

Group 1 and 13 complexes of aryl-substituted bis(phosphinimino)methyls

Michael S. Hill ^{a,*}, Peter B. Hitchcock ^b, Sophia M.A. Karagouni ^b

^a Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, UK

^b School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, UK

Received 14 October 2003; accepted 19 November 2003

Abstract

The organolithium reagent $[\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{Li}(\text{OEt}_2)]$ was easily obtained by deprotonation of $\text{H}_2\text{C}(\text{Ph}_2\text{P}=\text{NC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2$ with $n\text{BuLi}$ in diethyl ether solution. The crystal structure of $[\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{Li}(\text{OEt}_2)]$ has been determined and shown to consist a monomeric chelate structure that contains a distorted, trigonal planar lithium centre. The ligand precursor has also been deprotonated with both Me_3Al and Me_2AlCl to yield the tetrahedral organoaluminium complexes, $[\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{AlMe}_2]$ and $[\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{Al}(\text{Cl})\text{Me}]$. Reaction of $[\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{Li}(\text{OEt}_2)]$ with either AlX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) or GaCl_3 yielded a series of dihalo derivatives $[\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{MX}_2]$ all of which have been shown to exist as similar monomeric species containing four-coordinate group 13 centres.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Bis(phosphinimino)methyl; Group 13; X-ray structures

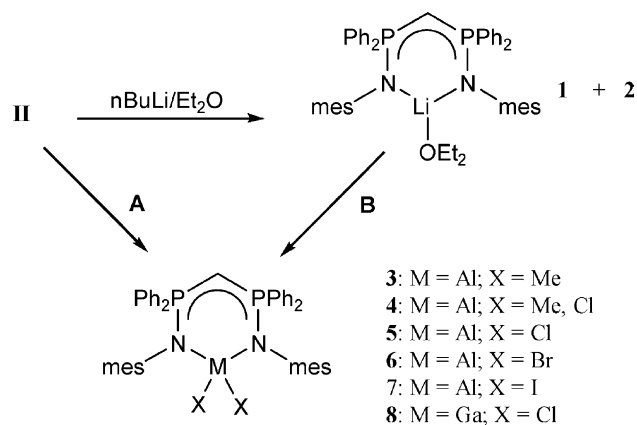
1. Introduction

We have recently initiated a program of research that aims to apply bulky and kinetically stabilising ligand systems to the study of low-coordinate metal centres [1,2]. A review of the recent literature revealed a widespread use of chelating, anionic ligands derived by deprotonation of bulky aryl-substituted β -aminoimines such as **I** and related ligands bearing other flanking N-substituents, which have the potential for precise steric and electronic ‘tuning’ of a reactive metal site. Ligands of this type have been used to support a variety of low-coordinate transition metal [3–13], main group element [14–20] and f-element complexes [21,22]. Furthermore, many of these systems have shown great utility in, for example, ring opening polymerisation catalysis [23–26] or as synthetic mimics for low-coordinate metal environments encountered in biological systems [27–30].

We were struck by the close resemblance, in both steric demands and denticity, between the aryl-substituted bis(phosphinimino)methanes, **II** and **III** [31], and ligands of type **I**. The trimethylsilyl-substituted bis(phosphinimino)methane, **IV**, has been the subject of a number of recent publications [32–38], most notably in its doubly deprotonated form for the synthesis of ‘pincer’ carbene complexes of the group 4 elements [39]. Use of the N-aryl substituted variants **II** and **III** however is restricted to a single account of their application as ancillary ligands for Co(II)- and Ni(II)-based olefin polymerisation catalysts [31] and our recent reports of their application in the support of three-coordinate mid and late first row (Mn–Zn) transition metal amides and alkoxides [1]. A number of group 13 derivatives of **I** and **IV** which include, as yet unique, examples of two-coordinate Al(I) and Ga(I), have also recently been described [40–42], while cationic aluminium alkyl complexes supported by **IV** have been identified as transition metal-free ethylene polymerisation catalysts [43]. We now wish to report our syntheses of a range of group 13 complexes derived from **II** (Scheme 1). This study allows detailed structural comparisons to be made with related

* Corresponding author. Tel.: +44-207-594-5709; fax: +44-207-594-5804.

E-mail address: mike.hill@imperial.ac.uk (M.S. Hill).



Scheme 1. Reagents: *Path A*; **3**, Me₃Al; **4** Me₂AlCl; *Path B*; **5** AlCl₃; **6** AlBr₃; **7** AlI₃; **8** GaCl₃.

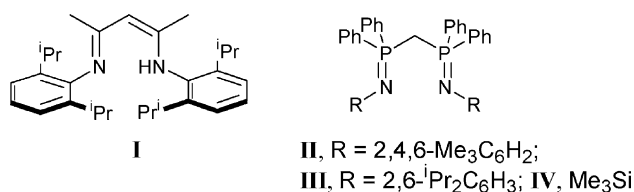


Fig. 1, II, III and IV.

derivatives and a further evaluation of the ligating behaviour of **II** toward electropositive metal centres (Figs. I, II, III and IV).

2. Results and discussion

The N-mesityl-substituted bis(diphenylphosphinimino)methane **II** (mesityl = 2,4,6-trimethylphenyl) was synthesised according to the literature method [31]. Crystallisation from diethyl ether resulted in colourless crystals which were subjected to an X-ray diffraction analysis. The molecular structure of **II** along with the numbering scheme used is illustrated in Fig. 1; selected bond lengths and angles are given in Table 1 and details of the X-ray analysis are given in Table 2. The structure is unremarkable and the observed P–N and P–C bond distances are comparable to values determined in other structurally characterised phosphiniminoethanes and bis(phosphinimino)methanes [1a,44].

Treatment of **II** with nBuLi in diethyl ether and crystallisation from a diethyl ether/hexane solvent system (≈10:1) at –30°C resulted in the isolation of **1** as large colourless block crystals suitable for X-ray diffraction analysis. The molecular structure of **1** along with the numbering scheme used is illustrated in Fig. 2. Selected bond lengths and angles are given in Table 1 and details of the X-ray analysis are given in Table 2. **1** is a monomeric lithium derivative of **II** in which the lithium centre is three-coordinate. This comprises a six-

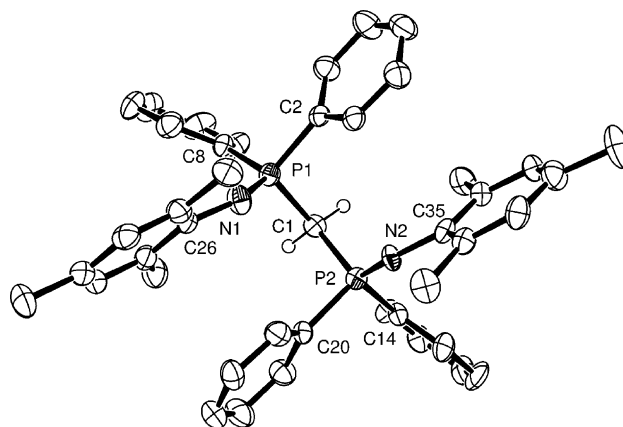


Fig. 1. The molecular structure of **II** (only hydrogen atoms attached to C(1) illustrated for clarity). 50% probability ellipsoids.

