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Methyl–hydride metathesis between $[Zr(cp)_2Me_2]$ and $[HAl(\mu_3\text{-}NBu^t)]_4$: molecular structures of $[Me_{1-x}H_xAl(\mu_3\text{-}NBu^t)]_4$ ($x = 0$, 0.78 or 1) and $[(cp)_2ZrMe(\mu\text{-}H)]_2$ ($cp = \eta^5\text{-}C_5H_5$)†

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The reaction of $[Zr(cp)_2Me_2]$ ($cp = \eta^5\text{-}C_5H_5$) with the cubane iminoalane, $[HAl(\mu_3\text{-}NBu^t)]_4$, yielded $[(cp)_2ZrMe(\mu\text{-}H)]_2$ and the alkyl-substituted iminoalanes $[Al_4MeH_3(\mu_3\text{-}NBu^t)_4]$ **1** and $[Al_4Me_2H_2(\mu_3\text{-}NBu^t)_4]$ **2**. The dimer $[(cp)_2ZrMe(\mu\text{-}H)]_2$ decomposes above 60 °C. The methyl–hydride exchange is first order with respect to each reactant concentration, and $\Delta H^‡$ and $\Delta S^‡$ have been determined as 104(1) kJ mol^{-1} and 18.8(4) J K^{-1} mol^{-1}, respectively. The molecular structures of $[(cp)_2ZrMe(\mu\text{-}H)]_2$, $[HAl(\mu_3\text{-}NBu^t)]_4$, $[MeAl(\mu_3\text{-}NBu^t)]_4$ and a cocrystallization disorder of compounds **1**, **2** and $[HAl(\mu_3\text{-}NBu^t)]_4$ have been determined by X-ray crystallography.

The accepted function of methylalumoxane $[(MeAlO)_n]$ (MAO) as a cocatalyst to $[Zr(cp)_2X_2]$ ($cp = \eta^5\text{-}C_5H_5$, X = Me or Cl) in Kaminsky–Sinn type olefin polymerization is two-fold.[1] First, MAO is assumed to alkylate the zirconocene metal fragments by ligand exchange, equation (1), although it should be

$$[Zr(cp)_2Cl_2] \xrightarrow{+\text{ MAO}} [Zr(cp)_2Me(Cl)] \qquad (1)$$

noted that there is no direct evidence of MAO acting as the alkylation agent since commercial MAO contains significant quantities of $AlMe_3$ which is known to alkylate $[Zr(cp)_2Cl_2]$.[2] Secondly, MAO abstracts the second chloride to generate a formally cationic zirconocene moiety, equation (2). We have

$$[Zr(cp)_2Me(Cl)] \xrightarrow{+\text{ MAO}} [Zr(cp)_2Me]^+ \qquad (2)$$

demonstrated that the second reaction occurs because of the latent Lewis acidity[3] of the alumoxane's cage structure.[4,5] The *tert*-butylalumoxanes show latent Lewis acidity towards methylzirconium,[3] palladium chloride and palladium acetate groups,[6] as well as β-lactones,[7] propylene oxide[8] and amines.[9] However, alkylation of transition-metal moieties by the *tert*-butylalumoxanes is either too rapid to study in detail,[6] or does not occur,[3] therefore for a more detailed study a model system is required to demonstrate that aluminium cage compounds can undergo metathesis reactions.

Isoelectronic analogues of alumoxanes include the sulfido cubanes, $[RM(\mu_3\text{-}S)]_4$ (M = Al or Ga).[10] We have shown[11] that as a consequence of the weaker Al–S bonds the reaction of $[Zr(cp)_2Me_2]$ with $[Bu^tAl(\mu_3\text{-}S)]_4$ leads to cleavage of the Al_4S_4 core resulting in abstraction of a monomeric 'Bu^tAlS' moiety and yielding $[(cp)_2Zr(\mu\text{-}S)(\mu\text{-}Me)AlBu^t(Me)]$. The remaining '$Bu^t_3Al_3S_3$' fragment reacts further with $[Zr(cp)_2Me_2]$ to give $[(cp)_2ZrAl_3(\mu_3\text{-}S)_3Bu^t_3Me_2]$. In contrast to the alumoxanes and aluminium chalcogenides, the iminoalanes only show cage-opening reactions with strong acids such as HCl, suggesting a significantly reduced latent Lewis acidity, *i.e.* increased cage stability. As such iminoalanes should allow for the metathetical ligand exchange on zirconium [*cf.* equation (1)] to be studied in isolation from cage-opening reactions. Iminoalanes, $[RAl(\mu_3\text{-}NR')]_n$ are readily prepared with a variety of cage sizes ($n = 4$, 6–8 or 10), and with a range of substituents (R, R′ = alkyl, halide, hydride, *etc.*).[12,13] This present study reports the reaction of $[Zr(cp)_2Me_2]$ with the iminoalane $[HAl(\mu_3\text{-}NBu^t)]_4$.

