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Full Paper

Aust. J. Chem. **2013**, *66*, 1219–1225
http://dx.doi.org/10.1071/CH13229

Aluminium Complexes of a Sterically Demanding Bis(iminophosphorane)methandiide

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The reaction of the sterically demanding bis(iminophosphorane)methane, $\{DipN{=}P(Ph_2)\}_2CH_2$, H_2L **1** (where Dip = 2,6-$i$$Pr_2C_6H_3$), with one or two equivalents of $AlMe_3$ in toluene under varying conditions led to the methanide complex [$HLAlMe_2$] **4**, and the methandiide complex [$L(AlMe_2)_2$] **5**, respectively. Iterative iodination of complex **5** with I_2 in toluene yielded the complexes [$L(AlMeI)_2$] **6** and [$L(AlI_2)_2$] **7**. The complexes **4**–**7** were structurally characterised. The methanide **4** forms a puckered six-membered ring without Al-C(methanide) contact and the complexes **5** and **6** show coordination of the methandiide ligand to two Al atoms forming two four-membered rings on the central spirocyclic carbon centre. Complex **7** shows an asymmetric coordination mode of the two Al centres to the methandiide ligand in the solid state with an almost planar, severely distorted three-coordinate methandiide carbon atom and only one short Al–C bond.

Manuscript received: 1 May 2013.
Manuscript accepted: 30 May 2013.

Introduction

Substituted bis(iminophosphorane)methanes (Fig. 1, where Mes = mesityl (2,4,6-trimethylphenyl) and Dip = 2,6-diisopropylphenyl) such as H_2L **1** (R = Dip), and related sterically less demanding chalcogen analogues, are CH acidic compounds that can be deprotonated to substituted methanide (Fig. 1a) complexes and even doubly deprotonated forming substituted methandiide (Fig. 1b, c) complexes with suitable organometallic reagents, and can undergo subsequent metathesis chemistry.[1] The methandiide complexes are of particular interest because of their unusual metal-carbon interactions including a varying degree of metal-carbon double bonding. In complexes with electropositive metal ions, the majority of charge accumulation on the metal-carbon fragment is located on the methandiide carbon atom having typical charges of ~ -1.7 to -1.9.[1] This dianionic charge (see Fig. 1c) is mainly located in two orbitals that can be described for most compounds as approximately sp^2 and p in character. The highly ionic character of the metal-carbon interaction for electropositive metal ions has led to descriptions that favour a methandiide formulation rather than a covalent metal carbene bond. In addition, these substituted methanide and methandiide ligands afforded a range of metal complexes with different and flexible metal-ligand coordination modes to the anionic C and N atoms.[1] For bis(iminophosphorane)methandiide complexes, a formulation with alternating negative and positive charges and a dianionic central carbon atom (Fig. 1c) seems to be the appropriate description.[1]

The majority of investigations into bis(iminophosphorane) methanide and methandiide complexes have been carried out with trimethylsilyl and mesityl substituents on the nitrogen atoms, while complexes with the more sterically demanding Dip aryl group are less common.[1] Methandiide complexes have also undergone reactions with (unsaturated) organic substrates though this reactivity has been described as modest[1b] taking the high negative charge of the methandiide into consideration. As sterically demanding and anionic ligands, these substance classes have also found their way into stabilising rare bonding modes and oxidation states of metal ions. For instance, some Zn–Zn bonded complexes of substituted bis(iminophosphorane)methanides were recently obtained by the facile reaction of Cp*ZnZnCp* with CH-acidic bis(iminophosphorane) methanes.[2]

In recent years, several aluminium complexes of bis (iminophosphorane)methanides and -methandiides have been reported,[3–7] as well as some chalcogen analogues and related complexes.[8–15] Along the study of metal-ligand, and especially metal-carbon interactions, these complexes are also of interest as transition metal free olefin polymerisation pre-catalysts,[4,7] e.g. compound **2** (Fig. 2), and have been found to add the methandiide fragment of **2** to heterocumulenes,[5] yielding **3** (Fig. 2). Herein, we report on new Al^{III} complexes derived from the sterically demanding compound **1**, their conversion to iodide complexes, and initial attempts to synthesise novel low oxidation state derivatives.

Results and Discussion

The reaction of H_2L **1** with one equivalent of $AlMe_3$ in toluene afforded the methanide complex [$HLAlMe_2$] **4** in good yield, see Fig. 3. The complex was structurally characterised (see Fig. 4), crystallographic details are summarised in Table 1, and selected interatomic distances and angles are collected in Table 2. The structure of complex **4** shows the expected distorted four-coordinate environment around the Al^{3+} centre with a puckered six-membered ring similar to previously characterised

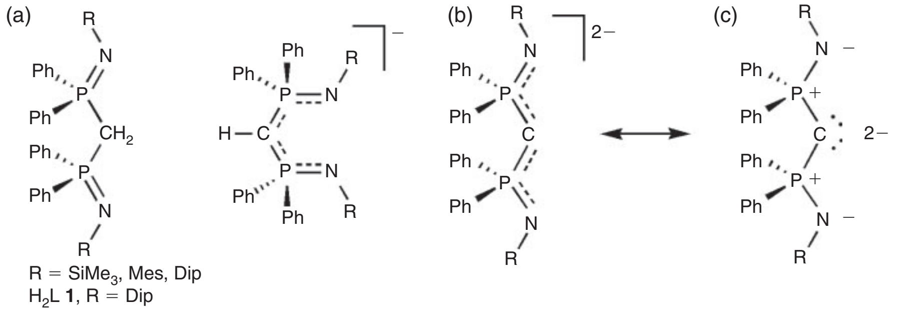

Fig. 1. Bis(iminophosphorane)methane, -methanide (a) and -methandiide (b, c).