Table 1
Selected bond lengths (Å) and angles (°) for compounds **II**, **1**, and **2**

| | II | 1 | 2 |
|----------------|-----------|------------|--|
| M–N(1) | | 1.952(5) | 1.953(7) ^a 2.036(7) ^b |
| M–N(2) | | 1.979(4) | 1.941(6) ^c 2.061(6) ^d |
| M–Cl/N(3)/O | | 1.965(5) | 2.521(6) ^e |
| P(1)–N(1) | 1.518(4) | 1.597(2) | 1.598(3) |
| P(2)–N(2) | 1.534(4) | 1.585(2) | 1.593(3) |
| P(1)–C(1) | 1.842(5) | 1.725(2) | 1.740(3) 1.702(3) ^f |
| P(2)–C(1) | 1.837(5) | 1.713(2) | 1.731(3) 1.763(3) ^g |
| N(1)–M–O/Cl/I | | 122.9(2) | 166.3(4) ^h |
| N(2)–M–O/Cl/I | | 122.1(2) | 134.0(3) ⁱ |
| N(1)–M–N(2) | | 114.9(2) | 76.2(2) ^j 115.5(3) ^k |
| M–N(1)–P(1) | | 111.72(17) | 97.1(2) ^l |
| M–N(2)–P(2) | | 110.69(17) | 102.5(2) ^m |
| N(1)–P(1)–C(1) | 114.3(2) | 112.90(12) | 106.90(15) 107.84(15) ⁿ |
| N(2)–P(2)–C(1) | 119.0(2) | 111.51(12) | 106.12(14) |
| P(1)–C(1)–P(2) | 115.8(2) | 134.58(16) | 130.74(19) 118.71(19) ^o |

^a Li(1)–N(1).

^b Li(1)–N(3).

^c Li(2)–N(2).

^d Li(2)–N(3).

^e Li(2)–P(4).

^f P(3)–C(44).

^g P(4)–C(44).

^h N(1)–Li(1)–N(3).

ⁱ N(2)–Li(2)–N(3).

^j N(1)–Li(1)–C(1).

^k N(3)–Li(1)–C(1).

^l Li(1)–N(1)–P(1).

^m Li(1)–N(3)–P(3).

ⁿ N(3)–P(3)–C(44).

^o P(3)–C(44)–P(4).

membered metallocyclic structure in which the bis (phosphinimino)methyl ligand behaves as a strictly bidentate chelate and the lithium coordination is completed

Table 2

Selected crystallographic and data collection parameters for compounds **II**, **1**, **2**, **3** and **4**

| | II | 1 | 2 | 3 | 4 |
|---|---|--|--|---|---|
| Chemical formula | C ₄₃ H ₄₄ N ₂ P ₂ | C ₄₇ H ₅₃ LiN ₂ OP ₂ | C ₇₇ H ₇₅ Li ₂ N ₃ P ₄ · 0.5 (C ₆ H ₁₄) | C ₄₅ H ₄₉ AlN ₂ P ₂ · 1.5 (C ₇ H ₈) | C ₄₄ H ₄₆ AlClN ₂ P ₂ · 2 (C ₇ H ₈) |
| Formula weight | 650.74 | 730.79 | 1223.25 | 844.98 | 911.47 |
| <i>T</i> (K) | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| Crystal size (mm ³) | 0.10 × 0.10 × 0.02 | 0.40 × 0.40 × 0.30 | 0.40 × 0.30 × 0.30 | 0.30 × 0.20 × 0.20 | 0.30 × 0.30 × 0.20 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> (No.14) | <i>P</i> 1̄ (No. 2) | <i>P</i> 2 ₁ / <i>n</i> (No.14) | <i>P</i> 1̄ (No. 2) | <i>P</i> 1̄ (No. 2) |
| <i>a</i> (Å) | 11.2554(16) | 10.5227(5) | 11.9297(3) | 12.4197(8) | 12.2018(2) |
| <i>b</i> (Å) | 23.545(5) | 11.2575(6) | 24.1662(7) | 12.8777(8) | 15.1001(3) |
| <i>c</i> (Å) | 13.5408(14) | 18.5988(10) | 24.0715(7) | 16.3104(11) | 15.7376(4) |
| <i>α</i> (deg) | 90 | 86.539(3) | 90 | 92.107(2) | 110.008(1) |
| <i>β</i> (deg) | 87.871(9) | 81.331(3) | 91.497(2) | 108.078(3) | 93.998(1) |
| <i>γ</i> (deg) | 90 | 70.183(3) | 90 | 101.181(4) | 109.626(1) |
| <i>Z</i> | 4 | 2 | 4 | 2 | 2 |
| <i>V</i> (Å ³) | 3586.0(10) | 2049.0(2) | 6937.3(3) | 2419.6(3) | 2509.86(9) |
| <i>d</i> _c (Mg m ⁻³) | 1.21 | 1.19 | 1.17 | 1.16 | 1.21 |
| <i>μ</i> (mm ⁻¹) | 0.15 | 0.14 | 0.15 | 0.15 | 0.20 |
| <i>θ</i> range (deg) | 4.16–21.97 | 3.71–21.96 | 3.77–23.00 | 3.78–23.02 | 3.76–24.84 |
| <i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] | 0.066, 0.117 | 0.045, 0.109 | 0.056, 0.133 | 0.095, 0.241 | 0.065, 0.161 |
| <i>R</i> ₁ ; <i>wR</i> ₂ all data | 0.124, 0.135 | 0.055, 0.116 | 0.079, 0.147 | 0.118, 0.258 | 0.088, 0.174 |
| Measured/independent | 13,185/4338/ | 9581/4833/ | 29,125/9563/ | 15,200/6309/ | 26,622/8576/ |
| Reflections/ <i>R</i> _{int} | 0.123 | 0.049 | 0.060 | 0.091 | 0.056 |
| Reflections with <i>I</i> > 2σ(<i>I</i>) | 2759 | 4142 | 7282 | 5010 | 6613 |

