	95.9(2)	AlC_3O AlO_2C_2	μO 192.8(6) C_{Me} 197.7(14,35) μO 186.0(6) O 184.2(7) C_{Me} 194.2(14,6)	- 125.0(3)	C,C 114.5(6,1.8) C,O 103.8(5,4.2) O,O 94.1(3) C,C 121.6(6) O,C 109.1(5,7.4)	177
$[Al_2\{\mu\text{-}Me_2N(H)CC(MeO)O\}(Me)_4Cl]$ (colourless)	m $P2_1/n$ 4	945.6(1) 1414.5(1) 1220.8(1)	103.78(1)	AlC_2ON AlC_2OCl	μO 187.0(2) N 203.9(2) C_{Me} 193.4(4,5) μO 189.5(5) C_{Me} 194.0(5,10) Cl 217.9(1)	- 126.6(1)	C,C 124.0(2) C,O 111.9(2,8) C,N 108.2(2,1) O,N 85.65(9)[d] C,C 122.2(2) C,O 108.5(2,8) C,Cl 109.8(2,7) O,Cl 94.61(7)	107
$Al_2(\mu\text{-}MeONNO)(Me)_5$ (colourless)	tr $P\bar{1}$ 2	670.6(1) 970.3(2) 1020.9(1)	82.37(1) 87.13(1) 72.97(1)	AlO_2C_2 AlC_3O	μO 190.9(6) O 188.1(6) C_{Me} 193.8(10,2) μO 200.4(6) C_{Me} 196.3(11,4)	- 132.9(3)	C,C 120.6(4) O,O 79.8(3)[d] O,C 112.8(4,1.0) C,C 117.1(5,0) C,O 99.9(4,2.7)	178
$Al_2(\mu\text{-}dhbp)(Me)_4$ (colourless)	or Aba2 4	1987.6(5) 805.7(4) 1699.6(5)		AlO_2C_2	μO 196(1) O 178(1) C_{Me} not given	- (not given)	C,C 124(1) O,O 92(1) O,C 105(1,13)	179
$[Al_2\{\mu\text{-}Bu^tNCHC(Me)_2O\}(Me)_5]$ (colourless)	m $P2_1/c$ 4	911.7(2) 1186.7(1) 1732.4(5)	- 101.91(2)	AlC_2ON AlC_3O	μO 182.5(5) N 200.2(6) C_{Me} 192(1,1) μO 191.0(5) C_{Me} 197(1,2)	- 120.3(3)	C,C 121.8(5) C,O 113.1(4,2) C,N 109.0(4,1.3) O,N 84.6(2)[d] C,C 112.8(4,2.5) C,O 105.8(3,4.1)	180
$Al_2(\mu\text{-}N(CH_2CH_2O)_5CH_2CH_2\}(Me)_5$ (colourless)	m $P2_1/m$ 2	970.9(2) 1169.7(3) 1076.7(2)	111.92(2)	AlC_3N AlO_2C_2N	μN 203.2(3) C_{Me} 196.4(4,7) μN 197.5(3) O 215.1(2,0) C_{Me} 195.1(3,18)	- 117.2(1)	C,C 109.6(2,2.3) C,N 107.4(1,3.6) C,C 130.2(2) C,O 94.2(1,2.3) C,N 114.9(1,4.2) O,N 79.94(5)[d]	181
$[K(dbz)\text{-}18\text{-}C\text{-}6)][Al_2(\mu\text{-}N_3)(Me)_6].1\frac{1}{2}Mena$ (colourless)	m $P2_1/c$ 4	1417.6(5) 1302.1(5) 2532.4(8)	98.23(4)	AlC_3N	μN 203(3,3) C_{Me} 200(5,3)	- 128(2)	C,C 113(2,5) C,N 103(2,3)	182
$Cs[Al_2(\mu\text{-}N_3)(Me)_6]$. p-xylene (colourless)	m C2/m 4	1914.3(6) 1622.7(6) 1039.2(5)	114.06(2)	AlC_3N AlC_3N	μN 198(1) C_{Me} 200(1,2) μN 198(1) C_{Me} 201(1,1)	- 131.4(9) - 132.5(9)	C,C 112.4(6,11.7) C,N 106.2(6,2.4) C,C 115.6(6,9.0) C,N 102.2(6,5.8)	182

Table 5 (continued)

$Al_2(\mu\text{-}CH_2)((Me_3Si)_2CH)_4$	or	2282.0(4)		AlC_3	μC 193.8(1)	-	C,C 120.0(9,2.0)		183
	Pcca	1700.9(2)			C 195.7(2,2)	129.6(6)			
(colourless) at 153(3)K	4	1164.6(2)							
$[Li(tmeda)_2][Al_2(\mu\text{-}CH_2)$	tr	1370.0(4)	85.13(2)	AlC_3	μC 191.1(4)	-	C,C 120.0(1,5.5)		184
	PT	1473.0(5)	70.45(3)		C 198.4(3,3)	144.4(2)			
$((Me_3Si)_2CH)_4(Me_3CCH_2)]$	2	1838.1(6)	81.42(2)	AlC_4	μC 205.4(4)		C,C 109.5(2,6.3)		
(colourless) at 218K					C 203.8(5)				
					209.0(31)				
$Al_2(\mu\text{-C-Pr})(C\text{-Pr})_5$	m	1457.3(3)		AlC_3	μC 206.2(7)	261.8(3)			185
	$P2_1/c$	942.2(2)	81.54(2)		C 193(1,3)	134.6(-,5)			
(colourless)	4	1371.9(6)		AlC_4	μC 209.8(8)				
					C 193(1,3)				
$[Al_2(\mu\text{-}C_6H_5NC)((Me_3Si)_2$	tr	1150.4(1)	104.18(1)	AlC_3	μC 200.3(3)	-	not given		186
	PT	1254.0(1)	95.37(1)		C 196.4(3,2)	162.6(2)			
$CH)_4].C_5H_{10}$	2	2065.0(2)	101.11(1)	AlC_3N	μC 200.7(3)		N,C 39.5(2)[h]		
					N 184.9(5)				
(colourless)					C 196.7(3,0)				
[K(dbz-18-C-6)](Al$_2$(μ-Cl)	m	2131.9(8)		AlC_3Cl	μCl 236.2(3,26)	-	C,C 115.4(4,7)		187
	$P2_1/c$	951.2(4)	93.79(3)		C_{Me} 197.8(8,34)	120.0(1)	C,Cl 102.6(3,5.1)		
$(Me)_6].2C_6H_6$	4	2108.1(8)							
$[Al_2(\mu\text{-Cl})Cl_{5.5}(Me)_{0.5}]$	m	941.9(2)		$AlCl_4$	μCl 223.6(2,5)	-	Cl,Cl 109.5(1,11.8)		188
	$P2_1/n$	2313.4(5)	110.66(2)		Cl 209.9(3,50)	118.5(1)			
$[Zr(Me_3Si)(Me_2SiCl)$	4	1741.8(4)							
$C_2H_4(in)_2]$									
$Al_2(\mu\text{-S})((Me_3Si)_2CH)_4$	or	2294.6(2)		AlC_2S	μS 218.7(4)	-	C,C 124.3(4)		189
	Pcca	1711.9(1)			C 193(1,1)	117.5(3)	C,S 117.8(3,2.7)		
(colourless) at 213K	4	1174.7(2)							
$Al_2(\mu\text{-}CS_2)((Me_3Si)_2CH)_4$[c]	tr	1529.1(7)	99.47(4)	AlC_3	C 205(1)		C,C 120.0(5,7.2)		189
	PT	1713.0(8)	97.10(4)		C 194.5(10.5)				
(colourless) at 173K	4	2018(1)	106.54(4)	AlC_2S_2	C 196.5(10,15)		C,C 118.9(5)		
					S 239.0(5)		S,S 73.7(2)[g]		
							C,S 114.0(4,1.4)		
				AlC_3	C 205(1)		C,C 120.0(5,9.0)		
					C 195(1,1)				
				AlC_2S_2	C 199.5(10,5)		C,C 121.6(5)		
					S 239.3(5,1)		S,S 74.2(2)[g]		
							C,S 113.0(4,4.0)		
$Al_2(\mu\text{-Te})((Me_3Si)_2CH)_4$	or	2385.5(5)		AlC_2Te	μTe 254.9(1)	-	C,C 125.7(2)		190
	Pcca	1657.9(3)			C 194.8(5,0)	110.40(6)	C,Te 117.0(2,2.2)		
(colourless)	4	1217.6(2)							
$K[Al_2(\mu\text{-}NO_3)(Me)_6]$[c]	m	797.5(8)		AlC_3O	C_{Me} 199(8,13)		C,C 102(3,9)		24
	$P2_1/m$	2451.2(12)	100.55(8)		O 198(5,3)		C,O 116(3,10)		
(colourless)	8	1460.1(10)		AlC_3O	C_{Me} 197(8,6)		C,C 101(3,5)		
					O 200.6(6,2)		C,O 117(3,8)		
$(NMe)_4[Al_2(\mu\text{-ac})(Me)_6]$	or	1020.2(3)		AlC_3O	O 187.1(8,3)		C,C 113.4(4,2.4)		191
	Pnma	1030.0(3)			C_{Me} 194(1,2)		C,O 104.2(4,1.6)		
(colourless)	4	1877.2(5)							
[Al$_2$(μ-MeNC(Ph)C(Ph)O)	m	2011.0(2)		AlC_3O	O 198.3(2)		C,C 116.1(2,2.2)		180
	C2/c	1381.9(1)	115.18(1)		C_{Me} 195.9(4,7)		C,O 101.5(1,5.6)		
$(Me)_6]$ (colourless)	8	1881.3(1)		AlC_3N	N 208.9(2)		C,C 114.7(2,4.1)		
					C_{Me} 194.9(4,6)		C,N 103.6(2,6.8)		
$K[Al_2(\mu\text{-SCN})(Me)_6]$	m	1857.9(8)	126.80(4)	AlC_3N	N 195.1(5)		C,C 113.7(2,1.2)		192
	C2/m	816.8(5)			C_{Me} 198.2(5,1)		C,N 104.8(2,1.7)		
(colourless)	4	1175.3(6)		$AlCl_3S$	S 248.9(2)		C,C 116.4(2,2.5)		
					C_{Me} 196.5(6,13)		C,S 101.1(2,1.5)		
[(Al$_2$Cl$_5$(Me))	tr	1000.9(3)	90.38(3)	$AlCl_3P$	Cl 212.4(2,14)		not given		193
	PT	1074.8(4)	103.36(2)		P 245.1(2)				
{μ-(Ph$_2$P)$_2$CH$_2$)]	2	1480.6(5)	96.89(3)	$AlCl_2CP$	Cl 205.7(4,37)				
					C_{Me} 199.8(5)				
(colourless)					P 249.7(2)				
$[Al_2(\mu\text{-}Ph_2PCH_2PPh_2)(Me)_6]$	tr	1005.3(6)	85.58(4)	AlC_3P	P 255.3(2,32)		C,C 115.6(3,1.6)		194
	PT	1101.7(6)	71.80(4)		C_{Me} 196.7(6,13)		C,P 102.2(2,5.8)		
(colourless)	2	1590.8(8)	77.49(4)						
[Al$_2$(μ-Ph$_2$P(S)CHP(S)Ph$_2$)	m	1812.6(2)		AlC_3S	S 238.8(2)		not given		195
	$P2_1/n$	956.9(2)	110.20(1)		C 209.7(4)				
$(Me)_6$	4	1939.4(3)			C_{Me} 194.6(6,3)				
				AlC_3S	S 246.0(2)				
(colourless)					C_{Me} not given				
$Al_2(\mu\text{-tmen})(Me)_6$	m	1071.9(3)		AlC_3N	N 207.4(2)		C,C 114.1(2,7)		196
	$P2_1/n$	764.8(2)	110.32(2)		C_{Me} 196.7(4,13)		C,N 104.3(1,6)		
(colourless)	2	1222.4(3)							
$[Al_2(\mu\text{-}(Me_2NCH_2)_2)$	tr	981.1(3)	108.39(3)	AlC_2NCl	C 196.2(5,1)		C,C 97.2(2)[d]		197
	PT	1525.2(8)	91.14(3)		N 204.5(3)		C,N 109.4(2,3.4)		
$(MeC(Me_3Si)HC)_4Cl_2]$[c]	2	1526.6(9)	95.95(3)		Cl 216.3(2)		C,Cl 121.5(2,2.1)		
							N,Cl 97.7(1)		
(colourless)				AlC_2NCl	C 195.9(5,1)		C,C 96.8(2)[d]		
					N 204.9(4)		C,N 110.5(2,2.0)		
					Cl 216.7(2)		C,Cl 120.4(2,1.4)		
							N,Cl 98.6(2)		
[Al$_2$(μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$)	tr	892.2(6)	68.870(2)	AlC_3P	C_{Me} 196.4(5,7)		C,C 115.8(3,1.3)		198
	PT	948.5(2)	84.001(3)		P 254.4(4)		C,P 102.0(2,3.3)		
$(Me)_6]$ (colourless)	1	1132.4(2)	66.808(3)						

Table 5 (continued)

$[Al_2(\mu\text{-}Ph_2P(S)(CH_2)_2P(S)$	tr	1207.6(3)	98.32(2)	AlC_3S	C_{Me} 196.2(7,3)	not given	195
	$P\bar{1}$	1314.8(3)	100.55(2)		S 250.6(3)		
$Ph_2(Me)_6]$ (colourless)	2	1311.4(3)	116.41(2)				
$[Al_2(\mu\text{-dhan})(Me)_4(thf)_2]\cdot$	tr	1012.2(1)	90.320(3)	AlC_3O	C_{Me} 197.8(4,16)	C,C 114.2(2,12.0)	199
	$P\bar{1}$	1135.2(1)	104.157(2)		C 203.1(3,2)	C,O 100.9(1,2.8)	
thf (colourless)	2	1289.3(1)	114.009(4)		O_{thf} 194.3(2,7)		
$Al_2(\mu\text{-}N(C_2H_4)_3N)(Me)_6$	trg	1122.3(2)		AlC_3N	C_{Me} 196.1(11,7)	C,C 115.0(3,7)	200
	R3m	-			N 206.6(8,1)	C,N 103.1(4,9)	
(colourless)	6	2275.7(8)					
$[Al_2(\mu\text{-}C_{14}H_{10})_2(Me)_4]$	m	2261.0(8)		AlC_4	C_{Me} 200.3(13,9)	C,C 109.5(5,10.7)	201
	$B2_1/c$	1125.6(10)	93.27(5)		C 206.1(11,5)		
$[Na(thf)_2]_2$ (colourless)	4	1758.9(15)					
$[Al_2(\mu\text{-}PhNCCNPh)$	m	2265.6(1)		AlC_3N	N 204.0(2)	N,C 65.78(6)[g]	186
	C_2/c	1974.3(2)	103.24(1)		C 207.5(2)		
$((Me_3Si)_2CH)_4]$ (dark red)	4	1335.3(1)			C 198.3(2,7)		
$[Al_2(\mu\text{-}(MeN)_2C_2$	m	1365.8(4)		AlN_2C_2	N 190.6(3,0)	N,N 85.7(1)[d]	202
	C2/m	910.4(4)	102.35(2)		C_{Me} 197.7(6,4)	C,C 117.2(2)	
$(NMe)_2)(Me)_4]$	2	653.9(1)				N,C 112.5(2,4)	
$[Al_2(\mu\text{-}MeNC(O)C(NMe)O)$	tr	574.38(9)	94.78(1)	AlC_2ON	O not given		203
	$P\bar{1}$	946.6(1)	111.02(1)		N not given		
$(Me)_4]$	1	657.50(8)	101.21(1)		C_{Me} not given		
$Al_2(\mu\text{-}C_4H_8O_2)(Me)_6$	m	1884		AlC_3O	O 202(2)	C,C 116.8(6,8)	204
	C2/m	1151	146.15		C_{Me} 197(2,1)	C,O 101.1(5,5)	
(colourless)	2	679					
$Al_2(\mu\text{-}C_4H_8O_2)((Me_3Si)N)_2$	m	1480.4(5)		AlC_2ON	O 200.1(6)	C,C 110.5(5)	205
	$P2_1/c$	747.5(3)	100.77(3)		N 184.8(8)	C,O 100.4(4,1.6)	
$(Me)_4$ (colourless)	2	1537.8(5)			C_{Me} 196(1,1)	C,N 120.1(4,3)	
						O,N 99.9(3)	
$Al_2(\mu\text{-}[12]\text{-crown-4})(Me)_6$	m	1134.2(7)		AlC_3O	O 197.7(3)	C,C 115.1(2,8)	206
	$P2_1/n$	1294(4)	95.48(4)		C_{Me} 196.2(5,7)	C,O 102.9(2,1.8)	
(colourless)	2	697.3(6)					
$Al_2(\mu\text{-}[15]\text{-crown-5})(Me)_6$	m	2213.4(8)		AlC_3O	O 200.5(6,0)	C,C 116.1(4,1.2)	207
	C2/c	1181.5(5)	135.07(4)		C_{Me} 194(1,5)	C,O 101.6(4,2.0)	
(colourless)	4	1834.7(7)					
$Al_2(\mu\text{-db-}[18]\text{-C-6})(Me)_6$	m	1150.0(4)		AlC_3O	O 196.7(3)	C,C 115.5(2,1.6)	207
	$P2_1/c$	1781.6(6)	105.39(4)		C_{Me} 196.0(4,22)	C,O 102.4(2,2)	
(colourless)	2	754.5(3)					
$Al_2(\mu\text{-dc-}[18]\text{-C-6})(Me)_6$[c]	m	1642.3(7)		AlC_3O	O 196.0(8)	not given	208
	$P2_1/a$	981.2(5)	107.41(5)		C_{Me} 200 - 201		
(colourless)	4	2093.5(8)		AlC_3O	O 193.6(8)		
					C_{Me} 200 - 201		
$Al_2(\mu\text{-bcme})(Me)_6$	tr	1114(1)	77.32(8)	AlC_3O	O 199(1)	C,C 116.1(4,2.1)	209
	$P\bar{1}$	1160(1)	67.91(8)		C_{Me} 198(1,2)	C,O 101.6(4,1.2)	
(colourless)	1	1202(1)	69.34(8)				
$[Al_2(\mu\text{-bcme})(Me)_2Cl_4]\cdot C_6H_6$	m	1211.6(2)		$AlCl_2OC$	Cl 212.6(5,5)	Cl,Cl 108.7(2)	209
	C2/c	2157.7(7)	104.05(2)		O 191.3(7)	Cl,O 103.1(3,5)	
(colourless)	4	2347.0(6)			C_{Me} 194(1)	Cl,C 116.1(4,1.0)	
						O,C 107.9(4)	
$[Al_2(\mu\text{-bcme})(Et)_2Cl_4]$	m	1206.2(4)		$AlCl_2OC$	Cl 212.4(3,4)	Cl,Cl 109.0(1)	209
	C2/c	2117.5(6)	100.78(4)		O 188.6(5)	Cl,O 103.1(2,4)	
(colourless)	4	2159.6(5)			C_{Et} 193.7(6)	Cl,C 115.2(3,8)	
						O,C 108.8(2)	
$Al_2(C_2H_{11}B_9)_2(Et)_2$	m	712.2(2)		AlH_2C_2	H not given	not given	210
	$P2_1/n$	2766.8(8)	96.246(5)		Cl not given		
	?	1162.9(3)		AlB_6C_4	B 218(5,5)	not given	
					C 226(4,2)		

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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] Five-member metallocyclic ring.