Results and Discussion

The iminoalane $[HAl(\mu_3\text{-}NBu^t)]_4$ reacts immediately and exothermically at room temperature with $[Zr(cp)_2Me_2]$ to yield the methyl–hydride transfer products, $[Al_4MeH_3(\mu_3\text{-}NBu^t)_4]$ **1** and $[(cp)_2ZrMe(\mu\text{-}H)]_2$[14–16] as the major products [equation (3)]. In

$$[HAl(\mu_3\text{-}NBu^t)]_4 + [Zr(cp)_2Me_2] \longrightarrow [(cp)_2ZrMe(\mu\text{-}H)]_2 + \underset{\mathbf{1}}{[Al_4MeH_3(\mu_3\text{-}NBu^t)_4]} \qquad (3)$$

addition, $[Al_4Me_2H_2(\mu_3\text{-}NBu^t)_4]$ **2** is also formed as a minor product (*ca.* 8%) from two methyl–hydride exchanges. In contrast to the results obtained for $[Zr(cp)_2Me_2]$, the reaction of $[Hf(cp)_2Me_2]$ with $[HAl(\mu_3\text{-}NBu^t)]_4$ does not occur below 60 °C, and no reaction is observed between $[Zr(cp)_2(CH_2Ph)_2]$ and $[HAl(\mu_3\text{-}NBu^t)]_4$.

A representative ^1H NMR spectrum of the reaction products is shown in Fig. 1, and clearly shows the presence of two methylated iminoalanes in addition to unreacted $[HAl(\mu_3\text{-}NBu^t)]_4$. Attempts to optimize the formation of either compound **1** or **2** were unsuccessful. The dimer $[(cp)_2ZrMe(\mu\text{-}H)]_2$ rapidly precipitates (as X-ray-quality crystals) from the benzene solution, and may be physically separated. The iminoalanes may be recrystallized from hexane. The molecular structure of the products has been confirmed by X-ray crystallography, see below. As has been previously reported, $[(cp)_2ZrMe(\mu\text{-}H)]_2$ rapidly decomposes above 60 °C to give a purple solid.[17]

The observed Me/H metathesis between $[Zr(cp)_2Me_2]$ and the iminoalane suggests that cage alumoxanes, such as MAO, may be able to perform the Me/Cl metathesis assumed to occur [*cf.* equation (1)] in the absence of $AlMe_3$. Although this is the first report of a metathesis reaction involving a transition-metal alkyl and an iminoalane, analogous reactions have been reported with main-group metal alkyls, *e.g.* the reaction of $[HAl(\mu_3\text{-}NR)]_4$ with $AlMe_3$ to yield $[MeAl(\mu_3\text{-}NR)]_4$.[13] In

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† *Supplementary data available* (No. SUP. 57193, 10 pp.): full kinetic data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

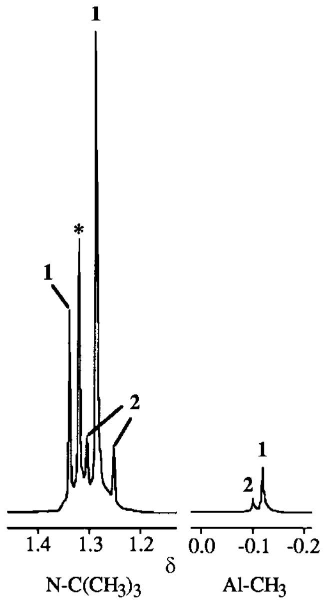


Fig. 1 Selected regions of the ^1H NMR spectrum of the iminoalane compounds $[Al_4MeH_3(\mu_3\text{-NBu}^t)_4]$ **1** and $[Al_4Me_2H_2(\mu_3\text{-NBu}^t)_4]$ **2** formed from the reaction between $[HAl(\mu_3\text{-NBu}^t)]_4$ (*) and $[Zr(cp)_2Me_2]$