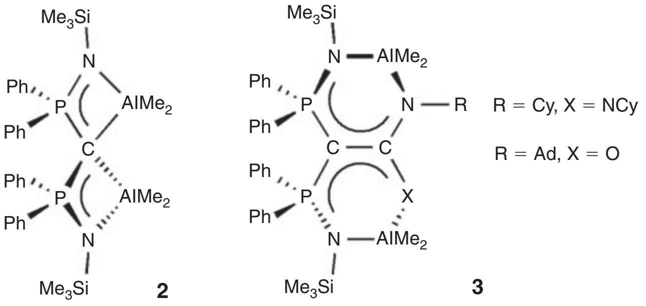

Fig. 2. Previously reported aluminium complexes **2** and **3**; Cy = cyclohexyl, Ad = 1-adamantyl.

examples,[3,6,7] though some known examples are found in a boat conformation. The Al–N and Al–C bond lengths are very similar to those found for related methanide-$AlMe_2$ complexes[6,7] though the Al–N bond lengths are longer than in related methanide-AlX_2 (X = Cl, Br, I) complexes.[3,7] The spectroscopic data of **4** is as expected and similar to related examples. Heating complex **4** in boiling toluene did not lead to further methane elimination which could form a mono-aluminium methandiide complex. Treatment of complex **4** with a second equivalent of $AlMe_3$ in toluene at ~100°C or under reflux afforded the bisaluminium methandiide complex $[L(AlMe_2)_2]$ **5** in good yield (Fig. 3). The crystal structure of complex $\mathbf{5} \cdot 3C_7H_8$ (Fig. 4, Table 1, Table 2) shows two spirocyclic Al-C-P-N rings about the central carbon atom, as found for the previously characterised related example **2**.[6] The least-square-planes of the two four-membered Al-C-P-N rings are twisted by ~72.4° which is close to the value for the related complex **2** (~75.3°). At 27°C, the ^1H NMR spectrum of **5** displays two very broad resonances for the *i*Pr methyl protons and one broad resonance for the *i*Pr methine protons. These two resonances merge at a coalescence temperature of ~40°C to one (broad) resonance and one sharp septet is observed for the *i*Pr methine protons. Between 27°C and 70°C, two singlets with an integration of 6H each are found for the Al-methyl protons, the broader resonance appears at highest field.

In order to substitute the Al-methyl groups in compound **5** with halide groups, we treated a solution of **5** with iodine (I_2) in toluene, see Fig. 5. The reaction was carried out as a titration experiment, following the decolourisation of iodine. The reaction proceeds rapidly at 0°C for the addition of the first two equivalents of I_2 and the mixed iodo methyl complex $[L(AlMeI)_2]$ **6** can be isolated and structurally characterised (Fig. 6, Table 1, Table 2). Complex $\mathbf{6} \cdot 2\,C_7H_8$ crystallised with a full molecule in the asymmetric unit and shows the same overall geometry as found for compound **5**. The two Al-C-P-N least-square-planes intersect at an angle of ~68.2°. The two large iodo ligands are arranged in a *trans*-like fashion on the LAl_2 core placing them almost as far as possible away from each other with an I-Al · · · · Al-I torsion angle of ~167°. The bond lengths and angles are comparable to those of **5** though with slightly shortened Al–N and Al–C(ligand) distances and slightly elongated Al-CH_3 and P–C(ligand) distances. The bond lengths ratio $M–C_{methandiide}/M–N$ for some dimeric complexes of the anionic ligand $\{(Me_3Si)NPPh_2\}C^{2-}$ have been compared and suggest increasingly covalent metal-ligand interactions with a lower ratio (<1.0).[1b] Complexes **5** and **6** show M–C/M–N ratios of ~1.13 and 1.14, respectively, which are close to the ratios for group 2 metal methandiides of ~1.11.[1b] If comparisons can be drawn with the complexes reported herein, then this underpins the highly ionic character of the metal-ligand interaction in **5** and **6**. Complex **6** shows four broad resonances for the *i*Pr methyl protons, two broad resonances for the *i*Pr methine protons and a singlet for the Al-methyl protons at 27°C in the ^1H NMR spectrum. Upon heating, the *i*Pr protons broaden significantly and start merging at around 60°C.