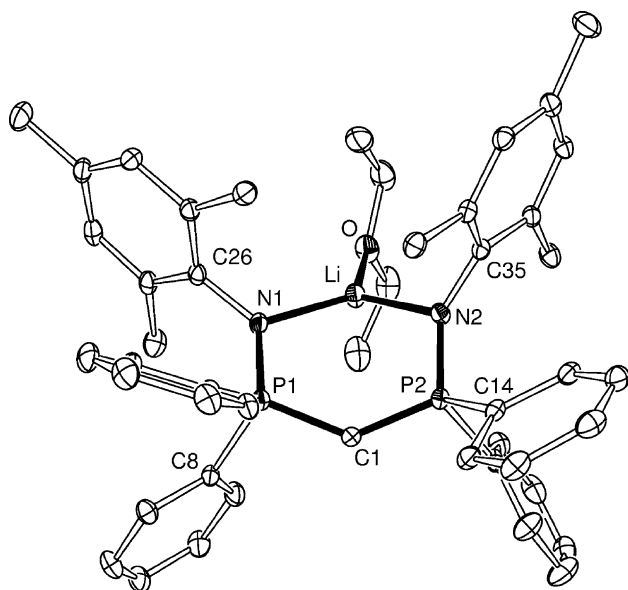


Fig. 2. The molecular structure of **1** (hydrogen atoms removed for clarity). 20% probability ellipsoids.

by a single molecule of diethyl ether. Although the chelated ligand adopts a boat conformation, the distance between the carbanionic methine carbon C(1) and the lithium centre is too long (2.999 Å to suggest any significant interaction. This is in contrast to our observations of similar three-coordinate derivatives of the later first row (Mn–Zn) transition elements where M–C(1) distances <2.4 Å have been observed [1]. As indi-

cated by the sum of angles subtended by the bonds around lithium [$\Sigma_{\text{angles}} = 359.9(2)^\circ$], the lithium coordination geometry is effectively trigonal planar and only slightly distorted by the ‘bite’ of the chelated ligand [N(1)–Li–N(2) = 14.9(2) $^\circ$]. The Li–N and Li–O bond lengths are within the range of those previously observed for three-coordinate lithium bound to amide and ether ligands and are similar to those reported for chelated β -diketiminato derivatives [14]. This latter observation illustrates the similar donation of charge that results from the two ligand types. The P–N and P–C bond lengths indicate considerable charge delocalisation around the chelate structure; the P–C(1) bonds are shortened in comparison to those of **II** while the P–N bonds are elongated.

The preparation of **1** was repeated on several occasions during the course of this study. Although yields were consistently high, in one instance, a small number of colourless crystals with a different needle-like morphology were observed to have formed along with the bulk product. Although a pure bulk sample could not be isolated for complete analytical and NMR spectroscopic characterisation, a further X-ray analysis revealed them to be the dimeric lithium derivative **2**. The structure of compound **2** is illustrated in Fig. 3, while selected bond lengths and angles are given in Table 1 and details of the X-ray analysis are given in Table 2. **2** consists of a deprotonated molecule of **II** which has co-aggregated along with the lithium derivative of the mixed P(III)/P(V) methane derivative **V**. We have previously reported **V** as an intermediate in the synthesis of an asymmetrically

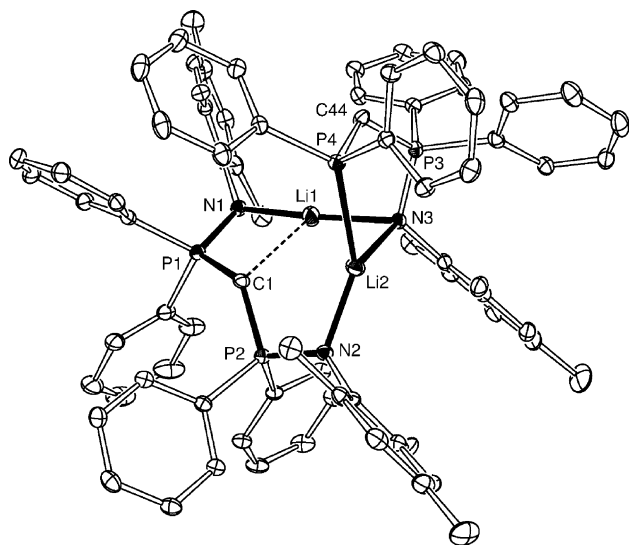


Fig. 3. The molecular structure of **2** (hydrogen atoms removed for clarity). 20% probability ellipsoids.

substituted bis(phosphinimino)methane [1], while several examples of (phosphinimino)methyl phosphines have been reported in the literature [45]. On this occasion we reason that a small contaminating quantity of **V** was present in our sample of **II** and that the deprotonated **V** forms **2** when crystallised in the presence of **1**. The dinuclear molecule contains two three-coordinate lithium ions. Li(1) is coordinated by the N(1) centre of the deprotonated bis(phosphinimino)methyl ligand and N(3) of the phosphinimino arm of the P(III)/P(V) fragment, subtending a N–Li–N angle of 166.3(4)°. This deviation from linearity is due to an additional Li(1)–C(1) interaction of 2.362(7) Å. There are no short contacts (<3 Å to the P(III)/P(V)-bridging C(44) methyl centre. Li(2) bridges the N(2) and N(3) positions of the two ligand moieties and is further ligated by the trivalent P(4) centre to form a five-membered metallocyclic P–C–P–N–Li chelate. The Li–N distances, while all falling within the normal range observed for lithium amides and lithium iminophosphoranes, reflect the differing coordination numbers of the nitrogen centres [46], as does the P(3)–N(3) bond length [1.635(3) Å] in comparison to the P(1)–N(1) [1.598(3) Å] and P(2)–N(2) [1.593(3) Å] distances. The Li(2)–P(4) distance of 2.521(6) Å is typical of Li–P interactions observed in other phosphorus-substituted methyl anions such as [Li(thf)C(SiMe₃)₂{SiMe₂CH [Li(thf)₂]PPh₂}] [2.517(8) Å] [47] and [LiC(SiMe₃)₂ PMe₂]₂ [2.519(4) Å] [48] (Fig. V).

Reaction of **II** with either Me₃Al or Me₂AlCl in toluene also resulted in deprotonation of the ligand and resulted in high yielding syntheses of the organoaluminium compounds **3** and **4** respectively. In both cases ³¹P NMR spectra of the final reaction mixtures demonstrated that quantitative consumption of **II** had occurred, presenting sharp singlets at 30.3 and 31.9 ppm

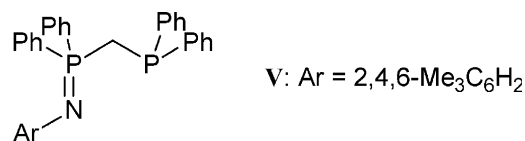


Fig. V.

respectively. X-ray crystallographic analyses were undertaken upon crystals of both compounds grown from toluene solution. Details of both analyses are given in Table 2. Crystals of the dimethylaluminium derivative **3** diffracted only weakly at higher angle resulting in high final *R* indices. The X-ray analysis of **4**, although resulting in acceptable residuals after refinement, was hampered by disorder of the chlorine and methyl groups with relative occupancy 0.71:0.29. Although detailed discussion of bond lengths and angles are not justifiable, the structures are unambiguous. Like the previously reported [HC(Ph₂PNSiMe₃)₂]AlMe₂ [49], both structures are monomers in which the phosphinimino units of the anionic ligands chelate to the four-coordinate aluminium centres to form a six-membered N–P–C–P–N–Al metallocyclic ring. Each ring adopts a distorted boat conformation, although the Al–C(1) distances are too long [**3**: 3.36; **4**: 3.24 Å] to formulate either structure as containing direct Al–C(1) bonds which would effectively raise the coordination number of each Al centre to five.