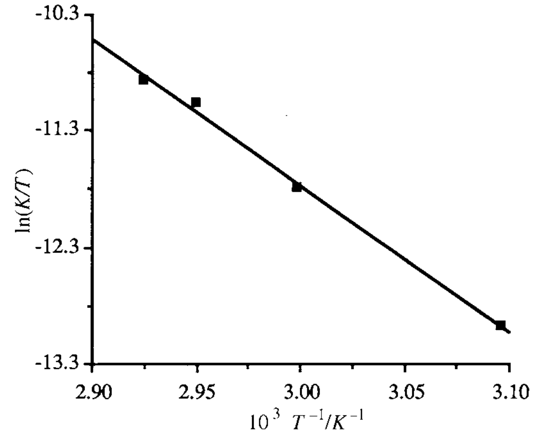
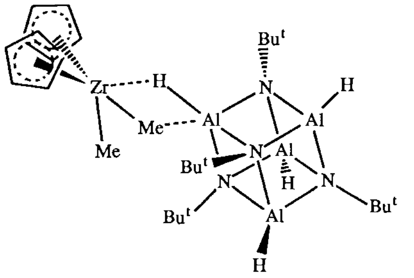


Fig. 2 Eyring plot for the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction between $[HAl(\mu_3\text{-NBu}^t)]_4$ and $[Zr(cp)_2Me_2]$ ($R = 0.997$)



I

addition, hydride–chloride metathesis is observed with $TiCl_4$.[18] However, kinetic data have not been reported in either case. As would be expected, the metathesis reaction between $[HAl(\mu_3\text{-NBu}^t)]_4$ and $[Zr(cp)_2Me_2]$ shows a first-order dependence (see Experimental section) on the concentration of both reagents, *i.e.* equation (4), consistent with either a concerted exchange (I_a) reaction or an associative (A) reaction.[19]

$$-d[Zr(cp)_2Me_2]/dt = k_2[Zr(cp)_2Me_2][Al_4H_4(NBu^t)_4] \quad (4)$$

Given the lack of evidence for cage opening in iminoalanes, we propose that metathesis would occur *via* an intermediate (A) or transition state (I_a) containing both five-co-ordinate aluminium and five-co-ordinate zirconium (*i.e.* **I**), both of which have clear precedents.[15,20]

The enthalpy ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were obtained from the appropriate Eyring plot (see Fig. 2), 104(1) kJ mol^{-1} and 18.8(4) J K^{-1} mol^{-1}. Although the small positive value for $\Delta S^{\ddagger}$ is difficult to interpret it is consistent with a late transition state.

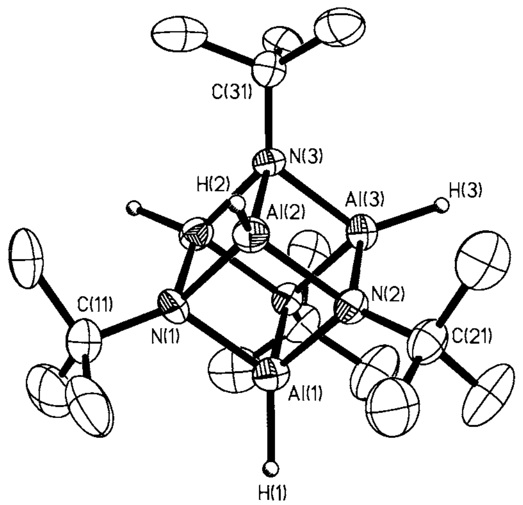


Fig. 3 Molecular structure of $[HAl(\mu_3\text{-NBu}^t)]_4$. Thermal ellipsoids are drawn at the 30% level, and the organic hydrogens are omitted for clarity