The first *bis*-iodination (**5** to **6**) is rapid at 0°C. Further iodination is slowed down and proceeds slowly at room temperature and a small excess of I_2 is required in the reaction mixture. After completion, workup afforded brown-yellow crystalline $[L(AlI_2)_2]$ **7** in moderate yield, see Fig. 5. Complex $\mathbf{7} \cdot 0.5\, C_6H_{14}$ crystallised with a full molecule in the asymmetric unit (Fig. 6; see also Tables 1 and 2 for further details). The two Al atoms coordinate to the methandiide ligand in an asymmetric fashion. Complex **7** comprises one Al-C-P-N four-membered ring and an Al-C-P-N-Al-I six-membered ring with a bridging iodide between the two Al centres. One Al–C bond is broken compared with the structures of **5** and **6** and replaced with an additional Al–I interaction to still yield two four-coordinate Al centres. This change in coordination environment is likely caused by an increased steric demand of the iodide ligands and possibly by a different ionic character of the AlI_2^+ fragments compared with the $AlMe_2^+$ or $AlMeI^+$ fragments in **5** and **6**, respectively. In addition, substituted bis(iminophosphorane)methanides and -methandiides have previously been described as very flexible ligands[1] and changes in the coordination mode are likely low in energy and could to some degree be influenced by crystal packing effects. The Al–I bond lengths for the bridging iodide are naturally longer compared with those for the terminal Al–I bonds, and the Al–I2 distance is somewhat shorter for Al1 than for Al2. The asymmetric coordination and the bond lengths suggest that $[L(AlI_2)_2]$ **7** approaches an intramolecularly ionised $[L(AlI^+)(AlI_3^-)]$ formulation. It is worthy to mention that the olefin polymerisation activity generated from pre-catalyst **2** stems from

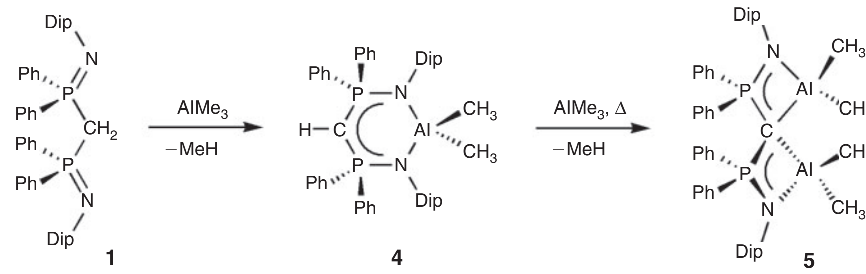

Fig. 3. Synthesis of complexes **4** and **5**.

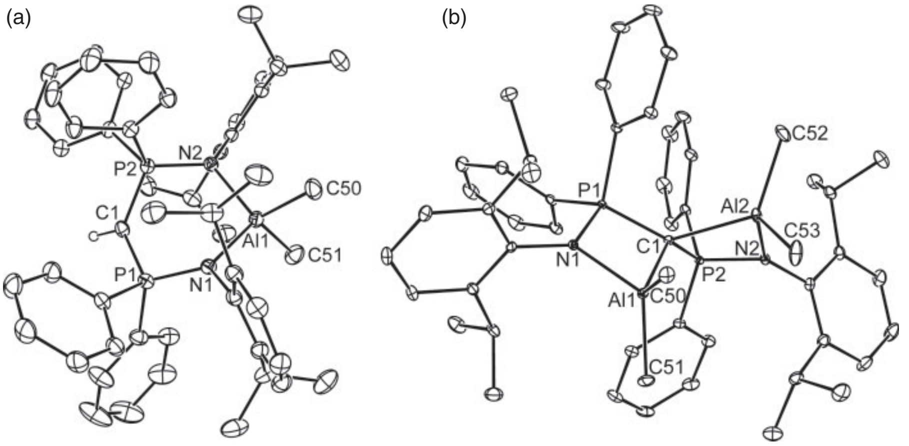

Fig. 4. Molecular structures of complexes (a) **4** and (b) **5** · $3C_7H_8$ (30 % thermal ellipsoids). Hydrogen atoms with the exception of C(1)H on **4** and solvent molecules are omitted for clarity.

its conversion to a cationic complex after a methyl anion abstraction in solution.[4] The methandiide carbon atom is three-coordinate with one acute (Al1-C1-P1 87.93(13)°) and two obtuse (Al1-C1-P2 135.74(14)° and P1-C1-P2 134.01(18)°) angles and is very close to a planar geometry (sum of angles ~358°). Notable is the short Al1–C1 bond length of 1.942(3) Å in complex **7**, that is ~0.2 Å shorter than the Al–C distances to the four-coordinate methandiide centres in **5** and **6** (2.126(3)-2.1607 (13) Å). To the best of our knowledge, the coordination of the two Al centres to the methandiide in the monomeric complex **7** represents a new structurally characterised coordination mode for this ligand class. A somewhat related asymmetric coordination mode of two metals to one methandiide unit has been characterised for the dimeric structure $[[(Ph_2PNSiMe_3)(Ph_2PS)CAlMe]_2]$.[9]

The ^1H NMR spectrum of compound **7** largely resembles that of complex **6** though without the Al-CH_3 peak and slightly shifted resonances. The four broad resonances for the *i*Pr methyl protons and two broad resonances for the *i*Pr methine protons broaden at elevated temperatures and the two methine resonances merge at ~65°C. Complexes **4** (δ 30.5), **5** (δ 31.6), **6** (δ 40.1), and **7** (δ 32.9) all display one sharp resonance in their $^{31}P\{^1H\}$ NMR spectra. This, together with ^1H NMR data, shows average symmetric solution behaviour for complex **7**. We further investigated this situation for the asymmetrically coordinated complex $[L(AlI_2)_2]$ **7** with a low temperature NMR study and found broadening of the resonances in the ^1H and $^{31}P\{^1H\}$ NMR spectra at very low temperatures in deuterated toluene down to −75°C, the limit of this experiment, though no splitting of the $^{31}P\{^1H\}$ resonance was observed. This shows that low energy exchange or isomerisation processes are responsible for the methandiide coordinated AlI_2^+ fragments in solution and further supports the high flexibility of the ligand class.[1] The $^{13}C\{^1H\}$ NMR spectra show a triplet for the methanide carbon atom of **4** at δ 15.1 with a large $^1J_{C\text{-}P}$ coupling constant of 138 Hz, though no comparable resonances were observed for the methandiide complexes **5**–**7** despite long acquisition times. This is not surprising given the coordination of this quaternary carbon atom to two ^{27}Al nuclei ($I = 5/2$) and further splitting by two ^{31}P nuclei. This has also previously been observed for the related complex **2**.[6]

