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Synthesis and characterization of group 13 dichloride (M = Ga, In), dimethyl (M = Al) and cationic methyl aluminum complexes supported by monoanionic NNN-pincer ligands†

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A series of group 13 dichloride species, supported by monoanionic NNN-pincer ligands, **L**MCl_2 (**L** = 2,5-(^{i}Pr$_2$P═NAr)$_2$N(C_4H_2); Ar = 4-^{i}PrC_6H_4 (**L^{Pipp}**), 2,4,6-$Me_3C_6H_2$ (**L^{Mes}**), 2,6-^{i}Pr$_2C_6H_3$ (**L^{Dipp}**); M = Ga (**1**), In (**2**)), were prepared *via* the reaction of Na**L** with MCl_3 and characterized by multinuclear NMR spectroscopy, elemental analysis and X-ray crystallography. Related organoaluminum complexes, **L**$AlMe_2$ (**3**), were synthesized by addition of $AlMe_3$ to **L**. Treatment with the Lewis acid $B(C_6F_5)_3$ afforded well-defined cationic aluminum methyl species, [**L**AlMe]$^+$[$MeB(C_6F_5)_3$]$^-$ (**4**), which were found to be thermally stable in both solid and solution state for days.

Introduction

Over the last several decades pincer ligands have become an increasingly popular scaffold for supporting metals across the periodic table,[1–4] with notable examples demonstrating superior capacity for mediating an array of stoichiometric and catalytic transformations, including asymmetric hydrophosphination, Friedel–Crafts alkylation and alkane dehydrogenation.[1–4] The vast majority of these systems incorporate neutral PNP and monoanionic PCP motifs. By comparison, there is a paucity of NNN-pincers, particularly those that bear a −1 charge, typically at the central nitrogen donor.[5,6] Nonetheless, this sub-group of pincer ligands has found growing utility, especially with noble,[3,4,7–18] rare-earth[19–26] and actinide[27–30] metals. Notably, reports of main group, particularly group 13, complexes containing monoanionic NNN-pincer ligands remain sparse.[5,6,31–33] The dearth of such species is most marked for the heavier group 13 elements, gallium and indium.[5,6,31–33] By contrast, far more work encompasses aluminum NNN-pincer complexes,[34–49] many of which have demonstrated competence mediating an impressive array of chemical transformations, including catalytic hydroboration,[44] and the ring-opening polymerization of lactones,[34,40,47–49] as well as the dehydrogenative coupling of amines.[35] Utility has also been found for aluminum pincer complexes in electrocatalysis.[36,39] From a more fundamental perspective, NNN-pincer ligands have led to the isolation of remarkable aluminum(III) complexes that exhibit square planar geometry.[37]

Recognizing the versatility of pincer ligands, and the suitability of hard nitrogen donors for electron deficient metals, we developed a family of pincer scaffolds constructed about a pyrrole core. Substitution of the 2- and 5-positions of the pyrrole ring with electron rich phosphinimine (R_3P═NR')[50,51] functionalities provides access to monoanionic NNN-pincers that can be readily fine-tuned at both the phosphorus and nitrogen atoms of the flanking groups.[52] These platforms have proven particularly effective at stabilizing organometallic rare-earth metal complexes,[19–23] and have also been utilized to access base-stabilized rhodium silylene and borylene species.[14,15] Because of the success garnered with these ligands and trivalent metals, we anticipated they would serve as ideal candidates from which novel group 13 complexes could be prepared. Herein we describe two new versions of our bis(phosphinimine)pyrrole framework that feature sterically demanding *N*-aryl groups, and detail the impact that such bulk has upon the thermal stability and solution and solid-state structures of dichloride complexes of gallium and indium, as well as neutral and cationic organoaluminum species.

Results & discussion

The NNN-pincer ligands 2,5-(^{i}Pr$_2$P═NAr)$_2$N(C_4H_2) (Ar = 2,4,6-$Me_3C_6H_2$ (**L^{Mes}**), 2,6-^{i}Pr$_2C_6H_3$ (**L^{Dipp}**)), which feature bulky *N*-aryl substituents, were prepared according to our previously reported protocol for 2,5-[^{i}Pr$_2$P═N(4-^{i}PrC_6H_4)]$_2$N(C_4H_2) (**L^{Pipp}**).[13] Addition of two equivalents of the requisite azide to 2,

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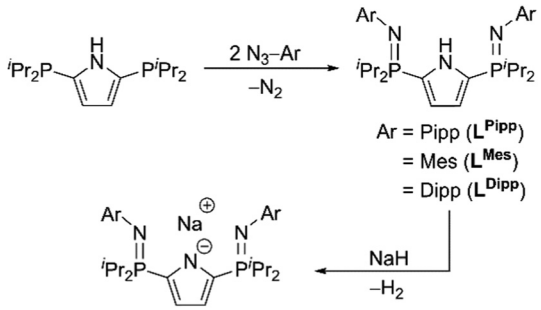


Scheme 1 Synthesis of Na**L**.