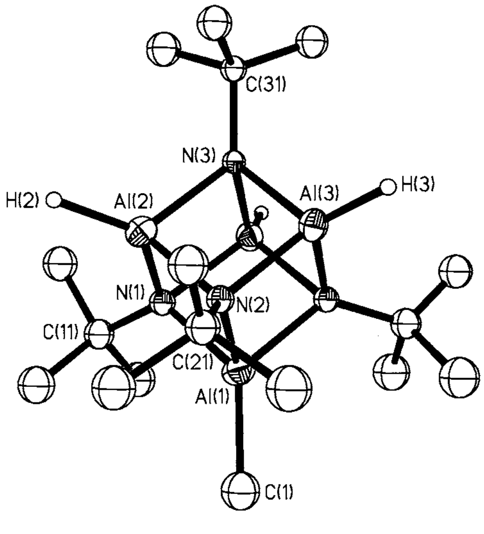


Fig. 4 Molecular structure of $[Al_4MeH_3(\mu_3\text{-NBu}^t)_4]$ **1**. Thermal ellipsoids are drawn at the 20% level. Only one of the positions for the disordered methyl group is shown, and the organic hydrogens are omitted for clarity

Crystallographic studies

The molecular structures of the products isolated from the metathesis of $[HAl(\mu_3\text{-NBu}^t)]_4$ and $[Zr(cp)_2Me_2]$ have been determined by X-ray crystallography, together with those of $[HAl(\mu_3\text{-NBu}^t)]_4$ and $[MeAl(\mu_3\text{-NBu}^t)]_4$ for comparison.

The molecular structures of $[HAl(\mu_3\text{-NBu}^t)]_4$, $[Al_4MeH_3(\mu_3\text{-NBu}^t)_4]$ **1** and one of the crystallographically independent molecules of $[MeAl(\mu_3\text{-NBu}^t)]_4$ are shown in Figs. 3, 4 and 5, respectively; selected bond lengths and angles are given in Table 1. The Al–N bond distances [1.89(1)–1.937(4) Å] and N–Al–N angles [89.3(5)–91.3(2)°] are essentially identical between each compound and are within the ranges found for other cubane iminoalanes, 1.913(1)–1.923(1) Å and 89.3(5)–90.6(4)°, respect-

Table 1 Selected bond lengths (Å) and angles (°) for $[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$, $[\mathrm{Me_{0.22}H_{0.78}Al}(\mu_3\text{-}\mathrm{NBu^t})]_4$ and $[\mathrm{MeAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$

	$[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$	$[\mathrm{Me_{0.22}H_{0.78}Al}(\mu_3\text{-}\mathrm{NBu^t})]_4$	$[\mathrm{MeAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$
Al–N	1.907(8)–1.929(6)	1.89(1)–1.918(9)	1.917(4)–1.937(4)
Al–H	1.45(7)–1.55(6)	1.55(8)–1.6(1)	
Al–C		1.88(3)	1.941(7)–1.959(6)
N–C	1.46(1)–1.50(1)	1.48(2)–1.52(2)	1.475(7)–1.494(6)
N–Al–N	90.3(3)–91.1(3)	89.3(5)–90.6(4)	89.8(1)–91.3(2)
N–Al–H	123(2)–128(2)	120(2)–128(2)	
N–Al–C		125(1)–126.9(9)	123.3(2)–126.2(2)
Al–N–Al	89.0(3)–89.6(3)	89.0(5)–90.4(4)	89.0(2)–90.1(2)
Al–N–C	125.3(6)–126.1(4)	123.0(8)–127.7(8)	124.5(3)–126.9(3)

Table 2 Selected bond lengths (Å) and angles (°) for $[(\mathrm{cp})_2\mathrm{ZrMe}(\mu\text{-}\mathrm{H})]_2$.