We carried out small scale experiments, monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, of complex **5** with I_2 in various stoichiometries including those with approximately one and three equivalents of I_2 in [D$_6$]benzene, respectively. These reactions afforded product mixtures and we assigned two broad resonances at ~δ 23 and ~δ 33 ($^{31}P\{^1H\}$ NMR) to the mixed species $[L(AlMe_2)(AlMeI)]$, and two doublets at δ 28.3 and δ 36.1 (br) with $J = 36.6$ Hz for $[L(AlMeI)(AlI_2)]$. These experiments also confirmed the generation of MeI (δ 1.44 by ^1H NMR) as the by-product in the iodination reactions. The end product $[L(AlI_2)_2]$ **7** can be synthesised in good yield according to these NMR experiments and work-up and possibly separation from small amounts of excess I_2 or polyiodinated products (e.g. with I_3^- ligands) only seemed to limit the isolated yield for the larger scale reactions. Initial reduction experiments of complexes **6** and **7** with potassium metal have so far only led to product mixtures. The attempted reduction of these compounds with the stoichiometric and hydrocarbon-soluble dimeric magnesium(I) complex[16] $[(^{Mes}nacnac)Mg]_2]$

Table 1. Selected crystallographic data for compounds 4–7

Compound	**4**	**5** · $3C_7H_8$	**6** · 2 C_7H_8	**7** · 0.5 C_6H_{14}
CCDC number	936379	936380	936381	936382
Empirical formula	$C_{51}H_{61}AlN_2P_2$	$C_{74}H_{90}Al_2N_2P_2$	$C_{65}H_{76}Al_2I_2N_2P_2$	$C_{52}H_{61}Al_2I_4N_2P_2$
Formula weight	790.94	1123.38	1254.98	1337.53
T [K]	173(2)	100(2)	123(2)	100(2)
λ [Å]	0.71073	0.71068	0.71073	0.71080
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$/n	$P2_1$/n	$P2_1$/n	$P2_1$/c
a [Å]	9.4621(19)	10.298(2)	13.6466(3)	12.920(3)
b [Å]	24.198(5)	27.243(5)	21.7276(3)	18.830(4)
c [Å]	19.854(4)	23.307(5)	20.5625(4)	22.100(4)
α [°]	90	90	90	90
β [°]	100.69(3)	100.40(3)	90.573(2)	96.39(3)
γ [°]	90	90	90	90
V [Å^3]	4467.0(15)	6431(2)	6096.6(2)	5343.2(19)
Z	4	4	4	4
ρ [Mg m^{-3}]	1.176	1.160	1.367	1.663
μ [mm^{-1}]	0.153	0.138	1.153	2.461
F(000)	1696	2416	2568	2620
Crystal size [mm^3]	0.30 × 0.12 × 0.12	0.04 × 0.03 × 0.03	0.50 × 0.45 × 0.40	0.04 × 0.03 × 0.02
Theta range [°]	3.09 to 25.99	1.16 to 27.09	1.98 to 28.00	1.42 to 27.18
Index ranges	$-11 \leq h \leq 11$, $-29 \leq k \leq 29$, $-24 \leq l \leq 24$	$-13 \leq h \leq 12$, $-28 \leq k \leq 28$, $-28 \leq l \leq 28$	$-18 \leq h \leq 18$, $-28 \leq k \leq 18$, $-27 \leq l \leq 27$	$-16 \leq h \leq 16$, $-24 \leq k \leq 24$, $-28 \leq l \leq 28$
Refl. collected	17210	91715	33728	84700
Indep. refl.	8746 [R(int) = 0.0401]	13803 [R(int) = 0.0597]	14697 [R(int) = 0.0248]	11858 [R(int) = 0.0562]
Completeness to theta max	99.8 %	99.2 % (at 25.00°)	99.9 %	99.7 %
Data/restraints/parameter	6280/0/369	13803/80/864	14697/52/735	11858/9/596
GooF	1.027	1.055	1.148	1.067
Final R indices, [I >2sigma(I)]	$R1 = 0.0454$, $wR2 = 0.1004$	$R1 = 0.0428$, $wR2 = 0.01143$	$R1 = 0.0400$, $wR2 = 0.0975$	$R1 = 0.0330$, $wR2 = 0.0832$
R indices (all data)	$R1 = 0.0788$, $wR2 = 0.1149$	$R1 = 0.0458$, $wR2 = 0.1167$	$R1 = 0.0567$, $wR2 = 0.1080$	$R1 = 0.0370$, $wR2 = 0.0853$
Largest diff. peak and hole [e · Å^{-3}]	0.331 and −0.433	0.375 and −0.582	1.931 and −1.419	0.953 and −1.593