[e] There are cis and trans isomers.

[f] Six-member metallocyclic ring.

[g] Four-member metallocyclic ring.

[h] Three-member metallocyclic ring.

[i] Refs. [2a,5,24,32c,39,50,71–74,90–101,103–109,110a,110b,111–173,175–210] are to be found in the reference list.

able deviation from the idealized geometry which requires 86.6° and 151.9° respectively. The L_{eq}–Al–L_{ap} angle in the ideal square pyramid is 104.1° compared to the observed range of 98 to 117°, also indicating a considerable deviation.

In five examples [76,80,81,84] the aluminium occurs in a distorted trigonal bipyramidal environment, created by combinations of mono-, bi- and tetradentate ligands. The observed interbond angles in these derivatives range from 115 to 125° for L_{eq}–Al–L_{eq}, 78 to 101° for

L_{eq}–Al–L_{ap} and 157 to 175.5° for L_{ap}–Al–L_{ap}. The idealized values are 120°, 90° and 180° respectively, indicating considerable distortions. In all of these cases, the distortions are primarily due to the chelating ligands, as noted previously.

The remaining three derivatives [73,79,82] have an intermediate geometry between the two extremes. Overall, the mean Al–L bond distances for monodentate ligands in the pentacoordinate organoaluminium series increase in the sequence: 196 pm (LC) < 207 pm (LO) < 220 pm (Cl) < 228 pm (Br). These values are somewhat higher than those found for the corresponding coordination derivatives of aluminium(III) which are: 186 pm (LO) < 216 pm (Cl) < 226 pm (Br) [1].

2.4. Coordination numbers six and higher

The data for coordination numbers six and higher are given in Table 4. There are three derivatives [85–87] in which the aluminium(III) atom is six coordinate. In yellow $Al(PhNNNPh)_2(3,5\text{-}Me_2py)(Me)$ [85] the triacenide ligands act as chelates, occupying four positions, and the two monodentate ligands finish the distorted octahedral environment about the aluminium. The presence of an elongated Al–N bond (215.5(2) pm) trans to the methyl group is characteristic of the strong trans influence of the latter.

The structure of $[Al(\eta^5\text{-}B_{11}H_{11})(Me)]^{2-}$ [86] is that of an icosahedron with Al–B bond distances ranging from 213.1(4) pm to 214.1(4) pm, an Al–C(Me) bond distance of 194.2(4) pm and B–Al–C bond angles from 131.5(2) to 134.7(2)°. A similar structure occurs for $Al(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})(Et)$ [87]. The resulting three-member metallocyclic ring angle has the value of 42.1° for C–Al–C, 46.2° for B–Al–C, and 49.6° for B–Al–B. This corresponds to the respective covalent radii of the C (77 pm) and B (86 pm) atoms.

The structure of the $[Al(\eta^3\text{-}C_2B_9H_{11})_2]^{2-}$ sandwich anion [88] is shown in Fig. 1. There are three crystallographically independent molecules, differing mostly by degree of distortion of the Al–L and L–Al–L parameters. This is typical of the general class of distortion isomerism [89].

3. Dimeric compounds

There are over 160, largely colourless, organoaluminium compounds of this type, for which the data are listed in Table 5. Several types of bridging are observed, including eight examples where two AlC_2 units [90–94], or two non-equivalent AlC_2 units plus an AlC_3 unit [92,94], or AlC_2 plus AlC_2H units [94] are held together by direct Al–Al bonds. The intermetallic bonding distance in these derivatives ranges from 247.0(2) to 275.2(3) pm. The mean Al–C bond distance for the AlC_2 chromophore (202.3 pm) is some 1.8 pm shorter than that of the AlC_3 chromophore (204.1 pm).

The distorted edge-shared tetrahedral arrangement is the most common form of bridging observed in this series. The bridging links found are: two H atoms [74]; two OL ligands [5,95–108]; two NL ligands [39,109,110a,110b,111–132]; two C-donor ligands [2a,32c,133–140]; two Cl atoms [118,141–147]; two SL ligands [148–150]; two PL ligands [71,151,152]; two bromine atoms [73]; two SeL ligands [72]; two AsL ligands [153,154]; two TeL ligands [155]; H plus C-donor [156]; OL plus C-donor [158]; NL plus C-donor [158,159]. The shortest distance between any two aluminium atoms found in this group of compounds is 260.0(4) pm [133] with two C-donor ligands as bridges, with values up to 281.7(2) pm for other 2-carbon-bridged units. The other Al · · · Al distances range from 276.0(4) to 315.5 pm (2-O bridges), 268.3 to 295.4(3) pm (2-N bridges), and 271.8 to 274.4 pm (mixed bridges). As the Al–Al distance increases, the Al–L–Al angle opens and the μL–Al–μL angle closes. For example, in the 2-O-bridged compounds the values are: 276.0(2) pm, 96.3(1)° and 83.7(1)° [95]; 286.6(1) pm, 100.8(1)° and 79.1(1)° [100]; 300.0(4) pm, 104.0(3)° and 74.8(3)° [104]; 305.5 pm, 105.3(3)° and 73.3(3)° [106]. For the 2-N bridges the values are: 268.3(1) pm, 84.6(1)° and 85.5(1)° [109]; 281.3(1) pm, 89.7(1)° and 90.3(1)° [111]; 287.0(5) pm, 93.1(3)° and 83.5(3)° [120]; 290.5(3) pm, 96.5(2)° and 80.6(2)° [122]. For the 2-C-bridged compounds the values are: 260.0(4) pm, 74.7(4)° and 105.3(4)° [133]; 266.4 pm, 77.2° and 102.8° [137]; 281.7(2) pm, 81.9(1)° and 98.1(1)° [32c].

The bridge angles and the covalent radii of the bridging atoms also correlate when comparisons are made between examples in which the Al–Al distances are almost the same. Here the Al–L–Al angle closes and the μL–Al–μL angle opens as the bridging atom radius increases, for example: 277.6(2) pm, 97.2(1)° and 82.8(1)° (O-donor, 73 pm) [99]; 277.7(3) pm, 89.3(1)° and 87.8(1)° (N-donor, 75 pm) [39]; 281.5(3) pm, 99.8(4)° and 80.3(4)° (O-donor) [98]; 281.5 pm, 91.6(3)° and 88.4(3)° pm (N-donor) [116]; 281.7(2) pm, 81.9(1)° and 98.1(1)° (C-donor, 77 pm) [32c].

The Al–L(bridge) distance gets longer as the covalent radius of the bridging atom increases, and also as the coordination number of the aluminium atom rises. Some examples of this effect are: 186 pm (4-coord.) and 189 pm (5-coord.) with oxygen bridges; 195 pm (3-coord.) and 197 pm (4-coord.) with carbon bridges; 227.5 pm (4-coord.) and 237 pm (6-coord.) with chlorine bridges. The mean value of the Al–L(bridge) distance for the four-coordinate derivatives can be seen to increase in the order: 186 pm (LO, 73 pm) < 197 pm (LN, 75 pm) < 212 pm (LC, 77 pm) < 227.5 pm (Cl, 99 pm) < 232 pm (LS, 102 pm) < 246 pm (LP,

112 pm) < 249 pm (Br, 114 pm) < 252 pm (LSe, 116 pm) < 255 pm (LAs, 122 pm) < 273 pm (LTe, 143pm).

There are five examples with aluminium(III) atoms in tetrahedral environments linked by two bidentate ligands to give two-atom bridges [161–165]. Another five examples have two bidentate ligands acting as three-atom bridges in a syn–syn configuration, with the aluminum(III) atoms in distorted tetrahedral geometries [166–170].

In several other derivatives, two aluminium(III) atoms are bridged by a single donor-atom, for example: hydrogen [171]; fluorine [192,173]; dioxygen (O_2) [174]; oxygen (O^{2-}) [175,176]; LO [50,107,177–180]; LN [181,182]; LC [183–186]; Cl [187,188]; LS [189]; Te [190]. The Al–L–Al bridge angle is linear (180°) when L is the H^-, F^- or O^{2-} anion, but only 128.3(7)° for the dioxygen case (which utilizes only one of its oxygen atoms). For donor atoms of ligands (LX) the observed ranges are: 120.3(3) to 132.9(3)° for LO; 117.2(1) to 132.5(9)° for LN; 129.6(6) to 162.6(2)° for LC; 118.5(1) to 120.0(1)° for Cl; 117.5(3)° for LS; 110.4° for Te. The trend is for the angle to close as the covalent radius of the bridging atom increases. The shortest Al–Al bond distance in this series is 261.8(3) pm, with an Al–C–Al bridge angle of 134.6° [185]. The mean Al–L(bridge) distance increases in the order: 165 pm (H) < 170 pm (O) < 180 pm (F) < 186 pm (O_2) < 190.5 pm (LO) < 200 pm (LN) < 201 pm (LC) < 219 pm (LS) < 230 pm (Cl) < 255 pm (Te).

Triatom bridges are found in several examples [180,191–195] in a syn–syn configuration with tetrahedral environments about each Al(III) atom (Table 5). Another four derivatives [195–198] have bidentate ligands with four atoms in the bridge between tetrahedral Al(III) atoms.

In the remaining derivatives [186,199–210] the bridges are unique, and the structure of one of them is shown in Fig. 2. The planar bonding faces of the two dicarbollide ligands are nearly parallel, with an angle of only 2.6° between them. Each is η^5-coordinated to a single aluminium atom. In addition, a diethylaluminium moiety is bonded to one of the dicarbollide cages via two B–H–Al bridges.

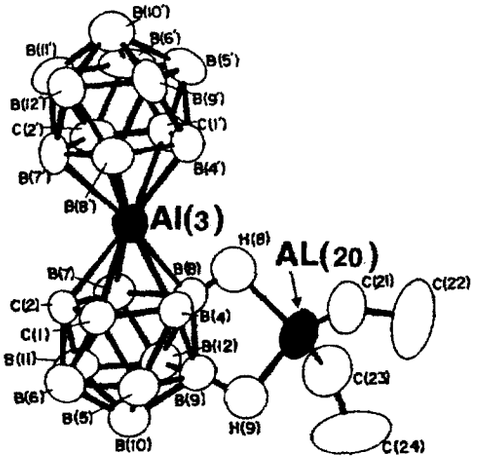

Fig. 2. Structure of $[Al_2(C_2H_{11}B_9)_2Et)_2$ [211].

The structures of the dimeric organoaluminium derivatives are thus very diverse, with the dominant bridging feature being distorted edge-shared tetrahedra. The shortest Al–Al bond length is 247.0(2) pm [90], which is much shorter than the value of 286.0 pm found in metallic aluminium. The most common coordination geometry is tetrahedral with varying degrees of distortion. However, there are examples of aluminium coordination from three to seven, and even ten. In several examples the two aluminium atoms differ in coordination environment, for example: $AlC_2 + AlC_3$ [92,94]; $AlC_3 + AlC_4$ [184,185]; $AlC_2 + AlC_2H$ [94]; $AlC_3 + AlC_3N$ [186]; $AlC_3 + AlC_2S_2$ [189]; $AlC_2ON + AlC_2OCl$ [107]; $AlN_3C + AlN_2C_2$ [109]; $AlC_3N + AlN_2C_2$ [158]; $AlC_3Cl + AlC_2ClP$ [160]; $AlN_2C_2 + AlC_2S_2$ [170]; $AlC_3O + AlO_2C_2$ [177,178]; $AlC_3O + AlC_2ON$ [180]; $AlC_3O + AlC_3N$ [180]; $AlC_3N + AlCl_3S$ [192]; $AlCl_3P + AlCl_2CP$ [193]; $AlC_3N + AlO_2C_2N$ [181]; $AlN_2C_2 + AlN_4C$ [132]; $AlN_2C_2 + AlN_4Cl_2$ [114,117]; $AlH_2C_2 + AlB_6C_4$ [210].

Both cis and trans isomers are found within the same crystal of $[Al(\mu\text{-}Pr^iNH)(Me)_2]$ [110a,110b]. There are also several examples which exhibit two crystallographically independent molecules in the same crystal, differing mostly by degree of distortion of the Al–L and L–Al–L parameters [24,90,98,103,125,148,156,182, 189,197,208]. There is one case with three such molecules [88].

The mean Al–L bond distances for tetrahedrally coordinated species with monodentate ligands increase in the sequence: 189 pm (LO) < 191 pm (LN) < 197 pm (LC) < 212 pm (Cl). For the bidentate ligands the order is 194 pm (LO) < 202 pm (LN) < 209 pm (LC) < 251 pm (LP). In general the latter are slightly larger than the former, with both reflecting the covalent radius of the ligated atom. The corresponding bridging ligand distances show a similar trend: 178 pm (H) < 180 pm (F) < 186 pm (LO) < 197 pm (LN) < 221 pm (LC) < 233 pm (Cl) < 234.5 pm (S) < 246 pm (LP) < 249 pm (Br) < 252 pm (LSe) < 255 pm (LAs) and 255 pm (Te) < 273 pm (LTe).

4. Trimeric compounds

Crystallographic and structural data for almost 30 colourless organoaluminium(III) trimeric derivatives are summarized in Table 6. A μ_3-O bridged unit of three non-equivalent tetrahedrally coordinated Al(III) atoms occurs [211], with mean Al–O bond distances and Al–O–Al angles of 181 pm and 119.5(4)° respectively. In another derivative [212], three $AlMe_3$ moieties are held together by μ_3-SeMe groups to complete a dis-

torted tetrahedral environment about the metal atoms (chromophore AlC_3Se). The mean values of the Al–Se distances and Al–Se–Al angles are 257.8(5) pm and 114.6(2)° respectively.

In a colourless example [213], the *N,N'*-bis(*o*-hydroxybenzyl)-1,2-diaminoethane(4-) ligand is in a cis geometry: one of the $AlBu^i_2$ units bridges the two nitrogen atoms and the other bridges the two oxygen

Table 6
Crystallographic and structural data for trimeric organo-aluminium compounds [a,e]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore		Al-L [pm]	Al-Al [pm] Al-L-Al [°] μL-Al-μL [°]	L-Al-L [°]	Ref
$[Al_3(\mu_3\text{-}O)(\mu\text{-}PhCO_2)$	or	2606.9(7)		AlC_3O	μ_3O[b]	181(1)	-	C,C[b] 109.6(6)	211
$(Me)_7][Na(bmc)(tl)]$	Pnma	1526.9(6)			C_{Me}	199(2,0)	119.5(4)	C,μ_3O 106.2(6,3)	
	4	1758.9(6)				204(2)			
(colourless)				AlO_2C_2	μ_3O	180.3(7)		C,C 121.1(8)	
				x2	O	185(1)		C,μ_3 113.1(7)	
					C_{Me}	not given		C,O 111.0(8)	
$K[Al_3(\mu_3\text{-}SeMe)(Me)_6]\cdot$	tr	1716.5(7)	119.26(5)	AlC_3Se	μ_3Se	257.8(5,16)	-	C,C 116.5(10,2.7)	212
$2C_6H_6$	PĪ	1014.4(7)	104.07(5)		C_{Me}	199(2,5)	114.6(2,1.0)	C,Se 100.8(7,3.9)	
	2	1015.6(7)	80.51(5)						
[(salean)$AlBu^i$	m	1721.8(3)		AlO_2N_2	μO	191.4(5,1)	285.5(3)	μO,μO 76.2(2)	213
	$P2_1/n$	965.7(2)	101.07(1)		μN	196.9(5,2)	O 102.5(2,2)	μN,μN 73.9(2)	
$(AlBu^i_2)_2]$	4	2383.7(4)					N 92.7(2,0)	μO,μN 88.9(2,6)	
								136.3(2,1)	
(colourless)				AlO_2C_2	μO	185.9(5,5)		μO,μO 78.9(2)	
					C	197.2(9,6)		C,C 124.4(3)	
								μO,C 111.1(3,4.2)	
				AlN_2C_2	μN	197.6(6,2)		μN,μN 73.6(2)	
					C	196.7(7,6)		C,C 114.0(3)	
								μN,C 115.9(3,3.8)	
$Al_3(\mu\text{-}en)_2(Me)_5$	m	1552.3(3)		AlN_4C	μN	199.1(2,3)	-	μN,C 111.3(1,6.7)	214
	P2/c	841.9(1)	109.00(2)			206.6(2,8)	94.5(1,1.5)	μN,μN 125.4(1)	
(White)	4	1346.4(3)			C_{Me}	195.8(2)	83.0(1,1.0)	149.2(1)	
				AlN_2C_2	μN	192.4(2,14)		μN,μN 88.0(1)	
				x2	C_{Me}	195.4(2,10)			
$[Al_3(\mu\text{-}dmen)_2(Me)_5]$	or	1466.8(9)		AlN_4C	μN	203.6(4,7)	291.1(2)	μN,C 110.9(2)	215
	Pnma	1668.2(2)			C_{Me}	195.9(8)	94.7(2,3)	μN,μN 139.0(2)	
(White)	?	816.0(3)					83.1(2,1.0)		
				AlN_2C_2	μN	192.6(4,0)		C,C 113.9(3)	
					C_{Me}	194.8(6,0)		μN,μN 88.2(2)	
								C,μN 113.7(2,8)	
$Al_3(\mu\text{-}bapen)(Me)_3Cl_2$	tr	923.4(3)	96.23(3)	AlN_4OCl	μN	200.2(4,20)	-	μN,N 89.5(2,7.1)	117
	PĪ	1068.1(3)	108.78(3)		N	201.3(4,10)	93.6(2,6)	μN,μO 96.2(2)	
(colourless)	2	1502.1(5)	97.34(3)		μO	194.4(4)	85.4(2)	μN,Cl 91.8(1)	
					Cl	236.8(2)	C	μO,N 88.6(2,8.9)	
								μO,Cl 86.7(1)	
				AlN_2C_2	μN	196.4(4,2)		μN,μN 87.5(2)	
					C_{Me}	196.0(6,4)		C,C 104.0(2)	
								μN,C 116.4(2,2.0)	
				AlONCCl	μO	181.8(3)		μO,N 85.5(2)	
					N	190.7(5)		μO,C 117.7(2)	
					C_{Me}	193.0(5)		μO,Cl 107.6(1)	
					Cl	213.0(3)		N,C 120.0(2)	
								N,Cl 113.0(2)	
								C,Cl 113.0(2)	
$Al_3(\mu\text{-}(Ph_2P(O))_2C)_2$	m	2615.7(9)		AlC_3O_2	μO	218.2(2,0)	-	C,C 120.0(5,10.2)	216
	C2/c	1026.1(3)	120.48(2)		C	197.9(5)	123.1(2)	O,O 163.9(2)	
$(Et)_5$	4	2460.7(9)			C_{Et}	198.3(10)		C,O 73.8(1)	
								97.9(6,3.4)	
(colourless)				AlO_2C_2	μO	183.9(2)		O,O 99.2(1)	
				(x2)	O	175.3(4)		C,C 116.3(3)	
					C_{Et}	195.6(7,5)		O,C 110.0(3,3.1)	
$Al_3(\mu\text{-}(Ph_2P(O))_2C)_2$	m	2575.6(4)		AlC_3O_2	μO	217.4(4)		C,C 120.0(2,2.0)	217
	C2/c	1012.6(2)	119.54(1)		C	198.2(6)		O,O 163.2(2)	
$(Me)_5$	4	2303.8(4)			C_{Me}	199.4(10)			
				AlO_2C_2	μO	not given			
(colourless)				(x2)	O	177.2(4)			
					C_{Me}	198.2(9,5)			
$MeSi(Bu^tNAlMe_2)_3$	m	1075(2)		AlN_2C_2	μN	202.0(5,6)	-	C,C 99.3(3)	218
	$P2_1/n$	1757(2)	90.5(1)		C_{Me}	195.5(6,23)	112.1(3)	C,N 119.4(4)	
(colourless)	4	1403.0(9)					81.43(6)		
$[Al(\mu\text{-}H)(Bu^t)_2]_3$	rh	1016.5(3)		AlH_2C_2	μH	172.6(5,0)	334	C,C 119.0(1)	219
	R3c	-			C	200.1(2,0)	151(1)	C,H 111.2(2,7)	
(colourless)	6	507.1(1)					89.2(8)		
at 153(3)K									
$[Al(\mu\text{-}OH)(Bu^t)_2]_3$	m	1769.7(6)		AlO_2C_2	μHO	184.8(4,3)	-	C,C 118.3(3,2)	176
	C2/c	1019.8(6)	109.37(2)		C_{Bu}	199.4(5,5)	142.0(2,1)	C,O 109.7(2,1.1)	
(colourless)	4	1778.1(5)					98.0(2,1)		
$[Al(\mu\text{-}OH)(Bu^t)_2]_3\cdot 2thf$	m	1146.3(3)		AlO_2C_2	μHO	184.3(3,12)	-	C,C 116.8(1,0)	176
	$P2_1/c$	1560.3(6)	95.63(2)		C_{Bu}	199.6(4,7)	140.5(1)	C,O 110.2(1,4.0)	
(colourless)	4	2226.3(6)					98.5(1,8)		
$[Al(\mu\text{-}OH)(Bu^t)_2]_3\cdot$	m	1140.6(2)		AlO_2C_2	μHO	184.6(2,11)	-	C,C 117.3(1,1.4)	176
	$P2_1/n$	2129.7(7)	96.76(2)		O_{Bu}	200.2(3,4)	141.7(1,7)	C,O 110.0(1,1.2)	
2MeCN (colourless)	4	1497.2(2)					97.8(1,1)		