A wide range of unusual cationic and low valent group 13 complexes have been reported which employ a β-diketiminato ligand as a sterically demanding and solubilising reaction platform [40–42,50–55]. Many of these interesting species employ dihalo-aluminium or gallium compounds as starting materials [50,56]. We therefore undertook the synthesis of analogous compounds derived from **II** through metathesis of **1** and the appropriate aluminium or gallium trihalide in diethyl ether solution. Compounds **5–8**, of the general form [HC(Ph₂PNC₆H₂Me₃-2,4,6)₂]MX₂ (**5**: M = Al, X = Cl; **6**: M = Al, X = Br; **7**: M = Al, X = I; **8**: M = Ga, X = Cl) were synthesised straightforwardly in this manner and obtained as colourless crystalline solids in high yield after crystallisation from diethyl ether solution at low temperature. In contrast to the methyl substituted organoaluminium compounds **3** and **4**, each of the dihalo derivatives displayed only limited solubility in toluene or benzene precluding collection of ¹H, ¹³C and ³¹P NMR data in these solvents. This necessitated the use of more polar *d*₈-THF for the collection of quality solution-state data which were consistent with time averaged C_{2v}-symmetric structures.

Crystals suitable for X-ray crystallographic analyses of all four dihalo complexes were isolated from concentrated diethyl ether solution. Selected bond lengths and angles are presented in Table 3 and crystal data are summarised in Table 4. While only compounds **5** and **6** are crystallographically isostructural, all four

Table 3
Selected bond lengths (Å) and angles (°) for compounds **5**, **6**, **7** and **8**

| | 5 | 6 | 7 | 8 |
|-------------------------|------------|------------|------------|------------|
| M–N(1) | 1.873(2) | 1.880(3) | 1.865(5) | 1.915(3) |
| M–N(2) | 1.881(2) | 1.868(3) | 1.867(5) | 1.914(3) |
| M–Cl/Br/I(1) | 2.1602(9) | 1.327(1) | 2.599(2) | 2.199(1) |
| M–Cl/Br/I(2) | 2.1369(9) | 2.297(1) | 2.531(2) | 2.169(1) |
| P(1)–N(1) | 1.650(2) | 1.648(3) | 1.648(5) | 1.642(3) |
| P(2)–N(2) | 1.647(2) | 1.649(3) | 1.651(5) | 1.642(3) |
| P(1)–C(1) | 1.711(2) | 1.701(3) | 1.713(5) | 1.710(4) |
| P(2)–C(1) | 1.700(2) | 1.713(3) | 1.707(5) | 1.700(4) |
| N(1)–M–Cl/Br/I(1) | 109.69(6) | 112.38(9) | 110.77(15) | 111.70(9) |
| N(2)–M–Cl/Br/I(2) | 106.64(6) | 108.73(9) | 107.92(16) | 107.11(9) |
| Cl/Br/I(1)–M–Cl/Br/I(2) | 106.46(4) | 104.2(4) | 103.78(6) | 105.91(4) |
| N(1)–M–N(2) | 113.01(8) | 113.90(13) | 111.8(2) | 111.21(13) |
| M–N(1)–P(1) | 116.98(10) | 117.15(15) | 119.2(3) | 118.91(17) |
| M–N(2)–P(2) | 117.91(10) | 116.26(15) | 119.4(3) | 118.53(17) |
| N(1)–P(1)–C(1) | 109.45(10) | 106.77(15) | 109.5(3) | 109.59(18) |
| N(2)–P(2)–C(1) | 107.14(10) | 108.97(15) | 108.7(3) | 109.48(17) |
| P(1)–C(1)–P(2) | 134.83(14) | 134.9(2) | 136.2(3) | 136.9(2) |

Table 4
Selected crystallographic and data collection parameters for compounds **5**, **6**, **7** and **8**

| | 5 | 6 | 7 | 8 |
|--|--|--|--|---|
| Chemical formula | C ₄₅ H ₄₃ AlCl ₂ N ₂ P ₂ · (C ₄ H ₁₀ O) | C ₄₃ H ₄₃ AlBr ₂ N ₂ P ₂ · (C ₄ H ₁₀ O) | C ₄₅ H ₄₃ AlI ₂ N ₂ P ₂ · 2(C ₄ H ₁₀ O) | C ₄₃ H ₄₃ Cl ₂ GaN ₂ P ₂ |
| Formula weight | 821.73 | 910.65 | 1078.75 | 790.35 |
| <i>T</i> (K) | 173(2) | 173(2) | 173(2) | 173(2) |
| Crystal size (mm ³) | 0.40 × 0.40 × 0.40 | 0.40 × 0.40 × 0.35 | 0.10 × 0.10 × 0.10 | 0.20 × 0.20 × 0.05 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>P</i> 2 ₁ / <i>c</i> (No.14) | <i>P</i> na2 ₁ (No. 33) | <i>P</i> 2 ₁ / <i>c</i> (No.14) |
| <i>a</i> (Å) | 12.0797(5) | 12.0912(2) | 30.8796(9) | 19.9063(7) |
| <i>b</i> (Å) | 19.2571(9) | 19.3900(4) | 15.8994(5) | 11.7084(7) |
| <i>c</i> (Å) | 19.0409(5) | 19.2706(3) | 10.2388(2) | 17.7565(10) |
| α (deg) | 90 | 90 | 90 | 90 |
| β (deg) | 100.329(2) | 99.288(1) | 90 | 109.871(3) |
| γ (deg) | 90 | 90 | 90 | 90 |
| <i>Z</i> | 4 | 4 | 4 | 4 |
| <i>V</i> (Å ³) | 4357.5(3) | 4458.7(1) | 5026.9(2) | 3892.1(3) |
| <i>d</i> _c (Mg m ⁻³) | 1.25 | 1.36 | 1.43 | 1.35 |
| μ (mm ⁻¹) | 0.28 | 1.95 | 1.37 | 0.96 |
| θ range (deg) | 3.72–25.02 | 3.73–25.68 | 3.80–25.04 | 3.73–23.03 |
| <i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] | 0.044, 0.106 | 0.048, 0.082 | 0.042, 0.079 | 0.047, 0.093 |
| <i>R</i> ₁ ; <i>wR</i> ₂ all data | 0.057, 0.114 | 0.077, 0.091 | 0.058, 0.085 | 0.066, 0.103 |
| Measured/independent | 16,777/7241/ | 35,556/7852/ | 19,788/8265/ | 15,136/5387/ |
| Reflections/ <i>R</i> _{int} | 0.046 | 0.061 | 0.055 | 0.064 |
| Reflections with <i>I</i> > 2 σ <i>I</i> | 5955 | 5925 | 6829 | 4185 |