Table 2. Selected interatomic distances [Å] and angles [°] for compounds 4–7
(av) describes an average value

	4	**5** · $3C_7H_8$	**6** · 2 C_7H_8	**7** · 0.5 C_6H_{14}
M–N/I	Al1–N1: 1.9461(18) Al1–N2: 1.9461(17)	Al1–N1: 1.9250(11) Al2–N2: 1.9095(12)	Al1–N1: 1.865(3) Al2–N2: 1.864(2) Al1–I1: 2.6115(9) Al2–I2: 2.5830(10)	Al1–N1: 1.858(3) Al2–N2: 1.854(3) Al1–I1: 2.5267(10) Al1–I2: 2.6145(11) Al2–I2: 2.6840(12) Al2–I3: 2.5067(10) Al2–I4: 2.5271(11)
M–C	Al1 · · · C1: *ca.* 3.383 Al-CH_3: 1.977 (av)	Al1–C1: 2.1565(14) Al2–C1: 2.1607(13) Al-CH_3: 1.972 (av)	Al1–C1: 2.134(3) Al2–C1: 2.126(3) Al–C50: 2.015(3)	Al1–C1: 1.942(3) Al2 · · · · C1: *ca.* 3.228
P–N	P1–N1: 1.6452(18) P2–N2: 1.6424(17)	P1–N1: 1.6323(11) P2–N2: 1.6300(11)	P1–N1: 1.640(2) P2–N2: 1.640(2)	P1–N1: 1.666(3) P2–N2: 1.670(3)
P–C	P1–C1: 1.702(2) P2–C1: 1.708(2)	P1–C1: 1.7552(13) P2–C1: 1.7399(13)	P1–C1: 1.775(3) P2–C1: 1.784(3)	P1–C1: 1.727(3) P2–C1: 1.695(3)
P–C–P	P1-C1-P2: 124.47(12)	P1-C1-P2: 126.48(7)	P1-C1-P2: 124.08(16)	P1-C1-P2: 134.01(18)
M–C–M	–	Al1-C1-Al2: 100.51(5)	Al1-C1-Al2: 100.40(12)	Al1-C1 · · · · Al2: *ca.* 87.9°

(^{Mes}nacnac = [HC(MeCNMes)$_2$])[17] at elevated temperatures also led to product mixtures and no reduced pure compound has been isolated so far.

Conclusions

We have successfully synthesised and characterised the bis(iminophosphorane)methanide aluminium complex [HLAlMe$_2$] **4** and the bis(iminophosphorane)methandiide aluminium complexes [L(AlMe$_2$)$_2$] **5**, [L(AlMeI)$_2$] **6**, and [L(AlI$_2$)$_2$] **7**, using a sterically demanding methandiide ligand. The latter two complexes were prepared in a facile manner from complex **5** and iodine. The single crystal structures of complexes **4**–**7** were determined and support largely ionic metal-ligand interactions and flexible coordination modes for the employed

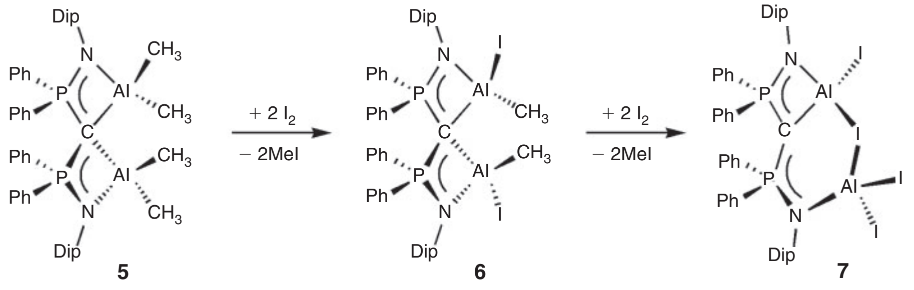

Fig. 5. Synthesis of complexes **6** and **7**.