Table 6 (continued)

[Al(μ-ONMe$_2$)(Me)$_2$]$_3$	tr	746.4(2)	86.90(2)	AlO_2C_2	μO 186.6(1,22)	-	C,C	120.5(1,1.1)	220
	PT	951.7(2)	83.40(2)		C_{Me} 196.1(2,4)	138.2(1,5.6)	C,O	110.2(1,1.8)	
(colourless)	2	1588.0(5)	74.28(2)			91.6(1,8)			
at 173K									
[Al(μ-NH$_2$)(Me)$_2$]$_3$	m	1210.5(4)		AlN_2C_2	μN 193.4(5,13)	338.2(3,47)	C,C	not given	221
	$P2_1/c$	885.3(2)	108.26(2)		C_{Me} 195.2(7,5)	122.0(2,3.4)	C,N	109.4(2,9)	
(colourless)	4	1434.3(4)				101.4(2,1.7)			
[Al(μ-NH$_2$)(Bu^t)$_2$]$_3$	rh	1040.1(3)		AlN_2C_2	μN 194.0(12,45)	359.2(20)	C,C	117.8(4)	221
	R3c	-			C_{Bu} 199.9(11,9)	133.9(5)	C,N	107.9(5,4)	
(colourless)	6	5078.3(39)				106.1(4)			
cis-[Al(μ-NHMe)	rh	998.3(4)	104.39(3)	AlN_2C_2	μN 194.1(12,10)	340.3(10)	C,C	117.6(6)	115
	R3				C_{Me} 197.2(12,3)	122.4(5)	C,N	108.3(5,1.8)	
(Me)$_2$]$_3$[d]	2					101.9(5)			
				AlN_2C_2	μN 193.9(9,9)	339.4(10)	C,C	116.2(6)	
(colourless)					C_{Me} 197.4(14,11)	122.1(4)	C,N	109.6(5,1.1)	
						102.4(4)			
trans-[Al(μ-NHMe)	m	1189.7(8)		AlN_2C_2	μN 190.1(12,68)	333.1(8,18)	C,C	117.5(9,2)	115
	C_2/c	1590.4(12)	107.50(3)		C_{Me} 198.2(20,23)	124.9(9,5.0)	C,N	108.9(7,1.8)	
(Me)$_2$]$_3$	4	977.8(7)				100.9(6,8)			
[Al(μ-NMe$_2$)(Me)$_2$]$_3$	m	1306.3(7)		AlN_2C_2	μN 193(1,3)	-	C,C	113.3(1.2,5)	222
	C2/c	983.4(6)	96.70(3)		C_{Me} 199(3,2)	119.9(5,4)	C,N	not given	
(colourless)	4	1505.0(7)				102.0(9,1.0)			
[Al(μ-PhN(CH$_2$)$_2$NH)Me]$_3$	tr	1644.1(7)		AlN_3C	μN 192(3,0)	-	μN,N	102(1,10)	55
	P$\bar{3}$	-			N 183(2)	124(1)	μN,C	109(1,4)	
(colourless)	2	1118.4(3)			C_{Me} 199(3)	107(1)	N,C	126(1)	
[Al(μ-Ndipp)(Me)]$_3$	trg	1903.5(6)		AlN_2C	μN 178.2(4,0)	-	not given		223
	P$\bar{3}$c1	-			C_{Me} 197.8(15)	124.7(5)			
(colourless)	6	2042.2(7)				115.3(5)			
[Al$_2$(μ-S(2-Bu^{t}C$_6$H$_4$))	m	932.4(7)		AlC_2S_2	μS 235.3(5,13)	-	C,C	120.6(5,1.3)	148
	$P2_1/c$	1863.2(5)	98.31(5)		C_{Me} 194(1,3)	117.6(2,5.6)	C,S	not given	
(Me)$_2$]$_3$	4	2395.9(9)				96.2(2,7.4)			
[Al$_2$(μ-S(2-SiMe$_3$)	tr	1014.9(4)	88.19(3)	AlC_2S_2	μS 236.4(2,13)	-	C,C	119.6(3,1.3)	148
	PT	1442.7(5)	89.39(3)		C_{Me} 194.5(7,13)	116.2(1,3.9)	C,S	not given	
C$_6$H$_4$)(Me)$_2$]$_3$	2	1515.9(4)	88.57(3)			96.5(1,7.1)			
[Al$_2$(μ-S(2-Pr^i)$_3$C$_6$H$_4$))	tr	1253.8(5)	74.38(1)	AlC_2S_2	μS 236.4(2,16)	-	C,C	121.8(2,2.2)	148
	PT	1318.0(2)	64.18(2)		C_{Me} 193.4(6,8)	117.5(1,5.0)	C,S	not given	
(Me)$_2$]$_3$	2	1387.3(2)	69.44(2)			97.2(1,7.0)			
[Al$_2$(μ-S(2-4,6-Pr^{i}C$_6$H$_2$))(Bu^t)$_2$]$_3$	m	1393.5(2)		Al_2S_2	μS 237(1,1)	-	C,C	130(1,1)	148
	$P2_1/c$	2256.3(4)	101.44(1)		C_{Bu} 196(3,5)	128.6(3,2.9)	C,S	not given	
	4	2504.4(4)				92.8(3,3.3)			
Al$_3$(μ-N$_4$ada)(Me)$_9$	m	741.6(2)		AlC_3N	C_{Me} 197.0(18,69)		C,C	116.0(6,3.0)	224
	$P2_1/c$	1668.7(6)	91.71(2)		N 211.3(5,14)		C,N	101.6(5,3.9)	
(colourless)	4	1914.3(6)							
Al$_3$(μ-tedta)(Me)$_8$	m	763.0(2)		AlN_2C_2	μN 195.9(9)	-	N,N	91.1(4)	80
	$P2_1/n$	2541.5(7)	97.46(2)		N 203(1)	114.6(5)	C,C	113.6(5)	
(colourless)	4	1450.8(3)			C_{Me} 195(1,2)		N,C	112.5(5,4.4)	
				AlC_3N	μN 204.4(9)		C,C	110.4(6,2.8)	
					C_{Me} 198(1,1)		C,N	108.5(5,3.1)	
				AlC_3N	N 210(1)		C,C	111.7(6,8)	
					C_{Me} 199(1,1)		C,N	107.1(6)	
[Al$_3$(μ-(Ph$_2$PCH$_2$CH$_2$)$_2$	tr	1996.8(4)	96.175(6)	AlC_3P	C_{Me} 196.4(5,7)		C,C	115.8(3,1.3)	198
	PT	1252.1(3)	93.917(6)		P 254.4(4)		C,P	102.0(2,3.3)	
PPh)(Me)$_9$·½C$_6$H$_6$	2	1034.6(9)	72.928(2)						
(colourless)									
Al$_3$(μ-db-[18]-C-6)(Me)$_9$	m	889.8(4)	74.86(3)	AlC_3O	C_{Me} 196.6(8,39)		C,C	115.8(4,2.3)	225
	PT	1184.8(5)	80.73(4)		O 199.3(5,31)		C,O	101.9(3,2.9)	
(colourless)	2	1906.0(6)	67.02(4)						

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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–O–Al = 97.9(2)°.

[d] There are two crystallographically independent molecules.

[e] Refs. [55b,80,115,117,148,176,198,211–225] are to be found in the reference list.

atoms. Each aluminium(III) is tetrahedrally coordinated (AlO_2N_2, AlO_2C_2 and AlN_2C_2). The Al–Al distance is 285.5(2) pm with mean Al–O–L and Al–N–Al bridge angles of 102.5(2)° and 92.7(2)° respectively.

There are two structures which contain a five-coordinate, square pyramidal, aluminium(III) atom in the middle of two tetrahedral aluminium(III) atoms. In both molecules the bidentate ligand, (en) [214] or (dmen) [215], serve both as chelates and double bridges between the central and outer aluminium atoms. Methyl groups complete the coordination spheres of all three aluminium atoms, one being in the apical position of the central metal atom.

Another derivative [117] contains a chloro-aluminium unit, a dimethylaluminium unit and a methylaluminium unit, as shown in Fig. 3. The macrocycle (bapen) as-

sumes a considerable distorted, folded 'envelope', conformation in accommodating the three different aluminium species. The core Al(1) atom has a pseudo-octahedral environment, while the outer Al(2) and Al(3) atoms are in tetrahedral environments with the chromophores AlN_2C_2 and AlONCCl respectively.

A pair of derivatives [216,217] of the composition $Al_3\{\mu\text{-}(Ph_2P(O)_2C\}_2(L)_5$, where L is methyl or ethyl, contain two bis(diphenylphosphinoyl)methanide units bridged by three organoaluminium (two dialkyl- and one monoalkylaluminium) moieties. The central aluminium atom is bonded to one methyl carbon and one oxygen atom of each ligand. The geometry about this aluminium(III) atom is trigonal bipyramidal (AlC_3O_2) with O atoms in apical positions. The O–Al–O bond angles are 163.9(2)° (methyl derivative) and 163.2(2)° (ethyl derivative), compared to the ideal value of 180°. The outer Al(III) atoms are both in tetrahedral environments (AlO_2C_2).

The most common feature of the trimeric organoaluminium derivatives is a planar six member $(Al–X)_3$ heterocyclic ring, with X being one of the following: μ-H [219]; μ-OH [176]; μ-$ONMe_2$ [220]; μ-NH_2 [221]; μ-NHMe [115]; μ-NMe_2 [222]; μ-Ndipp [223]; μ-$N(H)(CH_2)_2NPh$ [55b]; μ-SL [148]. Except for one case containing three-coordinate aluminium(III) [223], the aluminium atoms are found in tetrahedral environments. There is an interdependence between the Al–L(bridge) and Al–C(terminal) distances, the Al–L–Al, μL–Al–μL and C–Al–C bond angles, and the covalent radii of the bridging atoms. As the bridging atom gets larger, the Al–L(bridge) distance gets longer and the Al–C(terminal) distance decreases; for example: 173 pm and 200 pm for μ-H (33 pm); 185 pm and 199 pm for μ-OL (73 pm); 193 pm and 198 pm for μ-NL (75 pm); 236 pm and 195 pm for μ-SL (102 pm). The Al–L–Al and C–Al–C bond angles both close while the μL–Al–μL angle opens with increasing size of the bridge atom,

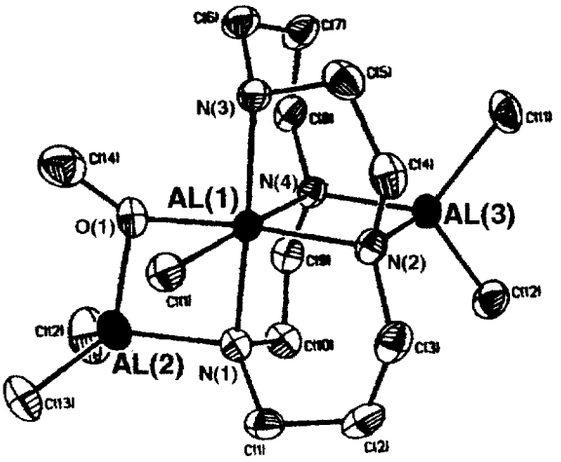

Fig. 3. Structure of $Al_3(\mu\text{-bapen})(Me)_3Cl_2$ [117].

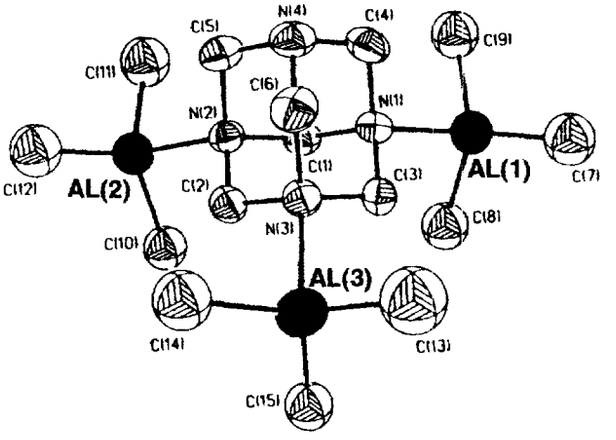

Fig. 4. Structure of $Al_3(\mu\text{-}N_4ada)(Me)_9$ [224].

except in the case of the S-donor ligands which are, of themselves, bulky and cause further distortions. The mean values for these angles are: 151°, 119.0° and 89.2° for μ-H; 140.6°, 118.3° and 96.5° for μ-OL; 124.2°, 116.5° and 102.5° for μ-NL; 120.0°, 123.0° and 95.7° for μ-SL.

The molecule $[Al(\mu\text{-NHMe})(Me)_2]_3$ [115] exists in two isomeric forms, cis and trans. The cis form even contains two crystallographically independent molecules, differing mostly by degree of distortion, within the same crystal.

The structure of $Al_3(\mu\text{-}N_4ada)(Me)_9$ [224] is shown in Fig. 4. The molecule approaches C_{3v} point symmetry, with the coordination of the aluminium atoms being distorted tetrahedral, probably a consequence of the associated steric demands.

Three different aluminium centres have been found in $Al_3(\mu\text{-tcdta})(Me)_8$ [80], with each metal atom being in tetrahedral environments with different degrees of distortion. In another trimeric derivative [198] the triphos ligand serves as a bridge in the manner [Al–P–C–C–P(Al)–C–C–P–Al]. Each aluminium atom is again tetrahedrally coordinated (AlC_3P). In another case, three $AlMe_3$ moieties bond with a 3,3-dibenzo-18-crown-6 ligand through its O donor atoms [225], giving tetrahedral coordination about each aluminium atom (AlC_3O).

5. Tetrameric compounds

Crystallographic and structural data for almost 40, mostly colourless, tetrameric organoaluminium compounds are listed in Table 7. These structures tend to be complex with several different structural types.

In $\{Al(\eta^5\text{-cp}^*)\}_4$ [226] the four Al(I) atoms form a regular tetrahedron, with the average Al–Al bond distance of 276.9 pm, which is about 9 pm shorter than that of metallic aluminium (286.0 pm). Each pentamethylcyclopentadienyl ring is η^5-coordinated to an Al(I) atom,

with the plane of each ring essentially parallel to the imaginary opposite face of the tetrahedron. The average Al–C distance is 233.4 pm.

There are seven derivatives [119,227,229–231] which have an Al_4X_4 cubane core structure, where X is N [119,227–229], P [230], Se [231], or Te [231]. The mean Al–μ_3L(bridge) distance increases with the covalent radius of the bridging atom in the sequence:

Table 7
Crystallographic and structural data for tetrameric organo-aluminium compounds [a,d]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Al-L [pm]	Al-Al [pm] Al-L-Al [°] μL-Al-μL [°]	L-Al-L [°]	Ref
$[Al^{I}(\eta^5\text{-}cp^*)]_4$	tr P$\bar{1}$ 2	1095.3(2) 1101.2(3) 1828.8(4)	83.83(2) 83.88(2) 66.80(2)	AlC_5	C^b 233.4(13,42) 201.5(-,18)[c]	276.9(5,4)	Al,Al 60.0(1,1)	226
$[Al(\mu_3\text{-}NPr^i)(Me)]_4$ (colourless)	tr P$\bar{1}$ 2	1692.4(11) 886.4(5) 947.1(9)	109.5(1) 110.9(1) 90.2(1)	AlN_3C	μ_3N 192.4(5,7) C_{Me} 194.6(7,28)	- 89.6(1) 90.4(1)	N,C 124.9(2)	227
$[Al(\mu_3\text{-}NPh)(Ph)]_4$ (colourless)	tg $I4_1/a$ 4	1993(5) - 1082(3)		AlN_3C	μ_3N 191(1,2) C_{Ph} 186(2)	- 89.8(4,2) 90.2(4,2)	N,C 126.7(5,3.5)	228
$[Al(\mu_3\text{-}Nmes)(Me)]_4 \cdot 3C_7H_8$ (colourless)	m $P2_1/c$ 4	1308.2(3) 1902.7(3) 2294.1(9)	101.04(3)	AlN_3C	μ_3N 194.8(7,0) C_{Me} 194.9(3)	275.3 89.9(6) 90.1(6)	N,C 116.7(1,2.5) 140.7(1)	119
$[Al(\mu_3\text{-}NSiPh_3)(Bu^i)]_4 \cdot$ ½hexane (colourless)	tr P$\bar{1}$ 2	1394.2(7) 1442.6(8) 2109.3(11)	93.23(1) 98.78(1) 93.84(1)	AlN_3C	μ_3N 195.4(5,16) C_{Bu} 195.5(6,8)	- 88.8(2) 91.2(2,8)	N,C 124.0(4,9)	229
$[Al(\mu_3\text{-}PSiPh_3)(Bu^i)]_4$ (white)	tg $P42_1c$ 2	1572.1(2) - 1718.6(3)		AlP_3C	μ_3P 241.4(4,5) C_{Bu} 196(1)	- 88.2(2,8) 91.8(2,9)	P,C 124.0(4,3.7)	230
$[Al(\mu_3\text{-}Se)(cp^*)]_4$ (colourless)	tg I4 2	1214.4(1) - 1437.3(2)		$AlSe_3cp^*$	μ_3Se 247.7(1,20) cp 194.9[c]	- 85.2(1,6) 94.6(1,7)	not given	231
$[Al(\mu_3\text{-}Te)(cp^*)]_4$	tg I4 2	1243.0(2) - 1454.6(3)		$AlTe_3cp^*$	μ_3Te 271.0(1,40) cp 196.5	- 84.7(1,1.0) 95.1(1,1.2)	not given	231
$([Al(\mu\text{-}Cl)((Me_3Si)_2CH)]_2(\mu\text{-}CH_2))_2$ (colourless) at 173K	tg $I4_1/a$ 4	1786.8(4) - 1786.8(3)		AlC_2Cl_2	μC 195.9(2) μCl 230.3(1,5) C 194.5(3)	122.6(2) 115.3(1)	μC,C 124.1(1) μC,μCl 108.6(1,3.3) μCl,μCl 97.3(1) μCl,C 104.3(1)	232
$Al_4(\mu_3\text{-}qui)_2(Me)_8$ (colourless)	m $P2_1/n$ 2	863.7(3) 1405.6(4) 1239.6(6)	108.17(3)	AlN_2C_2	μ_3N 196.7(7,26) C_{Me} 197(1,0)	278.8(5) 90.3(3) 89.7(2)	C,C 109.3(2)	233
				AlN_2C_2	μ_3N 193.0(7) N 199.3(6) C_{Me} 196(1,2)		N,N 85.6(3) C,C 117.5(4)	
$Al_4(\mu_3\text{-}qui)_2(\mu\text{-}OMe)(Me)_7$ (orange)	m $P2_1/c$ 4	1374.1(3) 1404.0(3) 1517.5(2)	92.02(2)	AlN_4	μ_3N 197.9(5,36) N 208.1(6,42) C_{Me} 195.3(7)	280.1(3) - 81.0(2)	μ_3N,N 125.0(2) 154.3(2) μ_3N,C 130.6(3) N,C 104.4(3)	233
				AlN_2C_2	μ_3N 194.1(5,18) C_{Me} 195.9(7,9)		N,N 83.0(2) C,C 115.2(3)	
				AlC_2ON (x2)	μ_3N 193.9(5,10) μO 186.3(4,6) C_{Me} 195.2(8,11)	- 136.6(3)	N,O 98.2(2,8) C,C 112.0(4,1)	
$[AsMe_4]_2[Me_2Al(\mu_3\text{-}O)AlMe_3]_2 \cdot C_6H_6$ (colourless)	m $P2_1/n$ 2	982.9(3) 1524.7(5) 1364.1(4)	97.37(2)	AlO_2C_2	μ_3O 180(2) C_{Me} not given		not given	234
				AlC_3O	μ_3O 178(2) C_{Me} not given		not given	
$[Bu^t_2Al(\mu_3\text{-}O)(AlBu^t_2]_2$ (colourless)	m C2/c 8	4162.2(3) 901.76(8) 2130.3(1)	99.250(5)	AlO_2C_2	μ_3O 186.5(4,6) C_{Bu} 202.1(6,8)	- 95.6(1,2) 84.5(1,3)	C,C 113.7(2,0) C,O 100.0(2,1.8) 128.3(2,8)	176
				AlC_2O	μ_3O 175.1(3,1) C_{Bu} 198.6(7,10)	- 132.5(2)	C,C 120.1(2,1) C,O 119.9(2,1)	
$[Al_2(\mu_3\text{-}N)\{(Me_3Si)N\}(cp^*)_2]_2$ (colourless)	tr P$\bar{1}$ 1	1122.5(2) 1173.3(2) 1370.3(2)	92.22(2) 109.57(2) 101.25(2)	AlN_3	μ_3N 181.1(-,8) N 179.0	- 84.3(-,1) 95.6(-,1)		235
				AlN_2C	μ_3N 181.0(-,7) C 198.5		N,C 131.7(-,6.9)	
				AlN_2C	μ_3N 178.1 N 181.8 C not given	- - 137.2(-,4.7)		
				AlC_2N	μ_3N 180.4 C not given			
$((AlMe_2)_3(\mu\text{-}tpm)_6Al)$ (colourless)	or Pbcn 4	1815.3(2) 1117.6(2) 2282.0(2)		AlO_6	μO 191.2(5,1)	- 102.2(2,8)	O,O 76.2(2,7) 167.3(2,3)	236
				AlO_2C_2 (x3)	μO 183.8(5,5) C_{Me} 196.9(8,9)		O,O 79.8(2,5) C,C 115.2(4,3)	

Table 7 (continued)

$(AlMe_2)(\mu\text{-}AlC_{10}H_{20}N_4)$	m	1764.3(7)		AlN_4Cl_2	μN	196.7(3,17)		N,N 170.0(2)	237
	C2/c	1122.0(6)	104.56(3)		μCl	250.9(2,0)		N,Cl 87.4(1,6.3)	
$(AlMe_2Cl)_2$	4	1306.9(5)		AlN_2C_2	μN	not given		not given	
					C_{Me}	198.6(6)			
				AlC_2NCl	μN	not given		not given	
				(x2)	μCl	225.8(2)			
					C_{Me}	195.4(4,12)			
$(AlEt)_2(\mu\text{-}C_{10}H_{20}N_4)$	m	1187.1(9)		AlN_3C	μN	195.0(6,5)	276.8(3)	not given	238
	$P2_1/n$	905.2(7)	115.19(4)		N	not given	90.4(4)		
$(AlEtCl_2)_2$	2	1429.9(1)			C_{Et}	not given	89.6(3)		
				$AlCl_2CN$	μN	not given		Cl,Cl 117.8(8)	
					C_{Et}	not given			
					Cl	216.8(4,5)			
$(AlMe)_2(\mu\text{-}C_{10}H_{20}N_4)$	m	815.2(6)		AlN_3C	μN	191.9(4,40)	273.5(2)	N,N 97.5(2,3.9)	239
	$P2_1/n$	1378.3(9)	90.18(6)		C_{Me}	192.8(5)	89.9(2)	N,C 121.6(2,6.3)	
$(AlMe_3)_2$	2	1101.8(8)					90.1(2)		
(colourless) at 173K				AlC_3N	μN	204.2(4)		C,C 113.1(3,1.0)	
					C_{Me}	197.7(5,14)		C,N 105.5(2,1.2)	
$(AlMe_2)_2(\mu\text{-}C_{10}H_{20}N_4)$	m	2516.6(2)		AlN_2C_2	μN	188.9(5)	335.7(3)	C,C 117.5(3)	240
	C2/c	726.8(4)	115.3(4)		N	205.8(5)	117.8(3)	N,C 109.5(2,6.6)	
$(AlMe_3)_2$	4	1731.6(4)			C_{Me}	195.3(6,14)	98.1(2)		
				AlC_3N	μN	203.0(5)		C,C 113.1(2,1.8)	
(colourless) at 173K					C_{Me}	197.8(7,18)		C,N 105.5(2,2.5)	
$(AlMe)_2(\mu\text{-}C_{10}H_{22}N_4)$	tr	797.8(2)	75.46(2)	AlN_3C	μN	193.3(2,30)	-	N,C 121.4(1,4.4)	241
	P1	942.8(2)	67.86(2)		C_{Me}	192.9(3)	89.7(1)		
$(AlMe_3)_2$	1	962.7(2)	73.84(2)				95.1(1,7.2)		
				AlC_3N	μN	203.7(2)	-	C,C 112.9(1,4)	
(colourless)					C_{Me}	198.2(3,8)	111.8(1)	C,N 105.8(1,7)	
$(AlBu^i)_2(\mu\text{-}C_{10}H_{20}N_4)$	tr	1044.3(2)	79.43(2)	AlN_3C	μN	193.5(5,23)	-		242
	P1	1056.2(2)	82.16(2)		C_{Bu}	not given	91.1(2)		
$(AlBu^i_3)_2$	1	1244.3(2)	68.06(2)				88.9(1)		
				AlC_3N	μN	not given			
(colourless)					C_{Bu}	not given			
$(AlMe)_2(\mu\text{-}[15]aneN_4)$	m	1082.6(2)		AlN_3C	μN	193.5(6,47)	278.5(3)	N,C 119.0(3,6.8)	243
	$P2_1/n$	1822.1(5)	102.23(2)		C_{Me}	193.4(9,12)	90.8(2)		
$(AlMe_3)_2$	4	1382.5(4)					97.9(2,8.8)		
				AlC_3N	μN	203.3(6,5)	-	C,N 106.3(3,4.1)	
(colourless)					C_{Me}	197(1,1)	112.8(2,3)		
$(AlMe)_2(\mu\text{-}C_6H_{20}N_6)$	m	2111.0(1)		AlN_4C	μN	200.8(2,32)	290.7(1)	not given	244
	C2/c	849.9(4)	115.19(4)		C_{Me}	196.2(4)			
$(AlMe_2)_2$	4	1363.5(8)		AlN_2C_2	μN	not given			
					C_{Me}	195.2(4,5)			
(colourless)									
$(AlEt)_2(\mu\text{-}C_6H_{20}N_6)$	tr	842.9(3)	102.39(2)	AlN_4C	μN	205.9(3,25)	-	N,C 111.5(2,8.4)	215
	P1	920.7(2)	86.92(2)		C_{Et}	197.6(4)	94.0(1)		
$(AlEt_2)_2$	?	980.4(1)	109.68(2)	AlN_2C_2	μN	190.4(3)	83.0(1,2.0)		
					C_{Et}	119.60(4)			
(colourless)								N,N 87.6(1)	
								C,C 118.9(1)	
								N,C 112.0(2,2.8)	
$(AlMe)_2(\mu\text{-}C_{12}H_{28}N_6)$	m	833.4(2)		AlN_4C	μ_3N	187.8(4)	285.7(3,27)	μ_3N,N 91.6(2)	245
	$P2_1/n$	1109.9(3)	90.99(2)			206.5(4)	92.5(2,1.3)	169.0(2)	
$(AlMe_2)_2$	2	1426.4(4)			μN	196.7(4)		μ_3N,C 127.9(2)	
					N	219.3(4)		N,C 89.8(2)	
(colourless)					C_{Me}	198.8(6)			
				AlN_2C_2	μ_3N	189.1(4)	-	C,C 111.0(3)	
					μN	194.4(4)	-		
					C_{Me}	198.1(7,7)	90.6(2)		
$(AlBu^i)_2$	m	1970.3(9)		AlC_2S_2	μ_3S	229.3(3,5)	-	not given	246
	$P2_1/n$	1346.2(8)	94.41(4)		μC	200.7(6)	83.7(1)		
$\{Ph_2P(S)CPPh_2(S)\}_2$	4	1992.4(9)			C_{Bu}	not given			
				AlC_2S_2	μS	225.4(3)		not given	
$(AlBu^i_2)_2$					S	not given			
					μC	205.9(6)			
(colourless)					C_{Bu}	not given			
				AlC_2S_2	μ_3S	234.6(3,4)		not given	
					C_{Bu}	not given			
				AlC_2SP	μ_3S	229.1(3)		S,P 94.0(1)	
					P	245.8(3)			
					C_{Bu}	not given			
$[Al\{MeC(CH_2NH)_3\}_2$	tg	1023.5(3)		AlN_6	μN	201.0(4,4)	-		247
	$P4_12_12$	-					92.6(2,1)		
$(AlMe_2)_3]$	4	2445(1)					90.0(2,4.8)		
				AlN_2C_2	μN	193.2(4,3)		N,N 89.7(2)	
(colourless)				(x3)	C_{Me}	196.8(6,5)			
$K_2[Al_4Me_{12}SO_4]$	m	1022.3(4)		AlC_3O	O	190(1,2)		C,C 115.1(8,2.4)	248
	$P2_1/c$	2022.5(7)	112.20(3)		C_{Me}	196(2,3)		C,O 102.9(7,6.0)	
(colourless)	4	1403.9(4)							
$K_2[Al_4Me_{12}SO_4]$.	m	977.3(3)		AlC_3O	O	191.0(9,67)		C,C 115.4(7,2.7)	248
	$P2_1/c$	1549.7(6)	92.51(3)		C_{Me}	196(2,7)		C,O 102.5(7,3.9)	
½p-xylene (colourless)	4	2044.2(9)							
$[\{N(CH_2CH_2O)_3\}$	m	937.2(6)		AlO_4NC	μO	194(9,10)		O,O 162.4(3)	249
	$P2_1/n$	1402.6(8)	92.35(4)		N	205.8(9)		O,N 158.0(4)	
$Al_2Me_3]_2$	2	961.0(4)			C_{Me}	199(1)		O,C 176.9(4)	
				AlO_2C_2	μO	184		O,O 108.0(4)	
(colourless) at 193K					C_{Me}	not given			

Table 7 (continued)

$[(N(CH_2CH_2O)_3)Al_2Me_3]_2$	m	953.73(6)		AlO_4NC		not given				250
	$P2_1/c$	984.72(6)	108.001(5)							
(colourless)	2	1435.5(1)		AlO_2C_2		not given				
$[(N(CH_2CH_2O)_3)$	tr	1024.6(4)	104.96(3)	AlO_4NCl	μO	179.8(4)	-	O,N	83.9(2,1.3)	251
	PT	1286.4(4)	89.92(3)			191.9(5,12)	100.9(2)	O,Cl	95.1(2,1)	
$Al_2(Bu^i)_2Cl]_2$	2	1468.1(6)	96.84(3)		N	200.3(5)	89.8(2,10.7)	N,Cl	97.5(2)	
(colourless)					Cl	224.3(3)				
				AlO_2C_2	μO	184.8(5,11)	-	O,O	104.4(2)	
					C_{Bu}	197.9(8,1)	122.2(2,9)	C,C	112.4(3)	
								O,C	109.9(3,1.7)	
$[Al(\mu\text{-}S\text{-}2,6\text{-}Me_2C_6H_3)$	tr	855.5(1)	96.546(8)	AlC_2S_2	μS	236.3(1,4)	-	C,C	123.2(2,2.9)	148
	PT	1186.9(1)	106.34(1)		C_{Me}	194.3(4,16)	128.8(1,1.9)			
$(Me)_2]_4$ (colourless)	1	1268.8(1)	109.06(1)				97.0(1,2.4)			
$[Al(\mu\text{-}NCOC_6H_4)$	tr	1275.3(3)	94.50(3)	AlO_2C_2	O	183.2(-,12)			not given	252
	PT	1281.8(3)	105.47(3)	AlN_2C_2	N	195.1(-,4)				
$\mu\text{-}O)Me_2]_4$	2	1350.6(3)	92.78(3)	AlC_2ON (x2)	C	195.3(-,10)				
(colourless)										
$[(AlMe_3)_4(18\text{-crown-}6)]$	or	1875.3(3)		AlC_3O	O	198.5(6)		C,C	115.6(4,2.9)	225
	Pbcn	1257.0(6)			C_{Me}	196.0(8,27)		C,O	102.3(3,1.4)	
(colourless)	4	1509.5(6)								
$[(AlMe_3)_4(18\text{-crown-}6)]$	m	1482.2(6)		AlC_3O	O	198.9(3,11)		C,C	114.8(2,1.1)	253
	$P2_1/n$	789.4(4)	105.40(4)		C_{Me}	196.5(6,14)		C,O	103.4(2,1.2)	
.p-xylene (colourless)	2	1880.5(6)								
$(AlMe_3)_4(Me_4cyclam)$	or	1392.8(5)		AlC_3N	N	209.8(3,5)		C,C	not given	254
	Pbca	1852.2(6)			C_{Me}	196.3(6,3)		C,N	104.3(2,2.8)	
(colourless)	4	1453.8(6)								
$(AlMe_3)_4([14]aneS_4)$	tr	803.2(5)	95.24(3)	AlC_3S	S	252.1(2,10)			not given	255
	PT	1033.0(4)	94.85(5)		C_{Me}	195.4(6)				
(colourless)	1	1120.5(3)	105.46(5)							
$\{[Al(\mu\text{-}MeCCMe)Cl]_2\}_2$	tr	1078(2)	97.9(1)	AlC_2Cl	C	199.0	300.5	C,C	115.1	256
	PT	1451(3)	109.4(1)		Cl	210.9		C,Cl	114.9	
(colourless) at 143K	1	1560(3)	104.2(1)		C#	235.5				

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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–cp centroid distance.

[d] Refs. [176,119,215,225–256] are to be found in the reference list.

193 pm (N, 75 pm) < 241 pm (P, 106 pm) < 248 pm (Se, 117 pm) < 271 pm (Te, 137 pm). At the same time, the Al–L–Al angle closes and the μL–Al–μL opens, for example: 89.5° and 90.6° (N-bridge); 88.2° and 91.8° (P-bridge); 85.2° and 94.6° (Se-bridge); 84.7° and 95.1° (Te-bridge). The mean Al–C distances also follow this trend: 193 pm (N) < 196 pm (P), for monodentate C-donor ligands; and 195 pm (Se) < 196.5 pm (Te), for Al–cp* (centroid). The structure of another tetramer has AlC_2Cl_2 units linked by a chlorine atom and methylene groups to give a heteroadamantane structure.

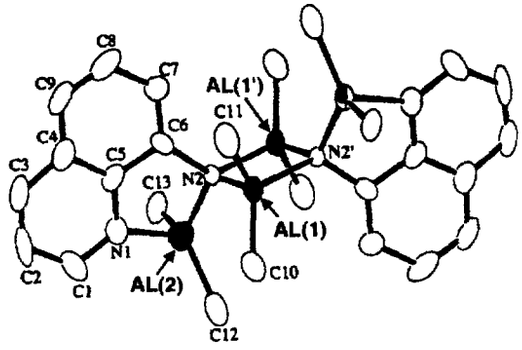

Fig. 5. Structure of $Al_4(\mu_3\text{-qui})_2(Me)_8$ [233].

Fig. 5 shows the structure of $Al_4(\mu_3\text{-qui})_2(Me)_8$ [233] which has an inversion centre. Each aluminium(III) atom is tetrahedrally coordinated (AlN_2C_2), with the 8-quinolylimide anion bridging three metal atoms through its imido atom N(2). The shortest Al–Al distance is 278.8(5) pm, and the most interesting property of this complex is its reaction with oxygen and conversion to $Al_4(\mu_3\text{-qui})_2(\mu\text{-OMe})(Me)_7$, the structure of which is shown in Fig. 6. The oxidation has caused a

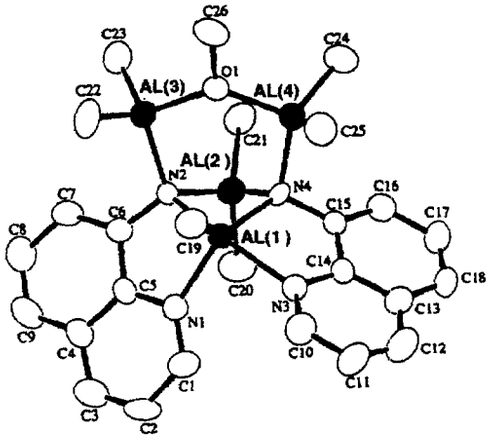

Fig. 6. Structure of $Al_4(\mu_3\text{-qui})_2(\mu\text{-OMe})(Me)_7$ [233].

dramatic change in the coordination environments, and arrangements, of the four Al(III) centres. The butterfly arrangement in Fig. 5 becomes an approximate tetrahedron of Al atoms in Fig. 6. The shortest Al–Al distance is now 280.1(3) pm for Al(1)–Al(2), and the longest distance is 346.0(3) pm for Al(3)–Al(4). The oxidized complex now contains a five-coordinate, trigonal bipyramidal aluminium, Al(1), with the other three metal centres remaining four-coordinate but with two different chromophores, AlN_2C_2 for Al(2) and AlC_2ON for Al_3 and Al_4.