5-(^{i}Pr$_2$P)NH(C$_4$H$_2$)[13] under standard Staudinger conditions[53] afforded $\mathbf{L}^{\mathbf{Mes}}$ and $\mathbf{L}^{\mathbf{Dipp}}$ in 93% and 95% yield, respectively (Scheme 1).

Single crystals of $\mathbf{L}^{\mathbf{Mes}}$ and $\mathbf{L}^{\mathbf{Dipp}}$ suitable for X-ray diffraction studies were grown from concentrated solutions of pentane and toluene (2 : 1), at −35 °C. Both $\mathbf{L}^{\mathbf{Mes}}$ (Fig. 1, top) and $\mathbf{L}^{\mathbf{Dipp}}$ (Fig. 1, bottom) are isostructural with $\mathbf{L}^{\mathbf{Pipp}}$ and feature similar P–N distances ($\mathbf{L}^{\mathbf{Pipp}}$: 1.564(1) Å, $\mathbf{L}^{\mathbf{Mes}}$: 1.563(2) Å, $\mathbf{L}^{\mathbf{Dipp}}$: 1.548(3) Å).[13]

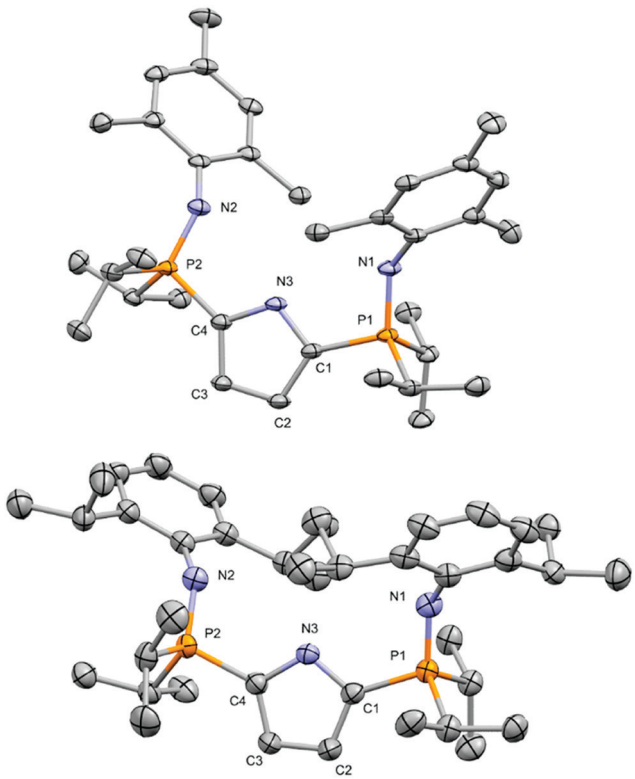


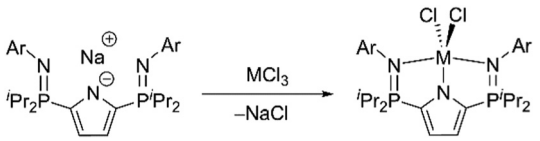
Fig. 1 Top: X-ray crystal structure of $\mathbf{L}^{\mathbf{Mes}}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): P1–N1 = 1.550(3), P2–N2 = 1.548(3), P1–C1 = 1.806(4), C1–C2 = 1.378(5), N3–C1 = 1.365(5), C2–C3 = 1.400(5), C1–P1–N1 = 111.7(2), C4–P2–N2 = 111.9(2), N3–C1–P1 = 123.0(3). Bottom: X-ray crystal structure of $\mathbf{L}^{\mathbf{Dipp}}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): P1–N1 = 1.563(2), P2–N2 = 1.559(2), P1–C1 = 1.797(2), C1–C2 = 1.386(2), N3–C1 = 1.365(5), C2–C3 = 1.413(3), C1–P1–N1 = 105.85(8), C4–P2–N2 = 107.81(8), N3–C1–P1 = 116.7(1).