compounds display similar features and only the structures of the diidoaluminium derivative **7** and the dichlorogallium derivative **8** are illustrated in Figs. 4 and 5. All four complexes adopt monomeric distorted tetrahedral structures with chelating bis(phosphinimino) methyl ligands. The N–M–N bite angles show little variation with changing metal or halide identity and range from 111.21(13)° in **8** to 113.9(13)° in **6**. These values are somewhat higher than those observed in related β -diketiminato derivatives such as the dichloroaluminium derivative of **I** [99.36(4)°] [56]. We have previously made similar observations with regard to

three-coordinate mid and late transition metal derivatives of **II** [1]. Despite this feature, both the M–N and M–X bond lengths of compounds **5–8** are very similar to those observed in analogous diketiminato derivatives indicating that charge donation from the deprotonated **II** is similar to that of the β -diketiminato ligand. The increased bite angle provided by the bis(phosphinimino)methyl ligand also results in a compression of the X–M–X bond angles by some 4–5° in comparison to similar β -diketiminato derivatives [50,56]. We have previously noted that three-coordinate metallated derivatives of **II** display close C(1)–M contacts. These result in

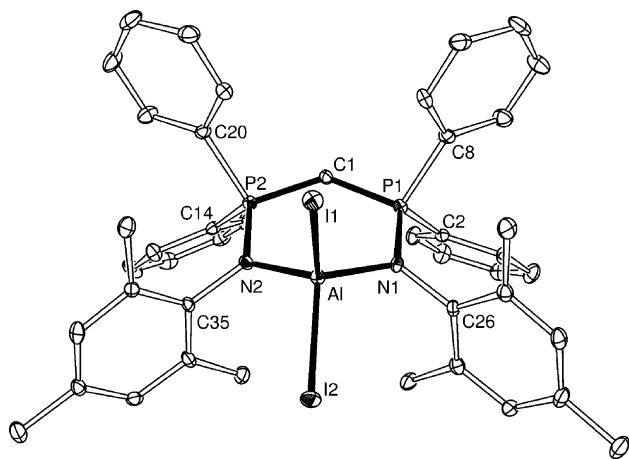


Fig. 4. The molecular structure of **7** (hydrogen atoms removed for clarity). 20% probability ellipsoids.

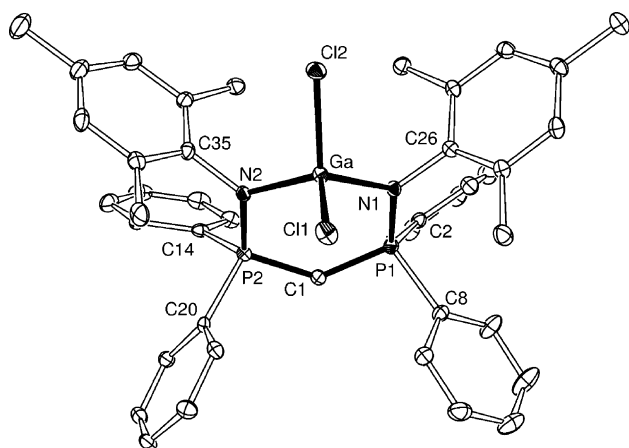


Fig. 5. The molecular structure of **8** (hydrogen atoms removed for clarity). 20% probability ellipsoids.

the adoption of a pronounced boat conformation of the chelating ligand but without major disruption of the overall metal coordination geometry [1]. As was the case for the methylaluminium derivatives **3** and **4**, the four coordinate dihalo derivatives **5–8** display no M–C(1) interactions $<3 \text{ \AA}$.

We are continuing to explore the reactivity of these compounds, particularly as synthons en route to cationic alkoxy and amido derivatives for application in the ring opening polymerisation of cyclic ethers and esters [1a].

3. Experimental section

3.1. General considerations

All reactions were conducted under an atmosphere of dry argon and manipulated either on a double manifold vacuum line or in a dinitrogen-filled drybox operating at

less than 1 ppm of O_2 . Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, diethyl ether from Na/benzophenone and hexane from Na/K alloy). NMR spectra were recorded at 300.13 (^1H), 125.8 (^{13}C), 194.5 (^7Li) and 121.5 MHz (^{31}P) from samples in C_6D_6 at 25 °C unless otherwise stated. Chemical shifts are relative to SiMe_4 for ^1H and ^{13}C NMR. ^{31}P and ^7Li NMR spectra were referenced externally to aqueous H_3PO_4 and LiCl respectively. Mass spectra were obtained at 70 eV. Mesityl azide and **II**, were synthesised in high yield by established literature procedures [31,57]. A sample of **II** suitable for a single crystal X-ray diffraction analysis was isolated from a concentrated diethyl ether solution at 5 °C.

3.2. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2\}\text{Li}(\text{OEt}_2)\}$ (**1**)]

$n\text{BuLi}$ (0.62 ml of a 2.5 M solution in hexane) was added at room temperature to a stirred solution of **II** (1.0 g, 1.54 mmol) in diethyl ether (30 ml). This resulted in gas evolution and the formation of a pale yellow solution that was stirred for a further 1 h. At this point the solution was concentrated to about 10 ml and then cooled to $-30 \text{ }^\circ\text{C}$. Storage at this temperature for one week produced **1** as colourless block crystals suitable for an X-ray diffraction analysis (0.99 g, 88%). In an analogous preparation, **2** was identified as a minor product by its contrasting morphology as colourless needles. A single crystal was mechanically separated and used in a further X-ray diffraction study. Analytical and spectroscopic data for **1**. Anal. Calc. for $\text{C}_{47}\text{H}_{53}\text{LiN}_2\text{OP}_2$: C, 77.24; H, 7.32; N, 3.83. Found: C, 77.35; H, 7.22; N, 3.85. ^1H NMR: δ 1.13 (t, 6H, Et_2O), 1.27 (t, 1H, P_2CH , $^2J_{\text{PH}} = 4.2 \text{ Hz}$), 1.84 (s, 12H, $o\text{-CH}_3$), 2.10 (s, 6H, $p\text{-CH}_3$), 3.34 (q, 4H, Et_2O), 6.56 (s, 4H, mesityl), 7.19 (m, 12H, $m, p\text{-PhP}$), 7.70 (m, 8H, $o\text{-PhP}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 15.7 ($p\text{-CH}_3$), 18.9 (t, $^1J_{\text{PC}} = 150.1 \text{ Hz}$, PCH), 20.8 (Et_2O), 21.4 ($o\text{-CH}_3$), 66.3 (Et_2O), 127.8 (dd, $^2J_{\text{PC}} = 9.4 \text{ Hz}$, $o\text{-Ph}$), 129.5 ($p\text{-Ph}$), 132.9 (dd, $^3J_{\text{PC}} = 9.4 \text{ Hz}$, $m\text{-Ph}$), 134.8, 140.6, 141.8, 144.6, 147.9. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 14.1. ^7Li NMR: δ -0.52.