There are three derivatives in which the Al_4O_2 [176,234] or Al_4N_2 [235] core is essentially planar, with intra-ring Al–O or Al–N distances of 186.5(4) pm (mean) [176], 180(2) pm [234] and 181.1 pm [235]. The exocyclic distances are shorter with values of 175.0(3) pm (mean) [176], 178(2) pm [234] and 180.0 pm [235]. In two cases [176,235] two of the aluminium atoms are three-coordinate and form the central, almost planar four-member rings of Al_2O_2 and Al_2N_4. The other two are four-coordinate (tetrahedral geometry) bonded to O or N atoms of the ring. In the remaining derivative [234] each aluminium atom is tetrahedrally coordinated, two AlO_2C_2 chromophores forming the central (almost planar) Al_2O_2 ring, with two AlC_3O found in peripheral positions.

The central core of another tetramer [236] contains an octahedral Al(III) atom bonded through six bridging alkoxide units to three organoaluminium $AlMe_2$ moieties. The coordination geometry about these aluminium atoms is tetrahedral (AlO_2C_2). A similar structure was found in another derivative [237], with a six-coordinate aluminium core (AlN_4Cl_2) linked to three peripheral tetrahedral aluminium atoms (one AlN_2C_2 and two AlC_2NCl chromophores).

A crystallographic centre of symmetry with a planar Al_2N_2 ring occupying the central cavity of the macrocyclic ligand is found in a number of examples [215,238,239,241–245]. The Al–Al distance in the four-member ring ranges from 273.5(2) to 290.7(1) pm (average 280.6 pm), indicating a metal–metal bond. The Al_2N_2 ring is asymmetric with independent Al–N distances (Table 7). The central aluminium conforms to a tetrahedral geometry [238–243] or square pyramidal geometry [215,244,245]. The outer pair of aluminium atoms are only found in tetrahedral geometries. The mean Al–L bond distances of the central, four-coordinate aluminium atom are shorter than those of the outer pair of atoms: the mean Al–N and Al–C bond distances for the former are respectively 193 pm and 194 pm. which increase to 203 pm and 198 pm respectively for the latter.

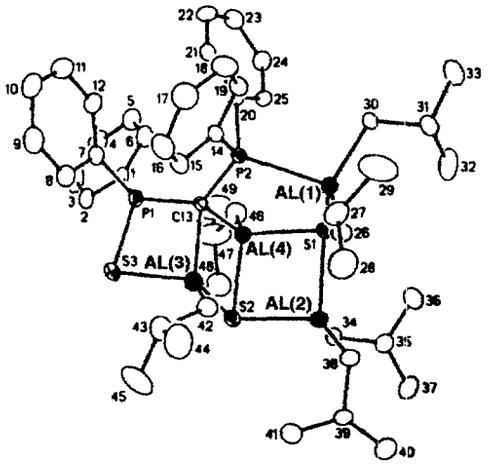

Fig. 7. A view of $(AlBu^i)_2\{Ph_2P(S)CPPh_2(S)_2\}(AlBu^i_2)_2$ [246].

The structure of $(AlMe_2)_2(C_{10}H_{22}N_4)(AlMe_3)_2$ [240] does not contain the customary Al_2N_2 fragments. Instead, it consists of a series of three, six-member, rings with an Al–Al separation of 335.7(3) pm. The central piperazine fragment, in a perfect chair conformation, serves to limit the flexibility of the amine skeleton (Al–N = 205.8(2) pm). Each aluminium is tetrahedrally coordinated (two AlN_2C_2 and two AlC_3N chromophores).

Fig. 7 [246] illustrates a tetramer with an unusual central core of S_2Al_4. This fragment and the bidentate phosphine ligand give rise to three adjoining four-member rings plus one five-member ring.

The molecular symmetry of $Al\{MeC(CH_2NH)_3\}_2(AlMe_2)_3$ [247] is C_2, with two tripodal ligands coordinating to the four aluminium atoms. These four atoms lie in a plane, three forming an equilateral triangle about the fourth. This central aluminium is in an octahedral geometry while the other three are essentially tetrahedral. The central aluminium atom is bonded to each of the others by two N atoms of the tripodal ligand to give a central AlN_6 unit. The other aluminium atoms are in AlN_2C_2 units.

A unique structure is found for an anion [248] in

Notes to Table 8:

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses 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] Two crystallographically independent molecules present.

[d1] Al–Al = 301.6, 310.0 and 385.6 pm.

[d2] Al–Al = 367.6(1) pm.

[e] Refs. [129,176,257–269] are to be found in the reference list.

Table 8
Crystallographic and structural data for oligomeric organo-aluminium compounds [a,c]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo-phore	Al-L [pm]	Al-L-Al [°]	L-Al-L [°]	Ref
$[Al_6(\mu_3\text{-}O)_4$	trg	1061.1(1)		AlO_4C	μ_3O 190.0(8)	103.7(9)	$\mu_3O,\mu O$ 75.6(3,8)	257
	$R\bar{3}$	-			$\mu\bar{R}O$ 190(1,5)	102.5(9)	122.1(3)	
$(\mu\text{-}OH)_4(Bu^t{}_6)]$	?	2973.6(3)			C_{Bu} 191.0(9)		μ_3O 116.6(6)	
							$\mu\bar{O},\mu O$ 77.9(3)	
(colourless)							125.3(3)	
$[Al(\mu_3\text{-}O)(Bu^t)]_6$ [c]	tr	1184.7(3)	103.83(2)	AlO_3C	μ_3O 178.3(6,23)	93.0(3,1.1)	O,O 86.5(2,1.3)	176
	$P\bar{1}$	1220.8(2)	109.02(2)		189.1(4,14)	127.4(3,3)	112.2(3,1)	
(colourless)	2	1371.1(4)	92.37(3)		C_{Bu} 193.1(10,29)		O,C 120.7(3,3.7)	
				AlO_3C	μ_3O 179.5(6,14)	92.2(2,1.9)	O,O 87.6(2,1.0)	
					188.8(4,13)	127.6(2,1.1)	112.4(3,8)	
					C_{Bu} 194.9(9,12)		O,C 120.3(3,1.9)	
$[Al(\mu_3\text{-}NPr^i)Cl]_6$	trg	1708.3(2)		AlN_3Cl	μ_3N 190.6(3,8)	88.1(1,2)	N,N 91.8(1,3)	258
	$R\bar{3}$	-			195.5(3)	122.0(1)	117.7(1)	
	3	965.2(1)			Cl 212.2(1)		N,Cl 117.0(1,3.7)	
$[Al(\mu_3\text{-}NPr^i)(Me)]_6$	trg	1737.8(3)		AlN_3C	μ_3N 191.7(2,9)	88.6(1,3)	N,N 91.4(1,3)	258
	$R\bar{3}$	-			196.4(2)	123.9(1)	115.7(1)	
$[Al(\mu\text{-}NPr^i)$	3	970,6(3)			C_{Me} 197.7(3)		N,C 117.7(1,2.8)	
$Me_{0.83}H_{0.17}]$								
(colourless)								
$[Al(\mu_3\text{-}NPh)(Me)]_6$	rh	1247.6(4)	62.35(3)	AlN_3C	μ_3N 191.2(5,10)	89.2(2,3)	N,N 90.5(2,3)	129
	$R\bar{3}$				195.1(6)	126.0(2)	113.7(2)	
(colourless)	2				C_{Me} 197.7(7)		N,C 117.9(2,5.2)	
$[(AlMe_2)_5(\mu_3\text{-}C_{11}H_5N_8)$	tr	1108.1(4)	91.95(3)	AlN_2C_2	μ_3N 197.4(6,17)	113.2(3,7.8)	N,N 96.6(2)	259
	$P\bar{1}$	1280.7(4)	104.86(3)		C_{Me} 196.2(7,5)		C,C 119.7(4)	
$(AlMe_3)].tl$	2	1651.9(5)	101.89(3)				N,C 109.5(3,2.4)	
				AlN_2C_2	μ_3N 197.6(6,62)		N,N 83.8(2,5)	
(colourless)				x4	N 198.9(6,67)		C,C 121.5(4,1.3)	
					C_{Me} 195.1(8,32)		N,N 110.4(4,11.5)	
				AlC_3N	N 206.0(6)		C,C 113.5(4,5.2)	
					C_{Me} 195.2(11,18)		C,N 105.1(3,4.3)	
$[Al(\mu\text{-}Cl)(\mu\text{-}dmb)]_6.tl$	m	975.9(2)		AlC_2Cl_2	μCl 229.2(1)	114.7(1)	C,C 128.1(3)	260
	$P2_1a$	4436.2(9)	93.19(2)		C 195.2(7)		Cl,Cl 99.2(2)	
(colourless)	4	1201.3(3)					C,Cl 103.0(2)	
$(Alcp^*)_6P_4$	tr	1120.74(13)	99.345(9)	AlP_3C	μ_4P 242.2(2)	80.1(1,4)	P,P 99.6(1,7)	261
	$P\bar{1}$	1290.80(16)	112.699(9)	x2	μ_3P 236.0(1)		P,C 116.8(1)	
(bright yellow)	2	1350.99(15)	111.496(9)		C 205.7	d1		
				AlP_2C_5	μ_4P 239.7(1,4)	117.6(1)		
				x4	μ_3P 231.0(2,2)	174.3(1)		
					C 227.6			
$[(AlMe_3)_6(came)].2tl$	tr	1369.0(8)	76.11(3)	AlC_3O	O 204(3,2)		not given	262
	$P\bar{1}$	1431.7(4)	62.36(4)		C_{Me} not given			
(colourless)	1	1473.8(6)	82.41(4)					
$[(AlMe_3)_6(bcme')].$	tr	1240.0(6)	96.17(3)	AlC_3O	O 199(1,1)		not given	262
$4C_6H_6$	$P\bar{1}$	1622.9(8)	107.25(3)		C_{Me} not given			
	1	1925.1(5)	101.54(3)					
(colourless)								
$K[Al_7O_6Me_{16}].C_6H_6$	tr	1209.5(5)	105.56(3)	AlO_3C	μ_3O 180.2(3,10)	120.5(2,2.4)	O,O 106.7(2,1.0)	263
	$P\bar{1}$	1222.2(5)	94.52(2)		C_{Me} 193.6(6)		O,C 112.1(2,3)	
(colourless)	2	1389.3(5)	83.98(2)	AlO_2C_2	μ_3O 184.5(3,50)	119.7(2,2.8)	O,O 98.4(2,1.5)	
				x6	$\mu\bar{O}$ 185.8(4,27)		O,C 111.4(3,5.6)	
					C_{Me} 194.9(7,21)			
$Cs[Al_7O_8Me_{16}].3PhMe$	c	1751.2(8)		AlO_3C	μ_3O 183(2)	121(1,2)	O,O 98(1)	263
	$P2_13$				C_{Me} 203(6)		O,C 111.7(8)	
(colourless)	4			AlO_2C_2	μ_3O 181(2,1)	120(1,2)	O,O 99(1,1)	
				x6	$\mu\bar{O}$ 184(3,1)		C,C 115(2,0)	
					C_{Me} 200(4,6)		O,C 111(2,4)	
$[Al(\mu_3\text{-}NMe)Me]_7$	m	1405.9(7)		AlN_3C	μ_3N 191(3,6)	88.8(11,2.9)	N,N 89.5(14,3.2)	264
	$P2_1/c$	1440.7(8)	93.10(5)		C_{Me} 198(4,10)	119.6(12,3.9)	110.2(12,1.5)	
(colourless)	4	1443.5(8)					N,C 118.8(15,10.3)	
$[Al(\mu_3\text{-}NMe)Et]_7$	or	1850		AlN_3C	μ_3N not given			264
	Pbca	3494			C_{Et} not given			
(colourless)	8	1097						
$((Me_2AlNHMe)_2$	or	1538.9(2)		AlN_3C	μ_3N 191.4(6,21)	88.4(3)	N,N 103.0(3,9.6)	265
	Abam	1974.7(4)		x4	C_{Me} 200.1(11)	115.3(3,5.4)	N,C 115.0(4,3.3)	
$(MeAlNMe)_6)$	4	1161.3(1)		AlN_3C	$\mu_3\bar{N}$ 186.4(6,0)	118.5(6)	N,N 106.8(3)	
				x2	$\mu\bar{N}$ 190.9(13)		N,C 112.3(6,2.3)	
(colourless)					C_{Me} 201.0(13)			
$K_2[Al_{12}(Bu^i{}_{12})].$	c	2639.3(7)		$AlAl'_5C$	Al 268.5(5,11)		Al,Al 60.0(2,4)	266
$(1.2tl)$	$Fa\bar{3}$				C_{Bu} 199.9(9)			
	8							
(colourless) at 208K								
$[Al(\mu\text{-}cp)Me_2]_n$	m	655.4(2)		AlC_4	C_{cp} 222.5(2,22)		C_{cp},C_{cp} 97.3(1)	267
	$P2_1/n$	915.6(2)	96.89(4)		C_{Me} 195.3(2,6)		C,C 100.1(1)	
(colourless)	4	1213.4(8)					C_{cp},C 114.0(1,7.8)	
$[Al(\mu\text{-}SMe)(Me)_2]_n$	or	2567.9(7)		AlC_2S_2	μS 234.8(2,3)	103.0(1)	S,S 100.1(1)	268
	Fdd2	794.2(2)			C_{Me} 194.5(8,1)		C,C 122.0(4)	
(colourless)	16	1200.4(3)				d2	S,C 108.2(3,2.6)	
$[(SeMe_3)(AlCl_3Me)]_n$	m	1121.8(3)		$AlCl_3C$	Cl 216.9(3,7)		Cl,Cl 105.6(1,7)	269
	$P2_1/c$	1111.9(3)	107.82(2)		C_{Me} 192.7(8)		C,C 113.1(3,1.7)	
	4	991.5(2)						

which four $AlMe_3$ units are linked to separate oxygen atoms of a central tetrahedral SO_4^{2-} group.

In three examples [249–251] the molecule resides about a crystallographic centre of symmetry coincident with the centre of an Al_2O_2 four-member ring. Two triethanolamine units, bridged by four aluminium moieties, create an Al_4O_6 aggregate composed of two fused six-member Al_3O_3 rings in which each oxygen atom bridges two aluminium atoms.

The derivative $[Al(\mu\text{-S-2,6-Me}_2C_6H_3)Me_2]_4$ [148] crystallizes in an extended chair conformation, with alternating (2,6-dimethylphenyl)thiolate ligands bridging $AlMe_2$ moieties to form an eight-member $(AlS)_4$ ring. The Al atoms are in apical positions, with a mean Al–S bond distance of 236.3(1) pm, Al–S–Al angle of 128.8(1)° and μS–Al–μS angle of 97.0(1)°. The C–Al–C bond angles of 126.0 and 120.3° show a difference between the two independent Al atoms.

An X-ray analysis of $[Al\{\mu\text{-NCO}(C_6H_4)\mu\text{-O}\}Me_2]_4$ [252] has revealed a tetramer with the largest, 16-member $(AlNCO)_4$, ring found in aluminium chemistry. The key feature of the structure is the alternation of the oxo-ligand and the $[N\ldots C\ldots O]^-$ coordinating units around the ring.

There are four derivatives [225,253–255] in which four $AlMe_3$ units have essentially changed the positions of the donor sites of the macrocycle by forcing the donor atoms (O [225,253], N [254] or S [255]) from the interior cavity to the macrocyclic perimeter. Each aluminium atom is tetrahedrally coordinated. The mean Al–L bond distance increases with the covalent radius of the coordinated atom in the sequence: 198.7 pm (O) < 209.8 pm (N) < 252.1 pm (S). The mean Al–C bond distance in the same sequence has the values: 196.3 pm ~ 196.3 pm > 195.4 pm.

Two non-planar 1,4-dialuminacyclohexadiene moieties, twisted through 90° with respect to each other [256], are coupled by an aluminium–olefin π-bond to each of the four aluminium atoms. (Al–Cπ = 235.5 pm). The pyramidal coordination of each aluminium atom by the chlorine atom (Al–Cl = 210.9 pm) and two σ-bonded C atoms (Al–C = 199.0 pm) clearly indicates the presence of an Al–olefin bond. The two σ-bonded carbon atoms of one aluminium provide the P-bond for another aluminium. The Al...Al separation is 300 pm. By contrast, the separation between the Al atoms within the dialuminacyclohexadiene ring is 337 pm.

The chemistry of tetrameric organoaluminium compounds is thus clearly quite complicated. The donor ligands range from mono- to hexadentate, and the stereochemistry about aluminium includes three to six coordination, with the tetrahedral four-coordinate geometry being the most common. The most common ligand is the methyl group, and ligands with O- or N-donor atoms most often serve as bridges. The Al(I)–Al(I) distance of 276.9(4) pm [226] is a little shorter than the value for Al(III)–Al(III) of 280 pm (ranging from 273.5(2) to 290.7(1) pm), excluding those over 300 pm).

6. Oligo- and polymeric compounds

Crystallographic and structural data for these derivatives are presented in Table 8. There are no pentanuclear organoaluminium compounds, the next group after tetramers (Table 7) being the hexamers, of which there are ten. The structure of colourless trigonal $[Al_6(\mu_3\text{-O})_4(\mu\text{-OH})_4(Bu^t)_6]$ [257] is shown in Fig. 8. It can be described as an octahedron of aluminium(III) atoms with each face capped by a μ_3-O or μ-OH moiety. Alternatively, it could be considered a cube of oxygen atoms face-capped by six $AlBu^t$ units.

Another four hexamers [129,176,258] are isostructural. The Al_6X_6 core can be described as a hexagonal prism with alternating Al and X atoms (X = O [176] or N [129,258]). The Al–X bonds in the six-member rings (mean Al–O = 178.9 pm, Al–N = 191.1 pm) are significantly shorter than the transverse bonds joining the rings (188.9 pm and 195.7 pm respectively). The Al_3X_3 hexagonal faces are essentially planar with significant trigonal distortion. The mean X–Al–X angle is 112.3° and Al–X–Al is 127.5° for the oxygen derivative [176], and 115.7° and 124° respectively for the nitrogen derivatives [129,258].

An eight-member $Al_2N_4C_2$ ring is found at the core of another hexamer [259], and is bisected by a bridging dimethylaluminium unit.

The structure of $[Al(\mu\text{-Cl})(\mu\text{-dmb})]_6$ [260] is remarkably symmetrical, giving the aesthetically appealing molecule shown in Fig. 9. Its lens-shaped architecture deviates only slightly from D_{3h} symmetry (a device often used in architectural design to catch the eye). The six aluminium atoms form a regular planar hexagon, bridged by six chlorine atoms in a trigonal prismatic arrangement. The bond angles at the metal atoms are considerably distorted, the C–Al–C angles being en-

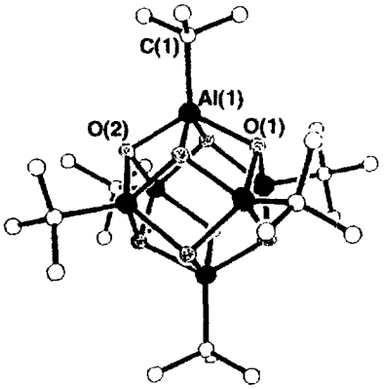

Fig. 8. Structure of $[Al_6(\mu_3\text{-O})_4(\mu\text{-OH})_4(Bu^t)_6]$ [257].