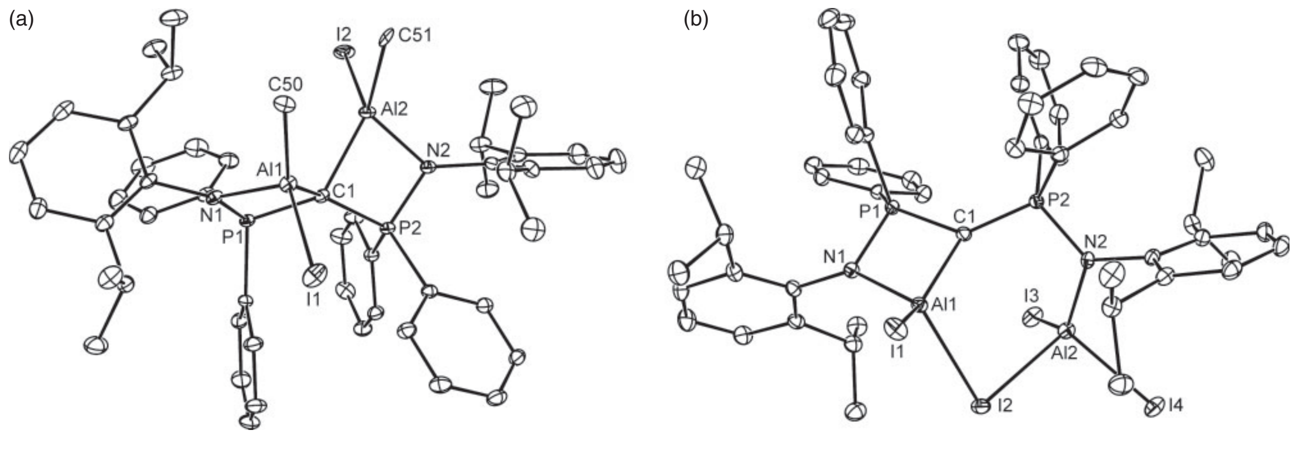

Fig. 6. Molecular structures of compounds (a) **6** · 2 C_7H_8 and (b) **7** · 0.5 C_6H_{14} (30 % thermal ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.

bis(iminophosphorane)methandiide ligand. An unusual asymmetric coordination mode of the Al atoms to the methandiide ligand in compound **7** was observed in the solid state with an almost planar, severely distorted three-coordinate methandiide carbon atom and one short Al–C interaction.

Experimental

General Considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Benzene, toluene, and hexane were dried and distilled over molten potassium. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 300 or Bruker Avance 400 spectrometer in dried and degassed deuterated benzene or toluene, were referenced to the residual ^1H or $^{13}C\{^1H\}$ resonances of the solvent used or external aqueous H_3PO_4 solutions, and were obtained at 303 K unless otherwise specified. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. H_2L **1**,[18] and $[[(^{Mes}nacnac)Mg]_2]$[17] were prepared according to literature procedures. All other reagents were used as received (Aldrich chemical company). Abbreviations: br = broad, vbr = very broad, vtr = virtual triplet, m = multiplet. Note that the P*C*P $^{13}C\{^1H\}$ resonances were not observed for compounds **5**, **6**, and **7**. The number of $^{13}C\{^1H\}$ Ar*C* resonances may be low due to overlap in broadened or multiplet resonances, or hidden by the strong residual solvent resonances.

Synthesis of [HLAlMe2] (**4**)

$AlMe_3$ (0.96 mL, 2.0 M in toluene, 1.92 mmol, 1.04 equiv.) was added to a cooled (∼ −30°C) solution of H_2L **1** (1.35 g, 1.84 mmol, 1.0 equiv.) in toluene (20 mL). The mixture was stirred at room temperature overnight and at ∼60°C for 4 h. The mixture was concentrated (to ∼8 mL) while still warm, hexane (15 mL) was added and cooled to 4°C. Precipitated product was filtered off and the supernatant solution was stored at −30°C to yield a second crop of **4** (1.18 g, 81 %); (Found: C 76.8, H 7.6, N 3.5. $C_{51}H_{61}AlN_2P_2$ requires C 77.4, H 7.8, N 3.5 %); ^1H NMR ([D$_6$]benzene, 400.2 MHz): δ 0.01 (s, 6H, AlC*H*$_3$), 0.42 (d, $J_{H\text{-}H} = 6.8$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.31 (d, $J_{H\text{-}H} = 6.8$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.37 (s, 1H, C*H*), 3.95 (sept, $J_{H\text{-}H} = 6.8$ Hz, 4H, C*H* (CH$_3$)$_2$), 6.91–7.18 (m, 18H, Ar-*H*), 7.52–7.61 (m, 8H, Ar-*H*); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 100.6 MHz): δ −3.8 (Al*C*H$_3$), 15.1 (t, $J_{C\text{-}P} = 138$ Hz, P*C*P), 23.0 (CH(*C*H$_3$)$_2$), 28.3 (CH (*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 124.9 (vtr, Ar-*C*), 125.5 (vtr, Ar-*C*), 130.7 (Ar-*C*), 133.9 (vtr, $J_{C\text{-}P} = 8.9$ Hz, Ar-*C*), 135.1 (dd, $J_{C\text{-}P} = 97.6$, 1.9 Hz, Ar-*C*), 140.2 (vtr, $J_{C\text{-}P} = 4.6$ Hz, Ar-*C*), 148.6 (vtr, $J_{C\text{-}P} = 2.7$ Hz, Ar-*C*); $^{31}P\{^1H\}$ NMR ([D$_6$]benzene, 162.0 MHz): δ 30.5 (s); ν_{max} (Nujol)/cm^{-1} 1589w, 1464s, 1433s, 1381m, 1311m, 1253m, 1236m, 1203m, 1171s, 1101s, 1051m, 1043m, 1032m, 1006m, 991s, 966s, 931m, 840m, 830m, 796s, 790s, 749m, 737m, 715m, 703s, 693s, 656s, 654s.