The sodium salt of $\mathbf{L}^{\mathbf{Mes}}$ was prepared in 92% yield by the straightforward reaction of one equivalent of NaH and $\mathbf{L}^{\mathbf{Mes}}$ in THF for two hours at ambient temperature. Formation of the salt was confirmed by the simultaneous disappearance of the pyrrole N–H resonance in the ^{1}H NMR spectrum (δ 10.50) and the characteristic downfield shift of the ^{31}P{^{1}H} signal from δ 4.1 to δ 19.2.[13] Much more forcing conditions (100 °C for 42 h), and a slight excess (1.3 equiv.) of NaH, were required to deprotonate the more sterically demanding ligand $\mathbf{L}^{\mathbf{Dipp}}$.

With three ligands in hand, we aimed to generate a family of group 13 complexes that vary systematically in steric protection of the metal centre. Initial attempts targeted aluminum; however, when AlCl$_3$ was treated with Na**L**, complex mixtures, from which single products could not be isolated, were consistently obtained. Notably, when the larger GaCl$_3$ and InCl$_3$ were utilized, analytically pure samples of all six combinations ($\mathbf{L}^{\mathbf{Ar}}$GaCl$_2$ (Ar = Pipp ($\mathbf{1}^{\mathbf{Pipp}}$), Mes ($\mathbf{1}^{\mathbf{Mes}}$), Dipp ($\mathbf{1}^{\mathbf{Dipp}}$))) and ($\mathbf{L}^{\mathbf{Ar}}$InCl$_2$ (Ar = Pipp ($\mathbf{2}^{\mathbf{Pipp}}$), Mes ($\mathbf{2}^{\mathbf{Mes}}$), Dipp ($\mathbf{2}^{\mathbf{Dipp}}$))) were isolated after reaction times of between 18 and 24 hours in benzene (Scheme 2).

Complexes **1** and **2** exhibit solution state structures, as indicated by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, consistent with C_{2v} symmetry. In each case only one aromatic resonance was observed for the pyrrole H, and notably, a downfield trend in chemical shift that correlates with *N*-aryl bulk, was observed ($\mathbf{1}^{\mathbf{Pipp}}$: δ 6.60, $\mathbf{1}^{\mathbf{Mes}}$: δ 6.77, $\mathbf{1}^{\mathbf{Dipp}}$: δ 6.78; $\mathbf{2}^{\mathbf{Pipp}}$: δ 6.60, $\mathbf{2}^{\mathbf{Mes}}$: δ 6.76, $\mathbf{2}^{\mathbf{Dipp}}$: δ 6.79). All complexes give rise to a single diagnostic ^{31}P NMR resonance (δ 33.0–35.9) that is shifted substantially downfield from both the corresponding sodiated (δ 18.6–28.0) and protio ligands (δ 2.9–13.5). Converse to the pyrrole ^{1}H NMR chemical shifts, all species in a given series exhibit an upfield pattern in their ^{31}P NMR spectra that is inversely correlated with *N*-aryl substituent size.

Dichloride complexes **1** and **2** readily crystallize; X-ray quality crystals of $\mathbf{1}^{\mathbf{Pipp}}$, $\mathbf{1}^{\mathbf{Dipp}}$, and **2** were obtained by slow evaporation of concentrated benzene solutions of each compound at ambient temperature. Representative solid-state structures of gallium ($\mathbf{1}^{\mathbf{Dipp}}$) and indium ($\mathbf{2}^{\mathbf{Dipp}}$) are depicted in Fig. 2 (see ESI,† for X-ray crystal structures of $\mathbf{1}^{\mathbf{Pipp}}$, $\mathbf{2}^{\mathbf{Pipp}}$ and $\mathbf{2}^{\mathbf{Mes}}$) and reveal 5-coordinate mononuclear complexes. These species feature a κ^3-bound pincer ligand and display distorted square pyramidal geometry about the metal centre with the three nitrogen donors and one chloride ligand comprising the base of the pyramid. While structures supported by the most bulky ligands ($\mathbf{L}^{\mathbf{Mes}}$, $\mathbf{L}^{\mathbf{Dipp}}$) lie far closer to square pyramid on the



M = Ga; Ar = Pipp ($\mathbf{1}^{\mathbf{Pipp}}$), Mes ($\mathbf{1}^{\mathbf{Mes}}$), Dipp ($\mathbf{1}^{\mathbf{Dipp}}$)
M = In; Ar = Pipp ($\mathbf{2}^{\mathbf{Pipp}}$), Mes ($\mathbf{2}^{\mathbf{Mes}}$), Dipp ($\mathbf{2}^{\mathbf{Dipp}}$)

Scheme 2 Preparation of group 13 metal chloride complexes, **L**MCl$_2$ (M = Ga (**1**), In (**2**); **L** = $\mathbf{L}^{\mathbf{Pipp}}$, $\mathbf{L}^{\mathbf{Mes}}$, $\mathbf{L}^{\mathbf{Dipp}}$).