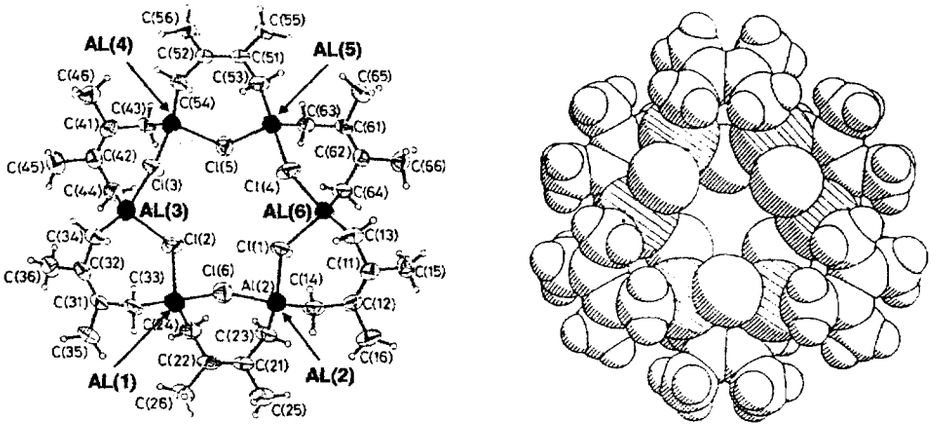

Fig. 9. Structure of [Al(μ-Cl)(μ-dmb)]$_6$ [260].

larged to 128.1(3)° and the Cl–Al–Cl angles diminished to 99.2(2)°. This seems inherent to the overall structure of the molecule in which the central Al/Cl core has to be spanned by the very rigid dimethylbutadiene moieties around it.

Bright yellow (Alcp*)$_6$P$_4$ [261] is shown in Fig. 10, where the structure can be seen to consist of Al_2P_2 rings forming a P_4Al_6 framework alternately occupied by aluminium and phosphorus. It can be described as two face-shared distorted Al_4P_4 cubes which lack P atoms at two diametrically opposite corners. The Al–P bond lengths vary with the coordination number of the Al atom involved.

The remaining two hexamers [262] differ from each other by the location of the $AlMe_3$ groups on the macrocyclic ring. In the one with the macrocycle-calix[8]arene methyl ether, all six of the $AlMe_3$ groups are on the outside of the macrocyclic ring. The one with the *p-tert*-butylcalix[8]arene methyl ether has only four $AlMe_3$ groups on the outside of the ring, the other two being inside the macrocyclic ring. The absence of a butyl para-substituent in the former case affords greater ring flexibility than in the latter case.

There are four heptanuclear derivatives [263,264], all containing seven aluminium(III) atoms. The anion $[Al_7O_8Me_{16}]^-$ [263] consists of an open Al_6O_6 cage capped by a seventh Al atom which is bonded to three alternate O atoms in the cage. The six aluminium atoms are bonded to two terminal methyl groups each, and the unique aluminium atom is bonded to only one methyl group, The bond angles at the Al atoms of the Al_6O_6 unit are near the tetrahedral value, with the exception of the interior O–Al–O angles which range from 97 to 99° (Table 8).

The structure of $[Al(NMe)(Me)]_7$ [264] is shown in Fig. 11. The molecule has a C_{3v} symmetry cage structure formed by aluminium and nitrogen atoms, as shown in Fig. 11. Each nitrogen is linked to one methyl group and three aluminium atoms. Each aluminium atom is linked to three nitrogen atoms and one methyl group. All the methyl groups are oriented away from the centre of the cage.

There is only one octameric organoaluminium derivative [265] whose orthorhombic structure is shown in Fig. 12. The molecule has a cage structure, apparently with C_{2h} symmetry. Each nitrogen and aluminium

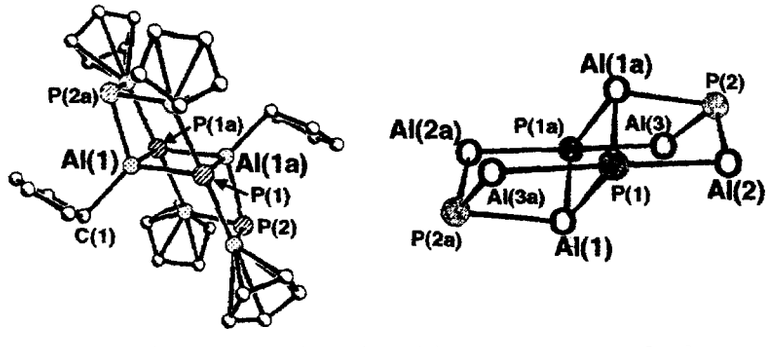

Fig. 10. (A) Structure of (Alcp*)$_6$P$_4$; (B) the P_4Al_6 framework [261].

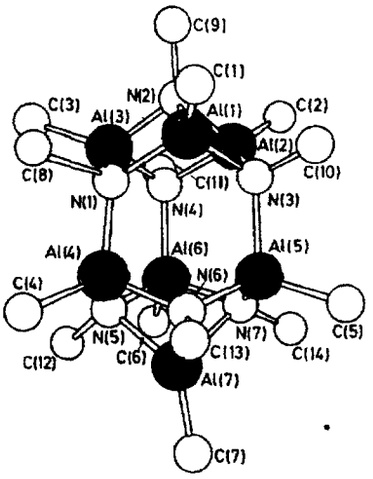

Fig. 11. Structure of $[Al(NMe)(Me)]_7$ [264].

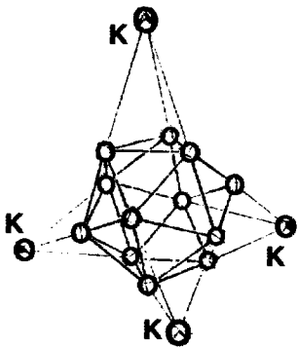

Fig. 13. Structure of $K[Al_{12}Bu^t_{12}]$ showing only the metal atoms [266].

atom is four coordinate (tetrahedral geometry), and all the methyl groups are oriented away from the cage.

The Al_{12} icosahedron of the dodecameric organoaluminium derivative is shown in Fig. 13. There are three, only slightly different, Al–Al bond lengths within the icosahedron (267.9, 268.0 and 269.6(5) pm). Moreover, the bond angles between the triangular sides deviate only by 0.4° from the ideal value of 60°, which is consistent with nearly perfect icosahedral symmetry.

There are only three extensively polymerized derivatives [267–269]. The structure of monoclinic colourless $[Al(\mu\text{-cp})Me_2]_n$ [267], shown in Fig. 14, consists of infinite chains composed of $AlMe_2$ groups bridged by C_5H_5 rings. The Al–C(cp) distances are unsymmetrical, with values of 220.3 and 224.8(2) pm. In another polymer [269], a two-dimensional structure of organoaluminium–organoselenium is found, $\{(SeMe_3)(AlCl_3\text{-}Me)\}_n$.

In the oligomeric species, hexameric organoaluminium compounds are the most common, as in the case of the heterometallic derivatives [270]. The ligands range from mono- to tetradentate, with some hexadentate ligands also. The most common ligand is the methyl group. The most common coordination about the aluminium atom is again tetrahedral. There is one example [257] which incorporates a five-coordinate (AlO_4C) aluminium atom. One hexameric example [261] contains a seven-coordinate (AlP_2C_5) metal atom in addition to the five tetrahedrally coordinated (AlP_3C) units. One example, $[Al(\mu_3\text{-}O)(Bu^t)]_6$ [176] contains two crystallographically independent molecules which represent the general class of distortion isomerism [89].

The mean Al–L(bridge) distance increases with the covalent radii of the donor atom in the order: 185 pm(O) < 191 pm(N) < 235 pm(S). For the triply bridged ligands, μ_3-L, the values are: 183 pm(O) < 197.5 pm(N) < 236 pm(P).

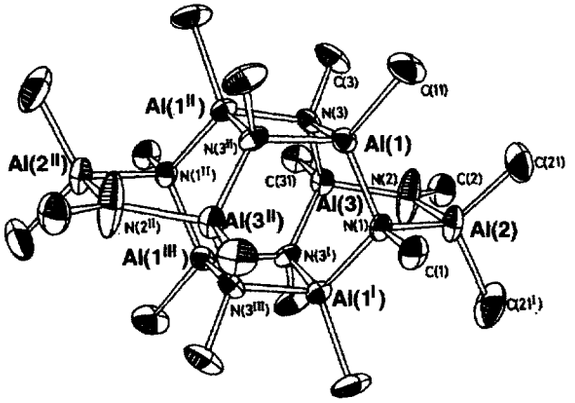

Fig. 12. Structure of $[(Me_2AlNHMe)_2(MeAlNMe)_6]$ [265].

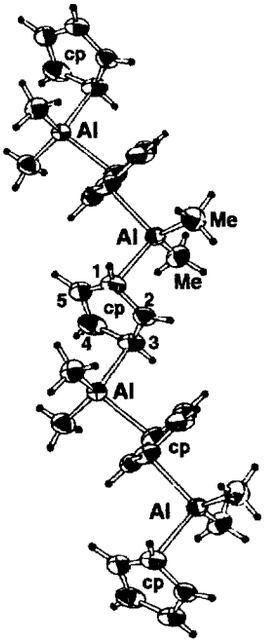

Fig. 14. View of a segment of the $[Al(\mu\text{-cp})Me_2]$ chain [267].

7. Conclusions

Over 350 organoaluminium compounds are surveyed in this review. Except for one example, $[Al(\eta^5\text{-cp}^*)]_4$ [226] in which an oxidation state of +1 is found, the aluminium atom is found in the oxidation state of +3. There are also many other examples with organoaluminium moieties present in the heterometallic derivatives of aluminium [270]. The coordination number (geometry) of the aluminium atom in these compounds decreases in the order: 4 (mostly tetrahedral) ≫ 5 (mostly trigonal bipyramidal) ~ 3 (Y-shaped) > 6 (various) > 7 (pentagonal bipyramidal) > 10. Coordination numbers 7 and 10 are rare. From a nuclearity point of view the derivatives are found as: dimers > monomers > tetramers > trimers > hexamers > heptamers > polymers > octamers > dodecamers. Only one example exists for each of the last two classes of derivative.

There are several examples [9,10,20,24,39,46,90,98, 103,125,148,156,176,182,189,197,208] which contain two crystallographically independent molecules within the same crystal, differing by degree of distortion. These are typical examples of distortion isomerism [89]. In one case there are three such molecules [88], and in another there are six [7]. Two isomeric forms are found for $[Al(Et)_2Cl_2][V_2(PMe_3)_6Cl_6]$ [61], and these also differ mostly by degree of distortion. There are two examples [110a,110b,115] which have cis and trans isomers. In one of these [115] the cis isomer also exhibits distortion isomerism within the same crystal.

A summary of the Al–L bond distances for different types of geometry is given in Table 9. The ligand atoms are listed in order of increasing covalent radii. In general, the mean values increase with coordination number and with covalent radius of the donor-atom. The mean values for terminal ligands are smaller than those of bridging ligands.

Aluminium(III) represents a typical 'hard' Lewis acid (acceptor) and, therefore, not surprisingly, shows a preference for 'hard' Lewis base (donor atom) ligands. In the examples with the π-bonding ligands, cyclopentadienyl and its derivatives, coordination in η^1- and η^2- as well as the η^5-mode is observed. The most common organic ligand is, however, the methyl group.

The shortest Al–Al bond distance in the organoaluminium derivatives are: (Al^{III}–Al^{III}), 247.0(2) pm [90] in the dimers; 273.5(2) pm [239] in the tetramers; 291.1(2) pm [215] in the trimers; and (Al^{I}–Al^{I}), 276.9(5) pm [226] in the dimers. By comparison, the lowest values of Al–Al bond distances found in almost 500 coordination derivatives of aluminium [1] are: 252.7(6) pm (Al^{II}–Al^{II}) < 264.3(3) pm (Al^{I}–Al^{I}) < 267.8(1) pm (Al^{III}–Al^{III}).

By far the most common geometry about aluminium, in both organometallic and other derivatives, is tetrahedral, and a summary of the Al–L bond distances for the most frequently occurring donors in such derivatives is given in Table 10. As can be seen, the mean Al–L bond distances in organoaluminium derivatives are often larger than for the coordination compounds.

This review and its related reviews [1,270] represent the first overview of the structural chemistry of aluminium. Despite increasing availability of data retrieval systems, the tracing of relevant material can be a difficult and expensive process. Much data is only available as supplemental material, which often includes the information required for comparative purposes. Some articles do not include full ligand details, and sometimes relevant bond distances and bond angles are missing.

Aluminium and its compounds are both chemically and biologically important, and structural information is

Table 9
Summary of the mean Al^{III}–L(atom) bond distances (pm) [a]

COORD. ATOM	Cov. Radius [pm]	COORDINATION 3	4	5
H	30	153	172(1,1)	
μH			175(10,12)	
L^2B	82		232(1,1)	
μF	70		180(2,2)	
L^1O	73	170.5(23,23)	184(14,16)	
L^2O			191(19,9)	190(5,5)
L^3O			199	
μLO^b			186(4,10)	
μ_3O			182(6,9)	
L^1N	75	184(6,4)	192(8,9)	
L^2		178	198(12,14)	202(3,5)
L^3			176(3,5)	
μLN			197(14,24)	
L^1C	77	198(5,3)	197(14,8)	197(6,2)
L^2C		197(6,9)	211(13,14)	
L^3C			221(11,11)	
μLC			196	
L^2S	102		250	
μS			235(16,7)	
L^2P	106		251(6,7)	
L^3P			254	
μLP			246(1,1)	
μ_3LP			241	
μ_3P			236	
μ_4P			241(2,1)	
Cl	99		216(14,6)	
μCl			232(7,13)	
μLSe	117		252	
μ_3Se			253(7,5)	
μLAs	120		255	
Br	114		234(3,5)	
μBr			249(1,1)	
μTe	136		255	
μLTe			273	
μ_3Te			271	

[a] The first number in parentheses is the difference between the shortest and the mean values, the second number is the difference between the highest and the mean.
[b] Al–O for μ_4-SO_4 group is 190.5 pm.

Table 10
Summary of the mean Al^{III}–L(atom) bond distances for four-coordinate aluminium compounds (pm) [a]

COORD. ATOM	Cov.Radius [pm]	Organometal Compounds	Coordination Compounds	Heterometal Compounds
H	30	172(1,1)	154(26,46)	150(15,15)
μH		175(10,12)	167(0,1)	168(24,42)
L^2B	82	232(1,1)		
F	70		164(4,7)	
μF		180(2,2)		
L^1O	73	184(14,16)	180(13,11)	176(11,22)
L^2O		191(19,9)	180(5,5)	
L^3O		199		
μLO		186(4,10)[b]	181(5,2)	180(11,9)
μ_3O		182(6,9)		
L^1N	75	192(8,9)	193(14,24)	192(15,21)
L^2N		198(12,14)	192(10,15)	
L^3N		176(3,5)		
L^4N		195(4,6)	190(9,8)	
μLN		197(14,24)	194(15,4)	192(11,15)
L^1C	77	197(14,8)		198(18,13)
L^2C		211(13,14)		
L^3C		221(11,11)		
μLC		196		221(10,19)
L^2S	102	250		
μS		235(16,7)		
L^2P	106	251(6,7)		
L^3P		254		
μLP		246(1,1)		
μ_3LP		241		
μ_3P		253(7,5)		
μ_4P		241(2,1)		
Cl	99	216(14,6)	212(7,9)	210(5,8)
μCl		232(7,13)	226(4,2)	221(7,27)
μLSe	117	252		
μ_3Se		253(7,5)		
μLAs	120	255		
Br	114	234(3,5)	227(7,30)	223(9,3)
μBr		249(1,1)	244(7,6)	234(3,14)
μTe	136	255		
μLTe		273		
μ_3Te		271		

[a] The first number in parentheses is the difference between the shortest and the mean values, the second number is the difference between the highest and the mean.
[b] In addition, Al–O for μ_4-SO_4 group is 190.5 pm.

often critical for the understanding of the roles these play. It is hoped that this review will serve to focus common structural features which may prove of interest in other areas of research.

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Appendix A. Abbreviations

ac	acetate
1-ad	1-adamantyl
ampo	2-allyl-6-methylphenoxidate
bamen	*N,N'*-bis(3-aminopropyl)ethylenediamine
bbp	N_2–$CH_2(Me)_2$C-4,6-Bu^t_2–C_6H_2NH
bcme	*tert*-butylcalix[4]arene methyl ether

bcme	*p-tert*-butylcalix[8]arene methyl ether
bhmap	3-*tert*-butyl-2-hydroxy-5-methylacetophenonate
bht	2,6-di-*tert*-butyl-4-methylphenolate
bmc	*p-tert*-butylmethoxycalix[4]arene
bo	borneolate
bp(H)N	aminobiphenyl
bpy	2,2′-bipyridyl
Bu^i	*iso*-butyl
Bu^t	*tert*-butyl
came	calix[8]arene methyl ether
$C_4H_8O_2$	1,4-dioxane
$C_6H_{16}NSi_2$	2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanate
$C_8H_{19}N_4$	*N,N′*-bis(aminopropyl)ethylenediaminate
$C_{10}H_{20}N_4$	1,4,8,11-tetraazacyclotetradecane (cyclam)
$C_{10}H_{22}N_4$	1,4-bis(3-aminopropyl)piperazine
$C_{12}H_{23}O_2$	$OC(Bu^t)CH_2C(Me)(Bu^t)O$
$C_{14}H_{10}$	9,10-dihydro-9,10-anthrylene
$C_{22}H_{22}N_4$	5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetra-azacyclotetradecinate
1,3-cod	1,3-cyclooctadienate
cp	cyclopentadienyl
cp^*	pentamethylcyclopentadienyl
cp′	tetramethylethylcyclopentadienyl
c-Pr	cyclpropylate
db-[18]-c-6	dibenzo-18-crown-6
dbmp	2,6-di-*tert*-butyl-6-methylphenolate
dc-[18]-c-6	dicyclohexano-18-crown-6
dha	9,10-dihydro-9,10-anthrylenate
dhan	9,10-dihydroanthracene
dhbp	2,2′-dihydro-3,3′-di-*tert*-butyl-5,5′-dibromo-benzophenonate
dipp(H)N	2,6-di-*iso*-propylC_6H_3(H)N
dk	1,2-cyclopentane-diol
dmap	*O*-[(dimethylamino)methyl]phenyl
dmb	3,3-dimethyl-1-buten-1-yl
dmen	$H_3CNCH_2CH_2NCH_3$
dmp	2,6-dimethylphenolate
dpb	2,6-di-*tert*-butylphenolate
en	ethylenediamine
eph	1-ephedrinate
idb	iminodibenzylate
Mena	1-methylnaphthalene
mes	mesityl
mop	2-methoxyphenolate
mpa	*N*-(*p*-methoxyphenyl)-2-(*p*-methoxyphenylimino)propylaminate
mt	methyltoluate
mto	mentholate
mtp	2-methylthiophenolate
naa	1-naphthylaminate
N_4ada	adamantane
nea	1-(1-naphthyl)ethylaminate
neo	neopentyl (CH_2CMe_3)
oea	2,3,7,8,12,13,17,18-octaethylporphinate
opn_2	1,3-bis(trimethylsilyl)-2-bis(trimethylsilyl)amino-2-phenyl-1,3,2,4-diazphosphate
opns	2-bis(trimethylsilyl)amino-3-*tert*-butyl-2-phenyl-1,3,2,4-triazaphosphate
oxo	2-oxobenoxazolate
pbi	*N*-phenylbenzimidate
pbia	*N*-phenylbenzimidate-acetaldehyde
pfp	pentafluorophenylate
pmo	2-pyridylmethanolate
qn	quinolidine
qui	8-quinolylimide
quo	8-quinolinolate
tbbo	2,4,6-tri-*tert*-butylbenzoxolate
tbp	2,4,6-tri-*tert*-butylphenolate
tbtas	2,4,6,7-tetra-*tert*-butyl-1,3,5-trimethyl-2,4,6-triaza-7-azonia-1,5-disilane
tedta	tetraethyldiethylenetriaminate
thf	tetrahydrofuran
tipa	*N*-(*p*-tolyl-2-(*p*-tolylimino)propylaminate
tl	toluene
tmcb	tetramethylcyclobutadiene
tmen	*N,N,N′,N′*-tetramethylethylenediamine
tmor	thimorpholine
tol	*o*-tolyl
tpi	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
tpm	2-thiophenemethanolate
trip	2,4,6-tri-*iso*-propylphenolate

References

[1] C.E. Holloway, M. Melnik, Main Group Met. Chem., 19 (1996) 411; 19 (1996) 619.