Synthesis of [L(AlMe2)2] (**5**)

$AlMe_3$ (1.50 mL, 2.0 M in toluene, 3.00 mmol, 2.32 equiv.) was added at room temperature to a solution of H_2L **1** (0.95 g, 1.29 mmol, 1.0 equiv.) in toluene (13 mL). The mixture was briefly stirred at room temperature and then at ∼105°C for 2 h. The mixture was concentrated (to ∼4–5 mL) while still warm and slowly cooled to −30°C to yield colourless crystals of **5** · nC_7H_8 (0.85 g, 64 %). Crystals suitable for structural determination show $n = 3$; after drying under vacuum, the solid contained $n = 2$. Mp ∼240°C softer, 245–248°C melts with foaming (Found: C 77.8, H 8.0, N 2.7. $C_{67}H_{82}Al_2N_2P_2$ requires C 78.0, H 8.0, N 2.7 %); ^{1}H NMR ([D$_6$]benzene, 400.2 MHz): δ −0.22 (br s, 6H, AlC*H*$_3$), 0.15 (br s, 6H, AlC*H*$_3$), 0.2–0.8 (vbr, 12H, CH(C*H*$_3$)$_2$), 0.9–1.5 (vbr, 12H, CH(C*H*$_3$)$_2$), 3.63 (br, 4H, C*H*(CH$_3$)$_2$), 6.45–6.79 (br m, 6H, Ar-*H*), 6.88–6.20 (br m, 16H, Ar-*H*), 7.77–7.86 (vbr, 4H, Ar-*H*); ^{1}H NMR ([D$_6$]benzene, 300.1 MHz, 343 K): δ −0.28 (br s, 6H, AlC*H*$_3$), 0.28 (s, 6H, AlC*H*$_3$), 0.85 (br, 24H, CH(C*H*$_3$)$_2$), 3.72 (sept, $J_{\text{H-H}} = 6.8$ Hz, 4H, C*H*(CH$_3$)$_2$), 6.55–6.80 (m, 6H, Ar-*H*), 6.96–7.24 (m, 16H, Ar-*H*), 7.70–8.00 (vbr, 4H, Ar-*H*); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.5 MHz, 333 K): δ −1.8 (br, Al*C*H$_3$), −0.2 (br, Al*C*H$_3$), 25.2 (vbr, CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 124.5 (br, Ar-*C*), 125.4 (vtr, $J_{\text{C-P}} = 1.5$ Hz, Ar-*C*), 130.9 (br, Ar-*C*), 131.8 (vtr, Ar-*C*), 133.6 (vtr, $J_{\text{C-P}} = 5.0$ Hz, Ar-*C*), 133.6 (vtr, $J_{\text{C-P}} = 4.6$ Hz, Ar-*C*), 138.0 (vtr, Ar-*C*), 147.7 (vtr, Ar-*C*); ^{31}P{^{1}H} NMR ([D$_6$] benzene, 162.0 MHz): δ 31.6 (s); $\nu_{\max}$ (Nujol)/cm^{-1} 1604w, 1590w, 1495m, 1463s, 1435s, 1383m, 1362m, 1318m, 1253m, 1203m, 1098s, 1049s, 976s, 838m, 796s, 729s, 719s, 694s, 666m, 648m, 597m.

*Synthesis of [L(AlMeI)$_2$] (**6**)*

A solution of I_2 (0.33 g, 1.30 mmol, 2.1 equiv.) in toluene (15 mL) was added dropwise (titration) to a cooled (0°C) solution of [L(AlMe$_2$)$_2$] **5** · 2 C_7H_8 (0.64 g, 0.620 mmol, 1.0 equiv.) in toluene (15 mL) in a way that the decolourisation of the iodine is reasonably fast at this temperature. The decolourisation slows down when ~90–95 % of the solution was added and the addition was stopped. The lightly coloured solution was briefly stirred at room temperature (resulting in complete decolourisation), concentrated to ~6 mL, and stored at 4°C to afford a first crop of colourless crystals of **6** · 2C_7H_8. Concentration of the supernatant solution to ~2 mL and cooling to −30°C afforded a second crop of **6** · 2C_7H_8 (0.40 g, 51 %). Mp 251–255°C; ^{1}H NMR ([D$_6$]benzene, 400.2 MHz): δ 0.28 (br, 6H, CH(C*H*$_3$)$_2$), 0.60 (br, 6H, CH(C*H*$_3$)$_2$), 0.62 (s, 6H, AlC*H*$_3$), 1.20 (br, 6H, CH(C*H*$_3$)$_2$), 1.55 (br, 6H, CH(C*H*$_3$)$_2$), 3.25 (br, 2H, C*H*(CH$_3$)$_2$), 4.47 (br, 2H, C*H*(CH$_3$)$_2$), 6.52–7.65 (br m, 22H, Ar-*H*), 8.02–8.18 (vbr, 4H, Ar-*H*); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.5 MHz, 333 K): δ 10.8 (br, Al*C*H$_3$), 23.4 (br, CH(*C*H$_3$)$_2$), 24.7 (br, CH(*C*H$_3$)$_2$), 27.2 (br, CH(*C*H$_3$)$_2$), 27.5 (br, CH(*C*H$_3$)$_2$), 28.6 (br, *C*H(CH$_3$)$_2$), 29.2 (br, *C*H(CH$_3$)$_2$), 125.0 (Ar-*C*), 126.6 (Ar-*C*), 127.3 (vtr, $J_{\text{C-P}} = 6.4$ Hz, Ar-*C*), 131.7 (Ar-*C*), 132.5 (Ar-*C*), 135.1 (vtr, $J_{\text{C-P}} = 5.6$ Hz, Ar-*C*), 135.8 (vtr, $J_{\text{C-P}} = 4.8$ Hz, Ar-*C*), 147.1 (m br, Ar-*C*), 148.0 (m br, Ar-*C*); ^{31}P{^{1}H} NMR ([D$_6$]benzene, 121.5 MHz): δ 40.1 (s); $\nu_{\max}$ (Nujol)/cm^{-1} 1603w, 1588w, 1494m, 1463s, 1436s, 1383m, 1365m, 1336m, 1317m, 1247m, 1232m, 1200m, 1192m, 1101s, 994s, 963s, 933m, 848s, 799s, 746m, 727s, 720s, 693s, 680m, 654m, 643m, 632m.