3.3. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2\}\text{AlMe}_2\}$ (**3**)]

A solution of trimethylaluminium (2.0 M in hexanes, 2.3 ml, 4.6 mmol) was added to **II** (3.00 g, 4.6 mmol) in toluene (30 ml) and the mixture was stirred at room temperature overnight. Concentration and cooling (5 °C) of this solution afforded **3** as colourless crystals. Reproducible CHN combustion analysis for this compound could not be obtained due to varying amounts of toluene solvate. Yield: 2.57 g, 80%. ^1H NMR: δ -0.25 (s, 6H, Me-Al), 1.80 (s, 12H, $o\text{-CH}_3$), 2.08 (s, 6H, $p\text{-CH}_3$), 6.69 (s, 4H, mesityl), 7.05 (m, 12H, $m, p\text{-PhP}$), 7.79 (m, 8H, $o\text{-PhP}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 2.1 ($\text{CH}_3\text{-Al}$), 20.08

(*p*-Me), 21.3 (*o*-Me), 21.8 (t, $^1J_{\text{PC}} = 150.1$ Hz, CHP), 125.2 (Ar), 128.4 (Ar), 130.2 (Ar), 134.6 (Ar), 136.5 (Ar), 140.2 (Ar). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 30.3. M.S. m/z : 691 [45%, M^+], 335 [20%, $\text{Ph}_2\text{PCH}_2\text{NMe}_3\text{H}$], 91 [100%, NPh].

3.4. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{Al}(\text{Cl})\text{Me}$] (**4**)

A solution of Me_2AlCl (1.0 M in hexanes, 4.6 ml, 4.6 mmol) was added to **II** (3.00 g, 4.6 mmol) in toluene (30 ml) and the mixture was stirred at room temperature overnight. Concentration and cooling (5 °C) afforded **4** as colourless crystals. Yield: 2.02 g, 60%. Anal. Calc. for $\text{C}_{44}\text{H}_{46}\text{AlClN}_2\text{P}_2 \cdot 2(\text{C}_7\text{H}_8)$: C, 76.42; H, 6.80; N 3.09. Found: C, 76.01; H, 6.51; N, 3.08. ^1H NMR: δ -0.50 (s, 3H, Me-Al), 1.84 (s, 12H, *o*-CH₃), 2.021 (s, 6H, *p*-CH₃), 2.30 (s, 1H, PCHP) 6.60 (s, 4H, mesityl), 7.40 (m, 12H, *m*, *p*-PhP), 7.90 (m, 8H, *o*-PhP). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 1.4 (CH₃-Al), 20.7 (*p*-Me), 20.9 (*o*-Me), 21.3 (CHP), 125.6 (Ar), 127.4 (Ar), 128.2 (Ar), 130.9 (Ar), 133.4 (Ar), 135.9 (Ar), 140.00 (Ar). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 31.9. M.S. m/z : 711 [100%, $\text{HC}(\text{Ph}_2\text{PNMe}_3)_2\text{AlCl}$], 594 [75%, $\text{HC}(\text{Ph}_2\text{PNMe}_3)_2\text{AlClH}_2$], 183 [45%].

3.5. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{AlCl}_2$] (**5**)

A solution of **1** (1.08 mmol) in Et₂O (20 ml) was added to a stirred suspension of AlCl₃ (0.14 g, 1.08 mmol) in Et₂O (20 ml) at -78 °C. This was allowed to warm to room temperature to produce a pale yellow solution and a colourless precipitate. Filtration and concentration to ≈ 10 ml produced **5** as an Et₂O solvate in the form of pale yellow needles (0.64 g, 80 %). Anal. Calc. for $\text{C}_{47}\text{H}_{53}\text{N}_2\text{AlOP}_2$: C, 68.69; H, 6.45; N, 3.41. Found: C, 68.61; H, 6.57; N, 3.38. ^1H NMR (*d*₈-THF, 25 °C): δ 1.12 (t, 6H, Et₂O), 1.85 (s, 12H, *o*-CH₃), 2.16 (s, 6H, *p*-CH₃), 3.37 (q, 4H, Et₂O), 6.64 (s, 4H, mesityl), 7.38 (m, 12H, *m*, *p*-PhP), 7.85 (m, 8H, *o*-PhP). $^{13}\text{C}\{^1\text{H}\}$ NMR (*d*₈-THF, 25 °C): δ 12.0 (t, $^1J_{\text{PC}} = 135.9$ Hz, PCH), 15.7 (*p*-CH₃), 20.8 (Et₂O), 21.4 (*o*-CH₃), 66.3 (Et₂O), 128.6 (dd, $^2J = 18.1$ Hz, *o*-Ph), 130.2 (*m*-C, Mes), 132.5 (*p*-C, Ph), 134.5 (*m*-C, Ph), 135.4 (*i*-C, Ph), 138.0 (*o*-C, Mes), 138.8 (*i*-C, Mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C), δ : 31.4. M.S., m/z : 746 [55%, M^+], 440 [60%, $\text{Ph}_2\text{PCH}_2\text{NMe}_3$], 317 [100%, $\text{Ph}_2\text{NMe}_3\text{H}$], 240 [35%], 210 [45%], 183 [80%], 164 [25%, PNMe_3], 121 [50%, MesH_2], 91 [40%, NPh].

3.6. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{AlBr}_2$] (**6**)

This was synthesised in an analogous manner from **I** (2.00 mmol) and AlBr₃ (0.53 g, 2.00 mmol). Yield: 0.552 g, 33%. Anal. Calc. for $\text{C}_{43}\text{H}_{43}\text{N}_2\text{P}_2\text{Al}_2\text{Br}_2$: C, 61.99; H, 5.88; N, 3.08%. Found: C, 61.83; H, 5.93; N, 3.01%. ^1H NMR (*d*₈-thf, 25 °C): δ 1.86 (s, 12H, *o*-Me), 1.92 (s, 6H, *p*-Me), 3.32 (d, PCHP, $^2J_{\text{PH}} = 7.02$ Hz), 6.75 (s, 4H, mes), 7.41 (t, 8H, *o*-Ph), 7.56 (t, 4H, *p*-Ph), 7.85 (t, 8H,

m-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C): δ 20.9 (*p*-Me), 21.8 (*o*-Me), 25.0 (PCH), 128.7 (*p*-C, mes), 130.3 (*o*-C, Ph), 132.6 (*m*-C, mes), 134.0 (*p*-C, Ph), 134.57 (*m*-C, Ph), 134.57 (*i*-C, Ph), 135.21 (*o*-C, mes), 139.0 (*i*-C, mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C): δ 32.8.