[2a] A. Almenningen, S. Halvorsen, A. Haaland, Acta Chem. Scand. 25 (1971) 1937.

[2b] G.H. Robinson, S.A. Sangokoya, J. Am. Chem. Soc. 110 (1988) 1494.

[2c] A.F.M. Maqsudeer Rahman, K.F. Siddiqui, J.P. Oliver, Organometallics 1 (1982) 881.

[3] J. Jerius, J.M. Hahn, A.F.M. Maqsudur Rahman, O. Mols, W.H. Ilsley, J.P. Oliver, Organometallics 5 (1986) 1812.

[4] A.P. Shreve, R. Mulhaupt, W. Fultz, J. Lalabrese, W. Robbins, S.D. Ittel, Organometallics 7 (1988) 409.

[5] R. Benn, E. Janssen, H. Lehmkul, A. Rufinska, K. Angermund, P. Benz, R. Goddard, C. Krüger, J. Organomet. Chem. 411 (1991) 37.

[6] A.H. Cowley, H.S. Isom, A. Decken, Organometallics 14 (1995) 2589.

[7] M.A. Petrie, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 113 (1991) 8704.

[8] K.M. Waggoner, K. Ruhlandt-Senge, R.J. Wehmschulte, X. He, M.M. Olmstead, P.P. Power, Inorg. Chem. 32 (1993) 2557.

[9] M.A. Petrie, K. Ruhlandt-Senge, P.P. Power, Inorg. Chem. 32 (1993) 1135.

[10] J.H. Medley, F.R. Fronczek, N. Ahmad, M.C. Day, R.D. Rogers, C.R. Kerr, J.L. Atwood, J. Crystallogr. Spectrosc. Res. 15 (1985) 99.

[11] J.H. Medley, N. Ahmad, M.C. Day, Can. J. Chem. 63 (1985) 2906.
[12] W. Uhl, Z. Anorg. Allg. Chem. 579 (1989) 75.
[13] D.M. Schubert, C.B. Knobler, W.S. Rees Jr., M.F. Hawthorne, Organometallics 6 (1987) 203.
[14a] D.M. Schubert, C.B. Knobler, M.F. Hawthorne, Organometallics 6 (1987) 1353. D.M. Schubert, M.A. Bandman, W.S. Rees Jr., C.B. Knobler, P. Lu, W. Nam, M.F. Hawthorne, Organometallics 9 (1990) 2046.
[14b] J.L. Atwood, R.E. Cannon, J. Organomet. Chem. 47 (1973) 321.
[14c] A.M. McPherson, G. Stuckey, H. Lemkull, J. Organomet. Chem. 152 (1978) 367.
[15] A.Y. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, J. Am. Chem. Soc. 114 (1992) 9724.
[16] M.B. Power, S.G. Bott, D.L. Clark, J.L. Atwood, A.R. Barron, Organometallics 9 (1990) 3086.
[17] M.B. Power, S.G. Bott, J.L. Atwood, A.R. Barron, J. Am. Chem. Soc. 112 (1990) 3446.
[18] G. Quinbert, H. Becker, M. Del Grosso, G. Dambacher, J.W. Bats, G. Dürner, Tetrahedron Lett. 34 (1993) 6885.
[19] M.B. Power, S.G. Bott, E.J. Bishop, K.D. Tierce, J.L. Atwood, A.R. Barron, J. Chem. Soc. Dalton Trans. (1991) 241.
[20] M.B. Power, A.W. Apblett, S.G. Bott, J.L. Atwood, A.R. Barron, Organometallics 9 (1990) 2529.
[21] M. Veith, F. Goffing, S. Becker, V. Huch, J. Organomet. Chem. 406 (1991) 105.
[22] G. Hencken, E. Weiss, J. Organomet. Chem. 73 (1974) 35.
[23] W. Uhl, E. Schnepf, J. Wagner, Z. Anorg. Allg. Chem. 613 (1992) 67.
[24] J.L. Atwood, K.D. Crissinger, R.D. Rogers, J. Organomet. Chem. 155 (1978) 1.
[25] R.D. Rogers, J.L. Atwood, J. Crystallogr. Spectr. Res., 14 (1984) 1.
[26] F.J. Feher, T.A. Budzechowski, K.J. Weller, Polyhedron 12 (1993) 591.
[27] J.L. Atwood, W.E. Hunter, K.D. Crissinger, J. Organomet. Chem. 127 (1977) 403.
[28] A.F.M. Maqsudur Rahman, K.F. Siddiqui, J.P. Oliver, J. Organomet. Chem. 319 (1987) 161.
[29] V. Srini, J. De Mel, J.P. Oliver, Organometallics 8 (1989) 827.
[30] T. Belgardt, J. Storre, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, Inorg. Chem. 34 (1995) 3821.
[31] D.M. Schubert, C.B. Knobler, W.S. Rees Jr., M.F. Hawthorne, Organomet. Chem. 6 (1987) 201.
[32a] H. Lehmkuhl, A. Shakoor, K. Mehler, C. Krüger, Y.-H. Tsay, Z. Naturforsch. Teil B: 40 (1985) 1504.
[32b] C. Krüger, J.C. Sekutowski, H. Holberg, R. Krause-Göing, J. Organomet. Chem. 141 (1977) 141.
[32c] M. Barber, D. Liptak, J.P. Oliver, Organometallics 1 (1982) 1307.
[33] R. Shakir, M.J. Zaworotko, J.L. Atwood, J. Cryst. Mol. Struct. 9 (1979) 135.
[34] S.K. Seale, J.L. Atwood, J. Organomet. Chem. 64 (1974) 57.
[35] J.L. Atwood, J.M. Cummings, J. Cryst. Mol. Struct. 7 (1977) 257.
[36] J.L. Atwood, W.R. Newberry III, J. Organomet. Chem. 87 (1975) 1.
[37] J.L. Atwood, S.K. Seale, D.H. Roberts, J. Organomet. Chem. 51 (1973) 105.
[38] C.D. Whitt, L.M. Parker, J.L. Atwood, J. Organomet. Chem. 32 (1971) 291.
[39] M. Taghiof, D.G. Hendershot, M. Barber, J.P. Oliver, J. Organomet. Chem. 431 (1992) 271.
[40] W.G. Feighery, R.U. Kirss, C.H. Lake, M.R. Churchill. ica, 218 (1994) 47.
[41] D.A. Wierda, A.R. Barron, Polyhedron 8 (1989) 831.
[42] A. Almenningen, L. Fernholt, A. Haaland, J. Organomet. Chem. 145 (1978) 109.
[43] R.D. Rogers, L.B. Stone, J.L. Atwood, Cryst. Struct. Commun. 9 (1980) 143.
[44] J.L. Atwood, D.C. Hrncir, W.R. Newberry III, Cryst. Struct. Commun. 3 (1974) 615.
[45] C. Krüger, P.J. Roberts, Y.H. Tsay, J.B. Koster, J. Organomet. Chem. 78 (1974) 69.
[46] B. Breit, U. Bergsträsser, G. Maas, M. Regitz, Angew. Chem. Int. Ed. Engl. 31 (1992) 1055.
[47] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, Angew. Chem. Int. Ed. Engl. 32 (1993) 1655.
[48] J.L. Atwood, H. Elgamal, G.H. Robinson, S.G. Bott, J.A. Weeks, W.E. Hunter, J. Inclusion Phenom. 2 (1964) 367.
[49] S.G. Bott, H. Elgamal, J.L. Atwood, J. Am. Chem. Soc. 107 (1985) 1796.
[50] M.J. Zaworotko, C.R. Kerr, J.L. Atwood, Organometallics 4 (1985) 238.
[51] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, Bull. Chem. Soc. Jpn. 45 (1972) 3388.
[52] P.B. Hitchcock, H.J. Jasim, M.F. Lappert, H.D. Williams, J. Chem. Soc. Chem. Commun. (1986) 1634.
[53] A. Steiner, D. Stalke, J. Chem. Soc. Chem. Commun. (1993) 444.
[54] R. Lechler, H.D. Hausen, J. Weidlein, J. Organomet. Chem. 359 (1989) 1.
[55a] J.A. Kanters, G.P.M. van Mier, R.L.M.M. Nijs, F. van der Steen, G. van Koten, Acta Crystallogr., Sect. C 44 (1988) 1391.
[55b] S.J. Trepanier, S. Wang, J. Chem. Soc. Dalton Trans. (1995) 2425.
[56] J.T. Leman, J. Braddock-Wilking, A.J. Cooling, A.R. Barron, Inorg. Chem. 32 (1993) 4324.
[57] W. Uhl, J. Wagner, D. Fenske, G. Baum, Z. Anorg. Allg. Chem. 612 (1992) 25.
[58] V.D. Romanenko, V.F. Shul'gin, V.V. Skopenko, A.N. Chernega, M.Y. Antipin, Y.T. Struchkov, I.E. Boldeskul, L.N. Markovskii, Zh. Obsh. Khim. 55 (1985) 282; Engl. Ed., p. 246. A.I. Chernega, M.Y. Antipin, Y.T. Struchkov, I.E. Boldeskul, V.F. Shul'gin, V.D. Romanenko, Zh. Strukt. Khim. 26 (1985) 120; Engl. Ed., p. 752.
[59] S.A. Sangokoya, W.T. Pennington, G.H. Robinson, J. Cryst. Spectrosc. Res. 19 (1989) 433.
[60] D.A. Atwood, S.G. Bott, J.L. Atwood, J. Coord. Chem. 17 (1987) 93.
[61] F.A. Cotton, S.A. Duraj, L.E. Manzer, W.J. Roth, J. Am. Chem. Soc. 107 (1985) 3850.
[62] M.R. Churchill, A.H. Reis, J. Chem. Soc. Dalton Trans. (1972) 1314.
[63] R.D. Rogers, J.L. Atwood, J. Cryst. Mol. Struct. 9 (1979) 45.
[64] R.E. Marsh, J. Cryst. Mol. Struct. 10 (1980) 163.
[65] M.D. Healy, J.W. Ziller, A.R. Barron, J. Am. Chem. Soc. 112 (1990) 2949.
[66] M.D. Healy, J.T. Leman, A.R. Barron, J. Am. Chem. Soc. 113 (1991) 2776.
[67] M.A. Petrie, P.P. Power, J. Chem. Soc. Dalton Trans. (1993) 1737.
[68] M.D. Healy, D.A. Wierda, A.R. Barron, Organometallics 7 (1988) 2543.
[69] M.L. Sierra, V. Srini, J. de Mel, J.P. Oliver, Organometallics 8 (1989) 2312.
[70] J.L. Atwood, P.A. Milton, J. Organomet. Chem. 52 (1973) 275.
[71] R.L. Wells, A.T. McPhail, M.F. Self, J.A. Laske, Organometallics 12 (1993) 3333.

[72] R. Kumar, D.G. Dick, S.U. Ghazi, M. Taghiof, M.J. Heeg, J.P. Oliver, Organometallics 14 (1995) 1601.
[73] M.A. Petrie, P.P. Power, H.V. Rasika Dias, K. Ruhlandt-Senge, K.M. Waggoner, R.J. Wehmschulte, Organometallics 12 (1993) 1086.
[74] H.S. Isom, A.H. Cowley, A. Decken, F. Sissingah, S. Corbelin, R.J. Lagow, Organometallics 14 (1995) 2400.
[75] A. Haaland, K.G. Martinsen, S.A. Shlykov, H.V. Volden, C. Dohmeier, H. Schnöckel, Organometallics 14 (1995) 3116.
[76] J. Lewin'ski, J. Zachara, B. Man'k, S. Pasynkiewicz, J. Organomet. Chem. 454 (1993) 5.
[77] R. Guilard, A. Zrinek, A. Tabard, A. Endo, B.C. Han, C. Lecompte, M. Souhassou, A. Habbou, M. Ferhat, K.M. Kadish, Inorg. Chem. 29 (1990) 4476.
[78] V.L. Goedken, H. Ito, T. Ito, J. Chem. Soc. Chem. Commun. (1984) 1453.
[79] S.G. Bott, A. Aloanipur, S.D. Morley, D.A. Atwood, C.M. Means, A.W. Coleman, J.L. Atwood, Angew. Chem. Int. Ed. Engl. 26 (1987) 485.
[80] S.J. Trepanier, S. Wang, Organometallics 13 (1994) 2213.
[81] G. Müller, J. Lachmann, A. Rufin'ska, Organometallics 11 (1992) 2970. G. Müller, J. Lachmann, Z. Naturforsch. Teil B: 48 (1993) 1544.
[82] M. Veith, M. Kross, J.F. Labaree, J. Mol. Struct. 248 (1991) 345.
[83] S.J. Dzugan, V.L. Goedken, Inorg. Chem. 25 (1986) 2858.
[84] J. Müller, U. Englert, Chem. Ber. 128 (1995) 493.
[85] J.T. Leman, A.R. Barron, Organometallics 8 (1989) 1828.
[86] T.D. Getman, S.G. Shore, Inorg. Chem. 27 (1988) 3439.
[87] M.R. Churchill, A.H. Reis, J. Chem. Soc. Dalton Trans. (1972) 1317.
[88] M.A. Bandman, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 27 (1988) 2399.
[89] M. Melnik, Coord. Chem. Rev. 47 (1982) 239 and references cited therein.
[90] R.J. Wehmschulte, K. Ruhlandt-Senge, M.M. Olmstead, H. Hope, B.E. Sturgeon, P.P. Power, Inorg. Chem. 32 (1993) 2983.
[91] C. Pluta, K.R. Pörschke, C. Krüger, K. Hildenbrand, Angew. Chem. Int. Ed. Engl. 32 (1993) 388.
[92] W. Uhl, H.H. Karsch, U. Schütz, A. Vester, Chem. Ber. 126 (1993) 2637.
[93] W. Uhl, Z. Naturforsch. Teil B: 43 (1988) 1113.
[94] W. Uhl, A. Vester, Chem. Ber. 126 (1993) 941.
[95] A.W. Apblett, A.R. Barron, Organometallics 9 (1990) 2137.
[96] R. Mulhaupt, J. Calabrese, S.D. Ittel, Organometallics 10 (1991) 3403.
[97] P. Bissinger, M. Paul, J. Riede, H. Schmidbaur, Chem. Ber. 126 (1993) 2579.
[98] M.L. Sierra, R. Kumar, V. Srini, J. de Mel, J.P. Oliver, Organometallics 11 (1992) 206.
[99] B. Cetinkaya, P.B. Hitchcock, H.A. Jasin, M.F. Lappert, H.D. Williams, Polyhedron 9 (1990) 239.
[100] R. Kumar, M.L. Sierra, V. Srini, J. de Mel, J.P. Oliver, Organometallics 9 (1990) 484.
[101] R. Benn, A. Rufin'ska, H. Lehmkuhl, E. Janssen, C. Krüger, Angew. Chem. Int. Ed. Engl. 22 (1983) 779.
[102] D.G. Hendershot, R. Kumar, M. Barber, J.P. Oliver, Organometallics 10 (1991) 1917.
[103] D.G. Hendershot, M. Barber, R. Kumar, J.P. Oliver, Organometallics 10 (1991) 3302.
[104] M.L. Sierra, V. Srini, J. de Mel, J.P. Oliver, Organometallics 8 (1989) 2486.
[105] M.R.P. van Vliet, P. Buysingh, G. van Koten, K. Vrieze, B. Kopic-Prodic, A.L. Spek, Organometallics 4 (1985) 1701.
[106] Y. Kai, N. Yusuoke, N. Kasai, M. Kakudo, Bull. Chem. Soc. Jpn. 45 (1972) 3397.
[107] F.H. van der Steen, G.P.M. van Mier, A.L. Spek, J. Kroon, G.P. van Koton, J. Am. Chem. Soc. 113 (1991) 5742.
[108] S.T. Dzugan, V.L. Goedken, Inorg. Chim. Acta 154 (1988) 169.
[109] K.M. Waggoner, M.M. Amstead, P.P. Power, Polyhedron 9 (1990) 257.
[110a]M. Jansen, I. Mobros, Z. Anorg. Allg. Chem. 612 (1992) 101.
[110b]S. Amirkhalili, P.B. Bitchcock, A.D. Jenkins, J.Z. Nyathi, J.D. Smith, J. Chem. Soc. Dalton Trans. (1981) 377.
[111] J.J. Byers, W.T. Pennington, G.H. Robinson, D.C. Hrncir, Polyhedron 9 (1990) 2105.
[112] J.B. Hill, T.A. Talley, W.T. Pennington, G.H. Robinson, J. Chem. Crystallogr. 24 (1994) 61.
[113] D.M. Choquette, M.J. Timm, J.L. Hobbs, M.M. Rahim, K.J. Ahmed, R.P. Planalp, Organometallics 11 (1992) 529.
[114] F. Moise, S.A. Sangokoya, W.T. Pennington, G.H. Robinson, J. Coord. Chem. 21 (1990) 129.
[115] G.M. McLaughlin, G.A. Sim, J.D. Smith, J. Chem. Soc. Dalton Trans. (1972) 2197.
[116] H. Hess, A. Hinderer, S. Steinhauser, Z. Anorg. Allg. Chem. 377 (1970) 1.
[117] S.A. Sangokoya, I. Moise, W.T. Pennington, M.F. Self, G.H. Robinson, Organometallics 8 (1989) 2584.
[118] S. Schulz, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, J. Organomet. Chem. 493 (1995) 69.
[119] K.M. Waggoner, P.P. Power, J. Am. Chem. Soc. 113 (1991) 3385.
[120] S.J. Schauer, W.T. Pennington, G.H. Robinson, Organometallics 11 (1992) 3287.
[121] M.F. Self, W.T. Pennington, J.A. Laske, G.H. Robinson, Organometallics 10 (1991) 36.
[122] J.A. Jensen, J. Organomet. Chem. 456 (1993) 161.
[123] B. Lee, W.T. Pennington, G.H. Robinson, Inorg. Chim. Acta, 190 (1991) 173.
[124] W.T. Pennington, G.H. Robinson, S.A. Sangokoya, Acta Crystallogr., Sect. C, 46 (1990) 1108.
[125] P.B. Hitchcock, H.A. Jasim, M.F. Lappert, H.D. Williams, Polyhedron 9 (1990) 245.
[126] G.H. Robinson, S.A. Sangokoya, R.D. Rogers, Polyhedron 7 (1988) 2727.
[127] M.G. Davidson, D. Elilio, S.L. Less, A. Martin, P.R. Raithby, R. Snaith, D.S. Wright, Organometallics 12 (1993) 1.
[128] J.J. Byers, B. Lee, W.T. Pennington, G.H. Robinson, Polyhedron 11 (1992) 967.
[129] A.-A.I. Al Wassil, P.B. Hitchcock, S. Sarisaban, J.D. Smith, C.L. Wilson, J. Chem. Soc. Dalton Trans. (1985) 1929.
[130] S.K. Seale, J.L. Atwood, J. Organomet. Chem. 73 (1974) 27.
[131] W.S. McDonald, Acta Crystallogr., Sect. B, 25 (1969) 1385.
[132] G.H. Robinson, S.A. Sangokoya, F. Moise, W.T. Pennington, Organometallics 7 (1988) 1887.
[133] R.G. Vranka, E.L. Amma, J. Am. Chem. Soc. 89 (1967) 3121.
[134] S.K. Byram, J.K. Fawcett, S.C. Nyburg, R.J. O'Brien, J. Chem. Soc. Chem. Commun. (1970) 16.
[135] J.C. Huffman, W.E. Streib, J. Chem. Soc. Chem. Commun. (1971) 911.
[136] W.H. Ilsley, M.D. Glick, J.P. Oliver, J.W. Moore, Inorg. Chem. 19 (1980) 3572.
[137] D.J. Brauer, C. Krüger, Z. Naturforsch. Teil B: 34 (1979) 1293.
[138] M.J. Albright, W.M. Butler, T.J. Anderson, M.D. Glick, P.J. Oliver, J. Am. Chem. Soc. 98 (1976) 3995.
[139] J.F. Malone, W.S. McDonald, J. Chem. Soc. Dalton Trans. (1972) 2646.
[140] G.D. Stucky, A.M. McPherson, W.E. Rhine, J.J. Eisch, J.L. Considine, J. Am. Chem. Soc. 96 (1974) 1941.
[141] G. Erker, M. Albrecht, C. Krüger, M. Nolte, S. Werner, Organometallics 12 (1993) 4979.