*Synthesis of [L(AlI$_2$)$_2$] (**7**)*

A solution of I_2 (0.58 g, 2.29 mmol, 4.71 equiv.) in toluene (30 mL) was slowly added to a cooled (0°C) solution of [L(AlMe$_2$)$_2$] **5** · 2 C_7H_8 (0.50 g, 0.485 mmol, 1.0 equiv.) in toluene (15 mL) for the first ~50 % of the I_2 solution. The mixture was allowed to warm to room temperature and the addition of the remaining I_2 solution was continued dropwise at room temperature over several hours in a way that the iodine colour of the solution is only light red. Once ~85 % of the solution was added, the mixture was stirred overnight giving a red-brown solution. The mixture was concentrated to ~4 mL, some warm hexane (20 mL) was added and the mixture was quickly filtered. Standing at room temperature afforded a crop of brown-yellow crystals of **7**.0.5 C_6H_{14}. Storing the supernatant solution at −30°C afforded a second crop (0.28 g, 43 %). Mp ~140°C softer, 150–155°C melts with gas formation; ^{1}H NMR ([D$_6$] benzene, 400.2 MHz): δ 0.34 (br, 6H, CH(C*H*$_3$)$_2$), 0.60 (br, 6H, CH(C*H*$_3$)$_2$), 1.35 (br, 6H, CH(C*H*$_3$)$_2$), 1.63 (br, 6H, CH(C*H*$_3$)$_2$), 3.38 (br, 2H, C*H*(CH$_3$)$_2$), 4.31 (br, 2H, C*H*(CH$_3$)$_2$), 6.67–7.20 (br m, 22H, Ar-*H*), 7.42–7.61 (m, 4H, Ar-*H*); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 75.5 MHz, 298 K): δ 23.1 (br, CH(*C*H$_3$)$_2$), 25.6 (br, CH(*C*H$_3$)$_2$), 26.8 (br, CH(*C*H$_3$)$_2$), 28.8 (br and sharp, CH(*C*H$_3$)$_2$, *C*H(CH$_3$)$_2$), 29.7 (br, *C*H(CH$_3$)$_2$), 125.0 (vbr, Ar-*C*), 127.2 (vtr, br, $J_{\text{C-P}} \approx 6.0$ Hz, Ar-*C*), 127.6 (vtr, $J_{\text{C-P}} = 6.0$ Hz, Ar-*C*), 131.4 (Ar-*C*), 131.7 (Ar-*C*), 134.2 (vtr, $J_{\text{C-P}} = 5.4$ Hz, Ar-*C*), 135.2 (vtr, $J_{\text{C-P}} = 4.7$ Hz, Ar-*C*), 147.7 (m br, Ar-*C*), 149.0 (m br, Ar-*C*); ^{31}P{^{1}H} NMR ([D$_6$]benzene, 121.5 MHz): δ 32.9 (s); $\nu_{\max}$ (Nujol)/cm^{-1} 1589w, 1459s, 1435s, 1381m, 1378m, 1364m, 1315m, 1308m, 1253m, 1144s, 1100s, 1042m, 946m, 925s, 885m, 868m, 839s, 800s, 771m, 745m, 716s, 693m, 616m.

X-Ray Crystallography

Suitable crystals were mounted in silicone oil and were either measured using a Nonius Kappa CCD diffractometer (**4**), an Oxford Xcalibur Gemini Ultra diffractometer (**6** · 2 C_7H_8) with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), or at the MX1 beamline at the Australian Synchrotron (**5** · 3 C_7H_8, **7** · 0.5 C_6H_{14}) with synchrotron radiation with a wavelength close to Mo$_{K\alpha}$ radiation. All structures were refined using *SHELX*.[19] All non-hydrogen atoms were refined anisotropically. Semi-empirical (multi-scan) absorption corrections were performed on all datasets. Two of the three toluene molecules are disordered in the structure of **5** · 3 C_7H_8, and were modelled with two positions for each carbon atom (75 % and 25 % occupancy) using geometry restraints. One of the two toluene molecules in the structure of **6** · 2 C_7H_8 is disordered and was modelled with two positions for each carbon atom (55 % and 45 % occupancy) using geometry restraints. C51 shows an asymmetric thermal ellipsoid and some residual electron density peaks are near this atom. The spectroscopic data of this sample fully support the formulation as a methyl group. In the structure of **7** · 0.5 C_6H_{14}, half a molecule of *n*-hexane is disordered in the asymmetric unit and was modelled using geometry restraints. Refinement details are summarised in Table 1 and further information can be found in the crystallographic information files. CCDC 936379 – 936382 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

A.S. is grateful to the Australian Research Council for support and a fellowship. C.P.S. thanks the DAAD for RISE program funding. The Monash University Research Accelerator Program is highly acknowledged. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, Victoria, Australia.

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