3.7. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{AlI}_2$] (**7**)

This was synthesised in an analogous manner from **I** (0.77 mmol) and AlI₃ (0.32 g, 0.78 mmol). Yield: 0.58 g, 80%. Anal. Calc. for $\text{C}_{43}\text{H}_{43}\text{N}_2\text{P}_2\text{Al}_2\text{I}_2$: C, 52.42; H, 5.90; N, 2.60%. Found: C, 52.30; H, 4.91; N, 2.51%. ^1H NMR (*d*₈-thf, 25 °C): δ 1.45 (s, 12H, *o*-Me), 1.72 (s, 6H, *p*-Me), 2.95 (d, PCHP, $^2J_{\text{PH}} = 6.95$ Hz), 6.26 (s, 4H, mes), 6.96 (t, 8H, *o*-Ph), 7.09 (t, 4H, *p*-Ph), 7.44 (t, 8H, *m*-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C): δ 20.78 (*p*-Me), 21.05 (*o*-Me), 22.7 (PCH₂), 128.7 (*p*-C, mes), 129.9 (*o*-C, Ph), 130.4 (*m*-C, mes), 132.6 (*p*-C, Ph), 134.1 (*m*-C, Ph), 134.2 (*i*-C, Ph), 135.3 (*o*-C, mes), 139.3 (*i*-C, mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C): δ 30.1. M.S. m/z : 929 [10%, M^+], 803 [55%, $\{\text{HC}(\text{Ph}_2\text{PNMe}_3)\text{AlI}\}$], 440 [35%, $\text{Ph}_2\text{PCH}_2\text{PNMe}_3$], 202 [100%], 318 [45%, Ph_2PNMe_3], 134 [45%, HNMe_3], 91 [45%, NPh].

3.8. [$\{\text{HC}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}\text{GaCl}_2$] (**8**)

This was synthesised in an analogous manner from **I** (2.00 mmol) and GaCl₃ (0.35 g, 2.00 mmol). Yield: 0.86 g, 54%. Anal. Calc. for $\text{C}_{43}\text{H}_{43}\text{N}_2\text{P}_2\text{GaCl}_2$: C, 65.34; H, 5.50; N, 3.55%. Found: C, 64.90; H, 5.00; N, 3.02%. ^1H NMR (*d*₈-thf, 25 °C): δ 2.01 (s, 12H, *o*-Me), 2.10 (s, 6H, *p*-Me), 2.30 (t, PCHP), 6.49 (s, 4H, Mes), 6.79 (t, 8H, *o*-Ph), 7.57 (t, 4H, *p*-Ph), 8.02 (t, 8H, *m*-Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C): δ 20.3 (*p*-Me), 21.0 (*o*-Me), 21.7 (PCH₂), 128.1 (*p*-C, Mes), 129.3 (*o*-C, Ph), 130.5 (*m*-C, Mes), 132.1 (*p*-C, Ph), 134.1 (*m*-C, Ph), 134.3 (*i*-C, Ph), 135.1 (*o*-C, Mes), 139.3 (*i*-C, Mes). $^{31}\text{P}\{^1\text{H}\}$ NMR (*d*₈-thf, 25 °C), δ : 36.0. M.S. m/z : 790 [5%, M^+], 755 [2%, $\text{M}^+\text{-Cl}$], 440 [15%, $\text{Ph}_2\text{PCH}_2\text{PNMe}_3$], 317 [30], 318 [30%, Ph_2PNMe_3], 134 [100%, HNMe_3], 91 [45%, NPh].

3.9. Crystallography

Data were collected at 173 K on a Nonius Kappa CCD diffractometer, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å; details are given in Tables 2 and 4. The structures were solved by direct methods (SHELXS-97) [58] and refined by full matrix least squares (SHELXL-97) [59] with non-H atoms anisotropic and H atoms included in riding mode. Crystals of **3** diffracted very weakly at high angle. The chlorine and methyl group attached to Al in **4** were disordered 0.71:0.29. One toluene molecule was also disordered and was refined with bond length constraints (SADI) with hydrogens omitted. In **7** two poorly defined molecules of diethyl ether were refined with bond length

constraints. An absorption correction (MULTISCAN) was applied to 5–8.

4. Supplementary Information

Crystallographic data for the structural analyses of **II**, 1–8 have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 209814–209822. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

The Royal Society is thanked for the provision of a University Research Fellowship (MSH).