Zr(1)–C(1)	2.533(5)	Zr(1)–C(2)	2.529(6)
Zr(1)–C(3)	2.484(7)	Zr(1)–C(4)	2.484(9)
Zr(1)–C(5)	2.521(6)	Zr(1)–C(11)	2.305(8)
Zr(1)–H(1)	1.939(8)	Zr(1)–H(1a)	2.161(8)
Zr(1)···Zr(1a)	3.467(2)	Zr(1)–Cp*	2.219(4)
C(1)–Zr(1)–C(2)	31.7(2)	C(1)–Zr(1)–C(3)	52.6(2)
C(2)–Zr(1)–C(3)	31.9(2)	C(1)–Zr(1)–C(4)	53.1(2)
C(2)–Zr(1)–C(4)	53.2(2)	C(3)–Zr(1)–C(4)	32.1(3)
C(1)–Zr(1)–C(5)	31.9(2)	C(2)–Zr(1)–C(5)	52.6(2)
C(3)–Zr(1)–C(5)	52.4(3)	C(4)–Zr(1)–C(5)	31.9(3)
C(1)–Zr(1)–C(11)	89.0(2)	C(2)–Zr(1)–C(11)	120.6(1)
C(3)–Zr(1)–C(11)	125.4(2)	C(4)–Zr(1)–C(11)	95.3(3)
C(5)–Zr(1)–C(11)	74.2(2)	Cp–Zr–Cp′	127.4(3)

* Cp = Centroid of C_5H_5 ligand.

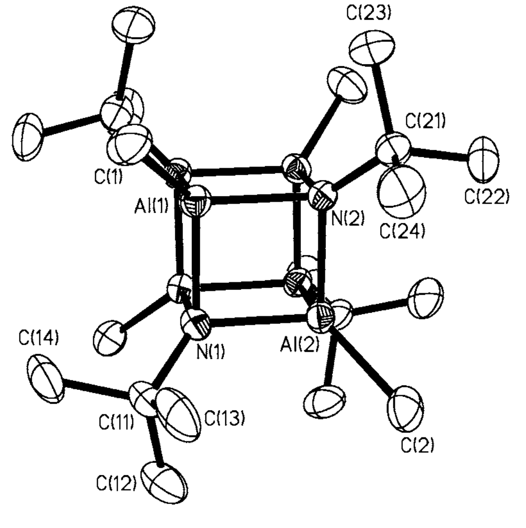


Fig. 5 Molecular structure of one of the crystallographically independent molecules of $[\mathrm{MeAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$, with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% level, and all hydrogens are omitted for clarity

Table 3 Selected kinetic data for the methyl–hydride metathesis reaction between $[\mathrm{Zr(cp)_2Me_2}]$ and $[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$[a]

T/K	$10^3k_2{}^b$/dm^3 mol^{-1} s^{-1}
323	0.7507
333	2.571
339	5.350
348	6.710

[a] From ^{1}H NMR spectra measured in $C_6D_5CD_3$. [b] Second-order rate constant, see text.

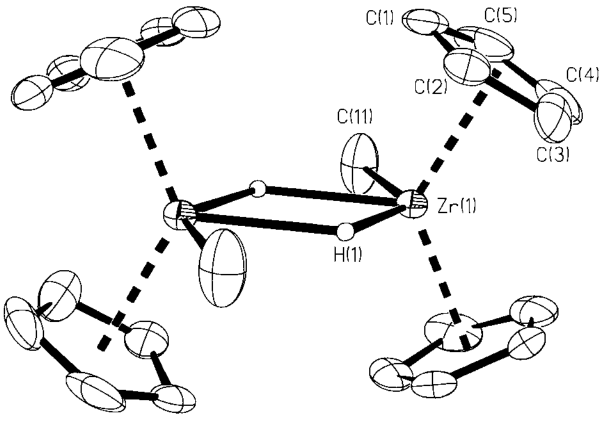


Fig. 6 Molecular structure of $[(\mathrm{cp})_2\mathrm{ZrMe}(\mu\text{-}\mathrm{H})]_2$. Details as in Fig. 3

ively.[21] The Al–H distances are in the range previously reported for aluminohydrides (1.4–2.0 Å).[22]