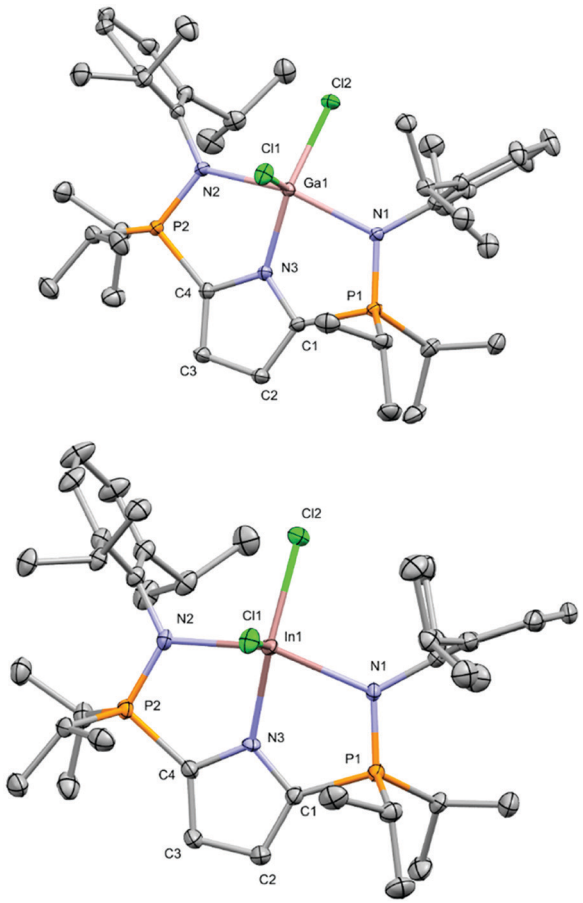


Fig. 2 Top: X-ray crystal structure of $\mathbf{1}^{\mathbf{Dipp}}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1–N1 = 2.160(1), Ga1–N2 = 2.152(1), Ga1–N3 = 1.948(1), Ga1–Cl1 = 2.1936(4), G1–Cl2 = 2.2223(4), P1–N1 = 1.626(1), P2–N2 = 1.634(1), N1–Ga1–N2 = 154.85(4), N3–Ga1–Cl1 = 146.89(4), N1–Ga1–Cl1 = 146.87(4), Cl1–Ga1–Cl2 = 103.73(2). Bottom: X-ray crystal structure of $\mathbf{2}^{\mathbf{Dipp}}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): In1–N1 = 2.287(2), In1–N2 = 2.289(2), In1–N3 = 2.131(2), In1–Cl1 = 2.3970(5), In1–Cl2 = 2.3590(5), P1–N1 = 1.629(2), P2–N2 = 1.625(2), N1–In1–N2 = 148.323(9), N3–In1–Cl1 = 146.779(8), N1–In1–Cl1 = 102.96(5), Cl1–In1–Cl2 = 102.875(10).

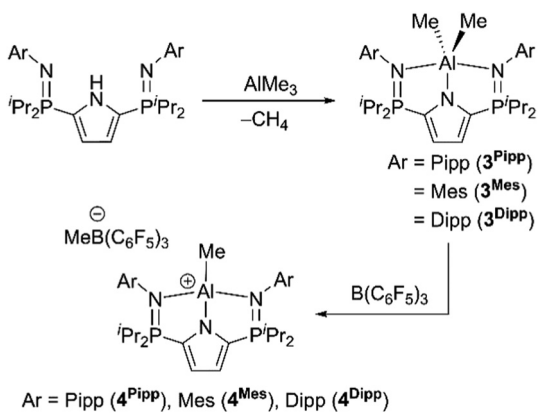
continuum with trigonal bipyramidal geometry, complexes of the larger indium more closely approach ideality (*e.g.* $\mathbf{2}^{\mathbf{Mes}}$: τ = 0.067;[54] $\mathbf{1}^{\mathbf{Dipp}}$: τ = 0.133; $\mathbf{2}^{\mathbf{Dipp}}$: τ = 0.026). Meanwhile, complexes $\mathbf{1}^{\mathbf{Pipp}}$ and $\mathbf{2}^{\mathbf{Pipp}}$, which lack *ortho*-substituents on the *N*-aryl groups, are more trigonal-bipyramid-like ($\mathbf{1}^{\mathbf{Pipp}}$: τ = 0.643; $\mathbf{2}^{\mathbf{Pipp}}$: τ = 0.459). In all cases the metal sits deep in the ligand binding pocket, resulting in M–$N_{pyrrole}$ distances that are markedly shorter than M–$N_{phosphinimine}$ lengths (*e.g.* For $\mathbf{1}^{\mathbf{Dipp}}$: Ga1–N1 = 2.160(1) Å, Ga1–N2 = 2.152(1) Å, Ga1–N3 = 1.948(1) Å). The remaining metal contacts are similar to those previously reported for five-coordinate gallium and indium complexes supported by monoanionic tridentate ligands.[33,55] Finally, it should be noted that while the P–N bond distances are elongated relative to the free ligands (1.604(6)–1.630(6) Å *vs.* 1.548(3)–1.564(1) Å), and hence, exhibit significant single bond character, they are comparable to lengths observed upon coordination to a variety of other metals, including rhodium (range = 1.608(2)–1.632(2) Å).[12–15]