References

- [1] (a) M.S. Hill, P.B. Hitchcock, *J. Chem. Soc., Dalton Trans.* (2002) 4694;
(b) M.S. Hill, P.B. Hitchcock, *Dalton Trans.* (2003) 570.
- [2] M.S. Hill, P.B. Hitchcock, *Organometallics* 21 (2002) 220.
- [3] J. Feldman, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese, S.D. Arthur, *Organometallics* 16 (1997) 1514.
- [4] P.G. Hayes, W.E. Piers, L.W.M. Lee, L.K. Knight, M. Parvez, M.R.J. Elsegood, W. Clegg, *Organometallics* 20 (2001) 2533.
- [5] W.-K. Kim, M.J. Fevola, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, *Organometallics* 17 (1998) 4541.
- [6] P.H.M. Budzelaar, A.B. van Oort, A.G. Orpen, *Eur. J. Inorg. Chem.* (1998) 1485.
- [7] B. Qian, W.J. Scanlon, M.R. Smith, D.H. Motry, *Organometallics* 18 (1999) 1693.
- [8] V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, *Eur. J. Inorg. Chem.* (2001) 1895.
- [9] J.M. Smith, R.J. Lachiotte, P.L. Holland, *Chem. Commun.* (2000) 1542.
- [10] J.M. Smith, R.J. Lachiotte, K.A. Pittard, T.R. Cundari, G. Lukat-Rodgers, K.R. Rogers, P.L. Holland, *J. Am. Chem. Soc.* 123 (2001) 9222.
- [11] A. Pa, M. Stender, R.J. Wright, M.M. Olmstead, P. Klavins, P.P. Power, *Inorg. Chem.* 41 (2002) 3909.
- [12] P.L. Holland, T.R. Cundari, L.L. Perez, N.A. Eckert, R.J. Lachicotte, *J. Am. Chem. Soc.* 124 (2002) 14416.
- [13] N.A. Eckert, E.M. Bones, R.J. Lachiotte, P.L. Holland, *Inorg. Chem.* 42 (2003) 1720.
- [14] M. Stender, R.J. Wright, B.E. Eichler, J. Prust, M.M. Olmstead, H.W. Roesky, P.P. Power, *J. Chem. Soc., Dalton Trans.* (2001) 3465.
- [15] W. Clegg, E.K. Cope, A.J. Edwards, F.S. Mair, *Inorg. Chem.* 37 (1998) 2317.
- [16] V.C. Gibson, J.A. Segal, A.J.P. White, D.J. Willams, *J. Am. Chem. Soc.* 122 (2000) 7120.
- [17] P.J. Bailey, S.T. Liddle, C.A. Morrison, S. Parsons, *Angew. Chem., Int. Ed.* 40 (2001) 4463.
- [18] M.H. Chisholm, J. Galluci, K. Phomphrai, *Chem. Commun.* (2003) 48.
- [19] Y. Ding, H. Hao, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* 20 (2001) 4806.
- [20] Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, P.P. Power, *Organometallics* 20 (2001) 1190.
- [21] P.B. Hitchcock, M.F. Lappert, S. Tian, *J. Chem. Soc., Dalton Trans.* (1997) 1945.
- [22] P.B. Hitchcock, J. Hu, M.F. Lappert, S. Tian, *J. Organomet. Chem.* 536 (1997) 473.
- [23] Review of lactide ring opening polymerisation: B.J. O'Keefe, M.A. Hillmeyer, W.B. Tolman, *J. Chem. Soc., Dalton Trans.* (2001) 2215.
- [24] B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, *J. Am. Chem. Soc.* 123 (2001) 3229.
- [25] M. Cheng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B. Lobkovsky, G.W. Coates, *J. Am. Chem. Soc.* 123 (2001) 8738.
- [26] A.P. Dove, V.C. Gibson, E.L. Marshall, A.J.P. White, D.J. Williams, *Chem. Commun.* (2001) 283.
- [27] D.J.E. Spencer, N.W. Aboeella, A.M. Reynolds, P.L. Holland, W.B. Tolman, *J. Am. Chem. Soc.* 124 (2002) 2108.
- [28] D.W. Randall, S.D. George, P.L. Holland, B. Hedman, K.O. Hodgson, W.B. Tolman, E. Solomon, *J. Am. Chem. Soc.* 122 (2000) 11632.
- [29] H. Andres, E.L. Bominaar, J.M. Smith, N.A. Eckert, P.L. Holland, E. Munck, *J. Am. Chem. Soc.* 124 (2002) 3012.
- [30] For a comprehensive review of β -diketiminatometal complexes, see: L. Bourget-Merle, M.F. Lappert, J.R. Severn, *Chem. Rev.* 102 (2002) 3031.
- [31] S. Al-Benna, M.J. Sarsfield, M. Thornton-Pett, D.L. Ormsby, P.J. Maddox, P. Brès, M. Bochmann, *J. Chem. Soc., Dalton Trans.* (2000) 4247.
- [32] A. Kasani, R. McDonald, R.G. Cavell, *Organometallics* 18 (1999) 3775.
- [33] M.J. Sarsfield, M. Said, M. Thornton-Pett, L.A. Gerrard, M. Bochmann, *J. Chem. Soc., Dalton Trans.* (2001) 822.
- [34] G. Aharonian, K. Feghali, S. Gambarotta, G.P.A. Yap, *Organometallics* 20 (2001) 2616.
- [35] P. Wei, D.W. Stephan, *Organometallics* 31 (2002) 1308.
- [36] M.T. Gamer, S. Dehnen, P.W. Roesky, *Organometallics* 20 (2001) 4230.
- [37] M.T. Gamer, P.W. Roesky, *J. Organomet. Chem.* 647 (2002) 123.
- [38] M.J. Sarsfield, M. Helliwell, D. Collison, *Chem. Commun.* (2002) 2264.
- [39] Review R.G. Cavell, R.P. Kamalesh Babu, K. Aparna, *J. Organomet. Chem.* 617 (2001) 158;
For a general review of iminophosphorane coordination chemistry, see A. Steiner, S. Zacchini, P.I. Richards, *Coord. Chem. Rev.* 227 (2002) 193.
- [40] C. Cui, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem., Int. Ed.* 39 (2000) 4274.
- [41] N.J. Hardman, C. Cui, H.W. Roesky, W.H. Fink, P.P. Power, *Angew. Chem., Int. Ed.* 40 (2001) 2172.
- [42] N.J. Hardman, B.E. Eichler, P.P. Power, *Chem. Commun.* (2000) 1991.
- [43] R.G. Cavell, K. Aparna, R.P. Kamalesh Babu, Q. Wang, *J. Mol. Cat., A* 189 (2002) 137.
- [44] (a) A. Müller, M. Möhlen, B. Neumüller, N. Faza, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* 625 (1999) 1748;
(b) M.W. Avis, C.J. Elsevier, N. Veldman, H. Kooijman, A.L. Spek, *Inorg. Chem.* 35 (1996) 1518.
- [45] (a) K.V. Katti, R.G. Cavell, *Inorg. Chem.* 28 (1989) 413;
(b) H. Schmidbaur, G.A. Bowmaker, O. Kumberger, G. Müller, W. Wolfsberger, *Z. Naturforsch b* 45 (1990) 476;
(c) K.V. Katti, R.G. Cavell, *Organometallics* 7 (1988) 2236;
(d) K.V. Katti, R.J. Batchelor, F.W.B. Einstein, R.G. Cavell, *Inorg. Chem.* 29 (1990) 808;
(e) K.V. Katti, B.D. Santarsiero, A.A. Pinkerton, R.G. Cavell, *Inorg. Chem.* 32 (1993) 5919.

- [46] A. Steiner, D. Stalke, *Angew. Chem., Int. Ed.* 34 (1995) 1752.
- [47] A.G. Avent, D. Bonafoux, C. Eaborn, M.S. Hill, P.B. Hitchcock, J.D. Smith, *J. Chem. Soc., Dalton Trans.* (2000) 2183.
- [48] H.H. Karsch, K. Zellner, P. Mikulcik, J. Lachmann, G. Müller, *Organometallics* 9 (1990) 190, and references therein.
- [49] K. Aparna, R. McDonald, M. Ferguson, R.G. Cavell, *Organometallics* 18 (1999) 4241.
- [50] B. Qian, D.L. Ward, M.R. Smith, *Organometallics* 17 (1998) 3070.
- [51] C.E. Radzewich, M.P. Coles, R.F. Jordan, *J. Am. Chem. Soc.* 120 (1998) 9384.
- [52] C.E. Radzewich, I.A. Guzei, R.F. Jordan, *J. Am. Chem. Soc.* 121 (1999) 8673.
- [53] F. Coslédan, P.B. Hitchcock, M.F. Lappert, *Chem. Commun.* (1999) 705.
- [54] C. Cui, H.W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem. Int. Ed.* 39 (2000) 1815.
- [55] V. Jancik, Y. Peng, H.W. Roesky, J. Li, D. Neculai, A.M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* 125 (2003) 1452.
- [56] M. Stender, B.E. Eichler, N.J. Hardman, P.P. Power, J. Prust, M. Noltemeyer, H.W. Roesky, *Inorg. Chem.* 40 (2001) 2794.
- [57] I. Ugi, H. Perlinger, L. Behringer, *Chem. Ber.* 91 (1958) 2324.
- [58] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, 1997.
- [59] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen, 1997.