The NMR spectroscopic characterization of the crystal obtained from the metathesis reaction and used for diffraction indicates it to be a mixture of $[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$, $[\mathrm{Al_4MeH_3}(\mu_3\text{-}\mathrm{NBu^t})_4]$ and $[\mathrm{Al_4Me_2H_2}(\mu_3\text{-}\mathrm{NBu^t})_4]$, in a 2.67 : 11.2 : 1 ratio. Based on the assumption that the methyl and hydride groups in $[\mathrm{Al_4MeH_3}(\mu_3\text{-}\mathrm{NBu^t})_4]$ are fixed [*i.e.* the methyl group is bonded to Al(1)], and a uniform crystal sample, a calculated site occupancy of a methyl attached to Al(1) and Al(2) would be 0.82 and 0.02, respectively. The independent refinement of 0.82 Me and 0.18 H for the ligand attached to Al(1) is therefore consistent with this prediction (see Experimental section), and consistent with a formulation of $[\mathrm{Me_{0.22}H_{0.78}Al}(\mu_3\text{-}\mathrm{NBu^t})]_4$. The cocrystallization of $[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$, $[\mathrm{Al_4MeH_3}(\mu_3\text{-}\mathrm{NBu^t})_4]$ and $[\mathrm{Al_4Me_2H_2}(\mu_3\text{-}\mathrm{NBu^t})_4]$, and hence resulting disorder of methyl and hydride groups, suggest that crystal packing is dominated by the *tert*-butyl groups. Further evidence of this is the isomorphous nature of $[\mathrm{Me_{0.22}H_{0.78}Al}(\mu_3\text{-}\mathrm{NBu^t})]_4$ and $[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$, see Experimental section. A similar observation has been reported for the hexameric iminoalanes.[23] It is noteworthy, however, that while $[\mathrm{MeAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$ is isostructural to $[\mathrm{HAl}(\mu_3\text{-}\mathrm{NBu^t})]_4$, $[\mathrm{Al_4MeH_3}(\mu_3\text{-}\mathrm{NBu^t})_4]$ and $[\mathrm{Al_4Me_2H_2}(\mu_3\text{-}\mathrm{NBu^t})_4]$ it is not isomorphous. A comparison of the bond lengths and angles in Table 1 suggests that the $\mathrm{Al_4N_4}$ core structure is insensitive to ligand effects, *i.e.* Al–H *versus* Al–CH_3. We have observed that the core of gallium sulfide cubane compounds, $[\{\mathrm{GaR}(\mu_3\text{-}\mathrm{S})\}_4]$, is similarly unaffected by the identity of the organic ligand.[24]

The molecular structure of $[(\mathrm{cp})_2\mathrm{ZrMe}(\mu\text{-}\mathrm{H})]_2$ is shown in Fig. 6; selected bond lengths and angles are given in Table 2. The molecule exists as a centrosymmetric dimer with asymmetrically bridging hydride groups [Zr(1)–H(1) 1.939(8), Zr(1)–H(1a) 2.161(8) Å], and is similar to the methylcyclopentadienyl dihydride, $[(\eta\text{-}\mathrm{C_5H_4Me})\mathrm{ZrH}(\mu\text{-}\mathrm{H})]_2$, previously reported.[25] The Cp–Zr–Cp angle (Cp = centroid of C_5H_5) of 127.4(3)° is similar to the values reported for other dicyclopentadienyl compounds of $\mathrm{Zr^{IV}}$.[26]