[142] M.D. Healy, J.W. Ziller, A.R. Barron, Organometallics 11 (1992) 3041.
[143] G. Allegra, G. Perego, A. Immirza, Makromol. Chem. 61 (1963) 69.
[144] W. Uhl, A. Vester, Z. Anorg. Allg. Chem. 589 (1990) 175.
[145] P.R. Schonberg, R.T. Paine, C.F. Paine, C.F. Campana, E.N. Duesler, Organometallics 1 (1982) 799.
[146] P.R. Schonberg, R.T. Paine, C.F. Campana, J. Am. Chem. Soc. 101 (1979) 7726.
[147] H.J. Koch, S. Schulz, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, A. Heine, R. Herbst-Inmer, D. Stalke, G.M. Sheldrick, Chem. Ber. 125 (1992) 1107.
[148] M. Taghiof, M.J. Heeg, M. Bailey, D.G. Dick, R. Kumar, D.G. Hendershot, H. Rahbarnooki, J.P. Oliver, Organometallics 14 (1995) 2903.
[149] A. Haaland, O. Stokkeland, J. Weidlein, J. Organomet. Chem. 94 (1975) 353.
[150] V. Srini, J. de Mel, R. Kumar, J.P. Oliver, Organometallics 9 (1990) 1303.
[151] E. Hey-Hawkins, M.F. Lappert, J.L. Atwood, S.G. Bott, J. Chem. Soc. Dalton Trans. (1991) 939.
[152] S.A. Sangokoya, W.T. Pennington, G.H. Robinson, D.C. Hrncir, J. Organomet. Chem. 358 (1990) 23.
[153] R.L. Wells, A.T. McPhail, T.M. Speer, Organometallics 11 (1992) 960.
[154] D.E. Heaton, R.A. Jones, K.B. Kidd, A.H. Cowley, C.M. Nunn, Polyhedron 7 (1988) 1901.
[155] A.H. Cowley, R.A. Jones, P.R. Harris, Angew. Chem. Int. Ed. Engl. 30 (1991) 1143.
[156] W. Uhl, M. Layh, Z. Anorg. Allg. Chem. 620 (1994) 856.
[157] A.V. Belyakov, A. Haaland, H.P. Verne, J. Weidlein, Acta Chem. Scand. 48 (1994) 169.
[158] M. Veith, H. Lange, O. Recktenwald, W. Frank, J. Organomet. Chem. 294 (1985) 273.
[159] V.R. Magnuson, G.D. Stucky, J. Am. Chem. Soc. 91 (1969) 2544.
[160] H. Schmidbaur, S. Lauteschläger, G. Müller, J. Organomet. Chem. 281 (1985) 33.
[161] H.D. Hausen, J. Tödtmann, J. Weidlein, Z. Naturforsch. Teil B: 49 (1994) 430.
[162] H. Hoberg, V. Gotor, A. Milchereit, C. Krüger, J.C. Sekutowski, Angew. Chem. Int. Ed. Engl. 16 (1977) 539.
[163] H. Schmidbaur, S. Lauteschläger, B. Milewski-Mahrla, Chem. Ber. 116 (1983) 1403.
[164] H.H. Karsch, A. Applet, F.H. Köhler, G. Müller, Organometallics 4 (1985) 231.
[165] H.H. Karsch, K. Zellner, J.Lachmann, G. Müller, J. Organomet. Chem. 409 (1991) 109.
[166] H.D. Hausen, F. Gerstner, W. Schwarz, J. Organomet. Chem. 145 (1978) 277.
[167] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, J. Organomet. Chem. 32 (1971) 165.
[168] U. Dembowski, M. Noltemeyer, J.W. Gilje, H.W. Roesky, Chem. Ber. 124 (1991) 1917.
[169] E.J. Corey, S. Sarshar, J. Bordner, J. Am. Chem. Soc. 114 (1992) 7938.
[170] R. Kumar, V. Srini, J. de Mel, J.P. Oliver, Organometallics 8 (1989) 2488.
[171] J.L. Atwood, D.C. Hrncir, R.D. Rogers, J.A.K. Howard, J. Am. Chem. Soc. 103 (1981) 6787.
[172] J.L. Atwood, W.R. Newberry III, J. Organomet. Chem. 66 (1974) 15.
[173] G. Allegra, G. Perego, Acta Crystallogr. 16 (1963) 185.
[174] D.C. Hrncir, R.D. Rogers, J.L. Atwood, J. Am. Chem. Soc. 103 (1981) 989.
[175] W. Uhl, M. Koch, W. Hiller, M. Heckel, Angew. Chem. Int. Ed. Engl. 34 (1995) 4971.
[176] M.R. Mason, J.M. Smith, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 115 (1993) 4971.
[177] Y. Kai, N. Yasuoka, N. Kasia, M. Kakudo, Bull. Chem. Soc. Jpn. 45 (1972) 3403.
[178] S. Amirkhalili, P.B. Hitchcock, J.D. Smith, J.G. Stamper, J. Chem. Soc. Dalton Trans. (1980) 2493.
[179] V. Sharma, M. Simard, J.D. Wuest, J. Am. Chem. Soc. 114 (1992) 7931.
[180] M.R.P. van Vliet, G. van Koten, M.A. Rottewell, M. Schrap, K. Vrieze, Organometallics 5 (1986) 1389.
[181] A.D. Pajerski, T.P. Cleary, M. Parvez, G.W. Gobel, H.G. Richey Jr., Organometallics 11 (1992) 1400.
[182] J.L. Atwood, W.E. Hunter, R.D. Rogers, J.A. Weeks, J. Inclusion Phenom. 3 (1985) 113.
[183] M. Layh, W. Uhl, Polyhedron 3 (1990) 277.
[184] W. Uhl, M. Koch, A. Vester, Z. Anorg. Allg. Chem. 619 (1993) 359.
[185] J.W. Moore, D.A. Sanders, P.A. Scherr, M.D. Glick, J.P. Oliver, J. Am. Chem. Soc. 93 (1971) 1035.
[186] W. Uhl, U. Schütz, W. Hiller, M. Heckel, Chem. Ber. 127 (1994) 1587.
[187] J.L. Atwood, D.C. Hrncir, R.D. Rogers, J. Inclusion Phenom. 1 (1983) 199.
[188] A.D. Horton, A.G. Orpen, Organometallics 11 (1992) 1193.
[189] W. Uhl, A. Vester, W. Hiller, J. Organomet. Chem. 443 (1993) 9.
[190] W. Uhl, U. Schütz, Z. Naturforsch. Teil B: 49 (1994) 931.
[191] M.J. Zaworatko, R.D. Rogers, J.L. Atwood, Organometallics 1 (1982) 1179.
[192] R. Shakir, M.J. Zaworotko, J.L. Atwood, J. Organomet. Chem. 171 (1979) 9.
[193] S.A. Sangokoya, B. Lee, M.F. Self, W.T. Pennington, G.H. Robinson, Polyhedron 8 (1989) 1497.
[194] G.H. Robinson, M.F. Self, S.A. Sangokoya, W.T. Pennington, J. Cryst. Spectrosc. Res. 18 (1988) 285.
[195] M.F. Self, B. Lee, S.A. Sangokoya, W.T. Pennington, G.H. Robinson, Polyhedron 9 (1990) 313.
[196] J.J. Byers, W.T. Pennington, G.H. Robinson, Acta Crystallogr. Sect. C: 48 (1992) 2023.
[197] M.G. Gardiner, C.L. Raston, Organometallics 12 (1993) 81.
[198] D.C. Bradley, H. Chudzynska, M.M. Factor, D.M. Frigo, M.B. Hursthouse, B. Hussain, L.M. Smith, Polyhedron 7 (1988) 1289.
[199] H. Lehmkuhl, W. Mehler, A. Shakoor, C. Krüger, Y.-H. Tsay, R. Benn, A. Rufin'ska, G. Schroth, Chem. Ber. 118 (1985) 4248.
[200] A.M. Bradford, D.C. Bradley, M.B. Hursthouse, M. Motevalli, Organometallics 11 (1992) 111.
[201] D.J. Brauer, G.D. Stucky, J. Organomet. Chem. 37 (1972) 217.
[202] F. Gerstner, W. Schwarz, H.D. Hausen, J. Weidlein, J. Organomet. Chem. 175 (1979) 33.
[203] P. Fischer, R. Gräf, J.J. Stezowski, J. Weidlein, J. Am. Chem. Soc. 99 (1977) 6131.
[204] J.L. Atwood, G.D. Stucky, J. Am. Chem. Soc. 89 (1965) 5362.
[205] T.Y. Her, C.C. Chang, G.H. Lee, S.M. Peng, Y. Wang, Inorg. Chem. 33 (1994) 99.
[206] G.H. Robinson, S.G. Bott, H. Elgamal, W.E. Hunter, J.L. Atwood, J. Inclusion Phenom. 3 (1985) 65.
[207] J.L. Atwood, D.C. Hrncir, R. Shakir, M.S. Dalton, R.D. Priester, R.D. Rogers, Organometallics 1 (1982) 1021.
[208] G.H. Robinson, W.E. Hunter, S.G. Bott, J.L. Atwood, J. Organomet. Chem. 326 (1987) 9.
[209] S.G. Bott, A.W. Coleman, J.L. Atwood, J. Inclusion Phenom. 5 (1987) 747.
[210] W.S. Rees Jr., D.M. Schubert, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 108 (1986) 5367.
[211] S.G. Bott, A.W. Coleman, J.L. Atwood, J. Am. Chem. Soc. 108 (1986) 1709.
[212] J.L. Atwood, S.K. Seale, J. Organomet. Chem. 114 (1976) 107.
[213] D.A. Atwood, D. Rutherford, Organometallics 14 (1995) 3988.

[214] Z. Yiang, L.V. Interrante, D. Kwon, F.S. Tham, R. Kullnig, Inorg. Chem. 30 (1991) 995.
[215] C.C. Chang, C.C. Huang, J.O. Tsai, M.D. Li, L.K. Liu, Polyhedron 12 (1993) 2125.
[216] B. Lee, S.A. Sangokoya, W.T. Pennington, G.H. Robinson, J. Coord. Chem. 21 (1990) 99.
[217] G.H. Robinson, B. Lee, W.T. Pennington, S.A. Sangokoya, J. Am. Chem. Soc. 110 (1988) 6260.
[218] M. Veith, A. Spaniol, J. Pöhlmann, F. Gross, Y. Hueh, Chem. Ber. 126 (1993) 2625.
[219] W. Uhl, Z. Anorg. Allg. Chem. 570 (1989) 37.
[220] H.D. Hausen, G. Schmöger, W. Schwarz, J. Organomet. Chem. 153 (1978) 271.
[221] L.V. Interrante, G.A. Sigel, M. Garbauskas, C. Hejna, G.A. Slack, Inorg. Chem. 28 (1989) 252.
[222] J.L. Atwood, G.D. Stucky, J. Am. Chem. Soc. 92 (1970) 285.
[223] K.M. Waggoner, H. Hope, P.P. Power, Angew. Chem. Int. Ed. Engl. 27 (1988) 1699.
[224] J.B. Hill, S.J. Eng, W.T. Pennington, G.H. Robinson, J. Organomet. Chem. 445 (1993) 11.
[225] J.L. Atwood, R.D. Priester, R.D. Rogers, L.G. Canada, J. Inclusion Phenom. 1 (1983) 61.
[226] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 30 (1991) 564.
[227] G. Del Piero, M. Cesari, G. Dozzi, A. Mazzei, J. Organomet. Chem. 129 (1977) 281.
[228] T.R.R. McDonald, W.S. McDonald, Acta Crystallogr. Sect. B: 28 (1972) 1619.
[229] D.M. Choquette, M.J. Timm, J.L. Hobbs, T.M. Nicholson, M.M. Amstead, R.P. Planalp, Inorg. Chem. 32 (1993) 2600.
[230] A.H. Cowley, R.A. Jones, M.A. Mardones, J.L. Atwood, S.G. Bott, Angew. Chem. Int. Ed. Engl. 29 (1990) 1409.
[231] S. Schulz, H.W. Roesky, H.J. Koch, G.M. Sheldrick, D. Stalke, A. Kuhn, Angew. Chem. Int. Ed. Engl. 32 (1993) 1729.
[232] W. Uhl, M. Layh, J. Organomet. Chem. 415 (1991) 181.
[233] S.J. Trepanier, S. Wang, Angew. Chem. Int. Ed. Engl. 33 (1994) 1265.
[234] J.L. Atwood, M.J. Zaworotko, J. Chem. Soc. Chem. Commun. (1983) 302.
[235] S. Schutz, L. Häming, R. Herbst-Irmer, H.W. Roesky, G.M. Sheldrick, Angew. Chem. Int. Ed. Engl. 33 (1994) 969.
[236] R. Kumar, V. Srini J. de Mel, M.L. Sierra, D.G. Hendershot, J.P. Oliver, Organometallics 13 (1994) 2079.
[237] G.H. Robinson, M.F. Self, S.A. Sangokoya, W.T. Pennington, J. Am. Chem. Soc. 111 (1989) 1520.
[238] G.H. Robinson, S.A. Sangokoya, Organometallics 7 (1988) 1453.
[239] G.H. Robinson, A.D. Rae, C.F. Campana, S.K. Byram, Organometallics 6 (1987) 1227.
[240] G.H. Robinson, F. Moise, W.T. Pennington, S.A. Sangokoya, J. Cryst. Spectrosc. Res., 18 (1988) 387.
[241] M.F. Self, W.T. Pennington, G.H. Robinson, Acta Crystallogr. Sect. C: 47 (1991) 1309.
[242] M.F. Self, W.T. Pennington, G.H. Robinson, Inorg. Chim. Acta 175 (1990) 151.
[243] G.H. Robinson, E.S. Appel, S.A. Sangokoya, H. Zhang, J.L. Atwood, J. Coord. Chem. 171 (1988) 373.
[244] G.H. Robinson, S.A. Sangokoya, J. Am. Chem. Soc. 109 (1987) 6852.
[245] G.H. Robinson, F. Moise, W.T. Pennington, S.A. Sangokoya, Polyhedron 8 (1989) 1279.
[246] G.H. Robinson, M.F. Self, W.T. Pennington, S.A. Sangokoya, Organometallics 7 (1988) 2424.
[247] M.D. Li, C.C. Chang, S.T. Liu, G.H. Lee, Y. Wang, S.M. Peng, Organometallics 13 (1994) 1504.
[248] R.D. Rogers, J.L. Atwood, Organometallics 3 (1984) 271.
[249] M.D. Healy, A.R. Barron, J. Am. Chem. Soc. 111 (1989) 398.
[250] J.L. Atwood, S.D. Christie, M.D. Clerk, D.A. Osmond, K.C. Sturge, M.J. Zaworotko, Organometallics 11 (1992) 337.
[251] B. Lee, F. Moise, W.T. Pennington, G.H. Robinson, J. Coord. Chem. 26 (1992) 187.
[252] C.M. Bird, C. Breheny, M.G. Davidson, A.J. Edwards, S.C. Llewellyn, P.R. Raithby, R. Snaith, Angew. Chem. Int. Ed. Engl. 32 (1993) 1483.
[253] H. Zhang, C.M. Means, N.C. Means, J.L. Atwood, J. Cryst. Spectrosc. Res. 15 (1985) 445.
[254] G.H. Robinson, H. Zhang, J.L. Atwood, J. Organomet. Chem. 331 (1987) 153.
[255] G.H. Robinson, H. Zhang, J.L. Atwood, Organometallics 6 (1987) 887.
[256] H. Schnöckel, M. Leimkühler, R. Lotz, R. Mattes, Angew. Chem. Int. Ed. Engl. 25 (1986) 921.
[257] C.C. Landry, C.J. Harlan, S.G. Bott, A.R. Barron, Angew. Chem. Int. Ed. Engl. 34 (1995) 1201.
[258] G. Del Piero, G. Perego, S. Cucinella, M. Cesari, A. Mazzei, J. Organomet. Chem. 136 (1977) 13.
[259] M.F. Self, W.T. Pennington, G.H. Robinson, J. Coord. Chem. 24 (1991) 69.
[260] C. Dohmeier, R. Mattes, H. Schnöckel, J. Chem. Soc. Chem. Commun. (1990) 358.
[261] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, Angew. Chem. Int. Ed. Engl. 33 (1944) 199.
[262] A.W. Coleman, S.G. Bott, J.L. Atwood, J. Inclusion Phenom. 5 (1987) 581.
[263] J.L. Atwood, D.C. Hrncir, R.D. Priester, R.D. Rogers, Organometallics 2 (1983) 985.
[264] P.B. Hitchcock, J.D. Smith, K.M. Thomas, J. Chem. Soc. Dalton Trans. (1976) 1433.
[265] S. Amirkhalili, P.B. Hitchcock, J.D. Smith, J. Chem. Soc. Dalton Trans. (1979) 1206.
[266] W. Hiller, K.W. Klinkhammer, W. Uhl, J. Wagner, Angew. Chem. Int. Ed. Engl. 30 (1991) 179.
[267] B. Teclé, P.W.R. Corfield, J.P. Oliver, Inorg. Chem. 21 (1982) 458.
[268] D.J. Brauer, G.D. Stucky, J. Am. Chem. Soc. 91 (1969) 5462.
[269] S.A. Sangokoya, W.T. Pennington, G.H. Robinson, J. Cryst. Spectrosc. Res. 20 (1990) 53.
[270] C.E. Holloway, M. Melnik, Main Group Met. Chem. 19 (1996) 411.