Table 4 Summary of X-ray diffraction data*

	$[HAl(\mu_3\text{-}NBu^t)]_4$	$[Me_{0.22}H_{0.78}Al(\mu_3\text{-}NBu^t)]_4$	$[MeAl(\mu_3\text{-}NBu^t)]_4$	$[(cp)_2ZrMe(\mu\text{-}H)]_2$
Empirical formula	$C_{16}H_{40}Al_4N_4$	$C_{17}H_{42}Al_4N_4$	$C_{20}H_{48}Al_4N_4$	$C_{11}H_{14}Zr$
Crystal size/mm	0.18 × 0.25 × 0.29	0.07 × 0.09 × 0.13	0.21 × 0.25 × 0.13	0.30 × 0.36 × 0.22
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pnma*	*Pnma*	*P*2/*c*	*Pnnm*
a/Å	10.3360(9)	11.157(1)	18.342(2)	7.289(4)
b/Å	15.081(1)	14.761(1)	9.5183(8)	9.516(3)
c/Å	16.632(1)	16.191(1)	33.812(4)	13.880(4)
β/°			94.300(8)	
U/Å^3	2592.6(4)	2666.5(4)	5886(4)	7962.7(7)
Z	4	4	8	4
D_c/g cm^{-3}	1.016	1.022	1.021	1.638
μ/mm^{-1}	0.181	0.178	0.166	0.082
2θ Range/°	2.0–44.0	2.0–44.0	2.0–50.0	4.0–40.0
No. data collected	1842	1900	11 286	902
No. independent data	1842	1900	10 955	477
No. observed data	859 ($\lvert F_o\rvert > 5.0\sigma\lvert F_o\rvert$)	617 ($\lvert F_o\rvert > 5.0\sigma\lvert F_o\rvert$)	4907 ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$)	443 ($\lvert F_o\rvert > 4.0\sigma\lvert F_o\rvert$)
Weighting scheme, w^{-1}	$\sigma^2(\lvert F_o\rvert) + 0.04(\lvert F_o\rvert)^2$	$\sigma^2(\lvert F_o\rvert) + 0.04(\lvert F_o\rvert)^2$	$\sigma^2(\lvert F_o\rvert) + 0.04(\lvert F_o\rvert)^2$	$\sigma^2(\lvert F_o\rvert)$
R	0.0550	0.0726	0.0482	0.0224
R'	0.0577	0.0747	0.0485	0.0250
Largest difference peak/e Å^{-3}	0.37	0.33	0.34	0.39

* Details in common: graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å); 298 K; refinement based on F^2.

Experimental

Mass spectra were obtained on a JEOL AX-505 H spectrometer operating with an electron beam energy of 70 eV (*ca.* 1.12 × 10^{-17} J) for electron impact, infrared spectra (4000–400 cm^{-1}) using a Nicolet 5ZDX-FTIR spectrometer for samples prepared as mulls on KBr plates and NMR spectra on Bruker AM-500, AM-400, AM-300 and AM-250 spectrometers using (unless otherwise stated) C_6D_6 solutions. Chemical shifts are reported relative to external $SiMe_4$. All procedures were performed under purified nitrogen. Solvents were distilled and degassed before use. The compounds $[Zr(cp)_2Me_2]$, $[Hf(cp)_2Me_2]$, $[MeAl(\mu_3\text{-}NBu^t)]_4$ and $[HAl(\mu_3\text{-}NBu^t)]_4$ were prepared by modifications of literature procedures.[27,28]

Reaction of $[Zr(cp)_2Me_2]$ with $[HAl(\mu_3\text{-}NBu^t)]_4$

Toluene (10 cm^3) was added to a mixture of $[HAl(\mu_3\text{-}NBu^t)]_4$ (0.400 g, 1.01 mmol) and $[Zr(cp)_2Me_2]$ (0.255 g, 1.02 mmol) at room temperature. It was stirred overnight and the volatiles removed under vacuum. The resulting solid was extracted with hexane (20 cm^3). The insoluble fraction was determined to be $[(cp)_2ZrMe(\mu\text{-}H)]_2$ by ^{1}H NMR spectroscopy. The solution was concentrated to *ca.* 5 cm^3 and cooled to −24 °C overnight to yield colourless blocks.

$[Al_4MeH_3(\mu_3\text{-}NBu^t)_4]$ **1**: EI mass spectrum *m/z* 409 ($M^+ - H$, 30%); ^{1}H NMR δ 1.33 [9 H, s, $NC(CH_3)$], 1.28 [27 H, s, $NC(CH_3)$] and −0.11 (3 H, s, Al–CH_3); ^{13}C NMR ($CDCl_3$) δ 51.80 [N*C*(CH_3)], 51.64 [N*C*(CH_3)], 34.71 [NC(*C*H_3)], 34.42 [NC(*C*H_3)] and −0.12 (Al–CH_3).

$[Al_4Me_2H_2(\mu_3\text{-}NBu^t)_4]$ **2**: EI mass spectrum *m/z* 423 ($M^+ - H$, 5%); ^{1}H NMR δ 1.30 [18 H, s, $NC(CH_3)$], 1.25 [18 H, s, $NC(CH_3)$] and −0.09 (3 H, s, Al–CH_3).

Kinetic studies

A series of samples of $[HAl(\mu_3\text{-}NBu^t)]_4$ was accurately weighed (± 0.005 g) into a series of 5 mm NMR tubes. To each tube was added an aliquot (*ca.* 0.25 cm^3) of a $C_6D_5CD_3$ solution of $[Zr(cp)_2Me_2]$ (13.2 mmol dm^{-3}), the mass of solution determined, and thus the concentration of $[HAl(\mu_3\text{-}NBu^t)]_4$. All the samples were prepared such that $[HAl(\mu_3\text{-}NBu^t)]_4$ was in excess (50–130 mmol dm^{-3}), and thus the reactions were run under pseudo-first-order kinetic conditions. All the samples were heated to the appropriate temperature within the NMR spectrometer, and a series of ^{1}H NMR spectra was collected every 10–30 min for up to 7 h. The temperature of the NMR spectrometer probe was calibrated using the chemical shifts of ethylene glycol. The integration of the Zr–cp proton resonances was used to determine the rate of reaction. A minimum of four samples, with varying concentrations of $[HAl(\mu_3\text{-}NBu^t)]_4$, were run at each of four temperatures. The pseudo-first-order rate constants (k_{obs}) were determined from plots of $-\ln[Zr(cp)_2Me_2]$ *versus* time. The second-order rate constants (k_2) were obtained from plots of k_{obs} *versus* the initial concentration of $[HAl(\mu_3\text{-}NBu^t)]_4$. Selected kinetic data are given in Table 3. Full data have been deposited as SUP. 57193.

Crystallography

Crystals of $[HAl(\mu_3\text{-}NBu^t)]_4$, $[Me_{0.22}H_{0.78}Al(\mu_3\text{-}NBu^t)]_4$ and $[MeAl(\mu_3\text{-}NBu^t)]_4$ were sealed in a glass capillary under argon and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Data collection and cell determinations were performed in a manner previously described.[4] The location of the majority of non-hydrogen atoms were obtained by using SIR,[29] while the remaining atomic coordinates were determined through the generation of Fourier-difference maps using MOLEN.[30] In the case of $[Me_{0.22}H_{0.78}Al(\mu_3\text{-}NBu^t)]_4$, refinement of the methyl carbon suggested a partial occupancy. On the basis of the ^{1}H NMR data the short Al(1)–C(1) bond distance and the large value of the thermal parameter ($B > 13$ Å^2) when C(1) was refined as full occupancy, a site-disordered crystal was assumed. Attempts to include a partial hydride attached to Al(1) and partial methyl groups attached to Al(2) and/or Al(3) all resulted in either unrealistic thermal parameters or convergence of the partial sites (regardless of any restraints used).[31] In the final model, therefore, a composite scattering factor was used for C(1) that was calculated based on the position being 82% C and 18% H. The aluminium hydrides, H(2) and H(3), were located and refined; all other hydrogen atoms were placed in calculated positions [d(C–H) = 0.95 Å, B(H) = 1.2 B_{eq} (attached carbon)]. No disorder was observed in the structure refinement of $[HAl(\mu_3\text{-}NBu^t)]_4$ or $[MeAl(\mu_3\text{-}NBu^t)]_4$. A summary of cell parameters, data collection, and structure solutions is given in Table 4. Scattering factors were taken from ref. 32.

A crystal of $[(cp)_2Zr(Me)(\mu\text{-}H)]_2$ isolated directly from the reaction mixture was mounted in glass capillary attached to the goniometer head of a Nicolet R3m/V four-circle diffractometer. Data collection, unit-cell and space-group determination were all carried out in a manner previously described in detail.[33] The structures were solved using the direct methods program XS[34] which readily revealed the positions of the Zr and some of the C atoms. Subsequent Fourier-difference maps revealed the positions of all the non-hydrogen atoms. The zirconium hydride was found on the difference map and freely refined, except in the final refinement. All the organic hydrogen atoms were placed in calculated positions [$U_{iso} = 0.08$ Å^2, d(C−H) = 0.96 Å] for refinement. Neutral-atom scattering factors were taken from the usual source.[32] A summary of cell parameters, data collection, and structure solutions is given in Table 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/300.

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