In an attempt to isolate organometallic indium and gallium complexes a plethora of reactions were undertaken wherein **1** or **2** were combined with the lithium reagents $LiCH_3$ and $LiCH_2SiMe_3$. Unfortunately, exhaustive efforts involving systematic variation of stoichiometry, solvent, reaction time and temperature afforded only complex mixtures from which pure compounds could not be obtained. Thus, these efforts were abandoned.

Given the difficulty encountered during efforts to functionalize chloride complexes **1** and **2**, we turned our attention to aluminum. Aluminum-mediated stoichiometric and catalytic chemical transformations are attractive because of the ready availability and low cost of aluminum compared with 2nd and 3rd row transition metals, which are much more often exploited for such purposes.[3,4] Accordingly, fundamental explorative investigations involving aluminum have recently been undertaken with increased frequency, revealing remarkable opportunities. For example, neutral and cationic aluminum alkyl species have demonstrated efficacy as catalysts for hydroboration,[44,56–59] ring-opening polymerization of cyclic esters,[45,47–49,55,60] and the guanylation of amines.[61] Hence, despite our lack of success generating complexes of the form $\mathbf{L}AlCl_2$, our aspirations were buoyed by commercial access to $AlMe_3$; thus, we sought to prepare aluminum methyl species *via* an alkane elimination protocol.

Upon reaction of protio ligands **L** with a 4.6 M hexanes solution of $AlMe_3$ effervescence, caused from liberated CH_4, was immediately observed. After 18 hours of stirring, trace THF was added, as it was discovered to effectively eliminate undesired dinuclear species. Recrystallization of the crude products from pentane at −35 °C provided analytically pure $\mathbf{L}AlMe_2$ (**3**) as pale coloured powders in 92–94% yield (Scheme 3).

Similar to complexes **1** and **2**, dimethyl **3** exhibit single resonances in the respective ^{31}P NMR spectra ($\mathbf{3}^{\mathbf{Pipp}}$: δ 35.0, $\mathbf{3}^{\mathbf{Mes}}$: δ 28.5, $\mathbf{3}^{\mathbf{Dipp}}$: δ 23.6). Diagnostic sharp peaks integrating as 6H were observed slightly upfield of δ 0 in the ^1H NMR



Scheme 3 Synthesis of neutral ($\mathbf{L}AlMe_2$ (**3**)) and cationic ($[\mathbf{L}AlMe]^+[MeB(C_6F_5)_3]^-$ (**4**)) aluminum NNN-pincer complexes.

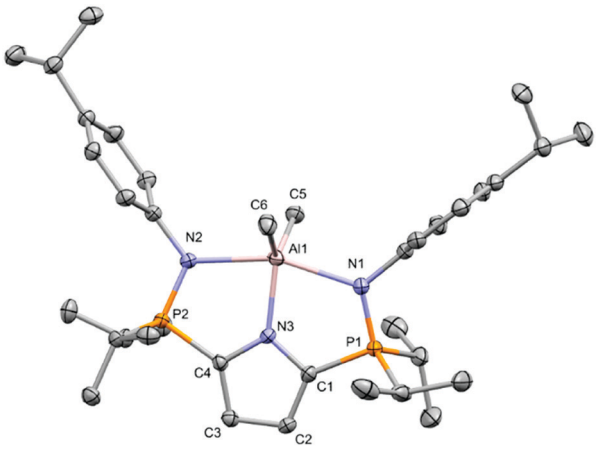


Fig. 3 X-ray crystal structure of $\mathbf{3}^{\mathbf{Pipp}}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–N1 = 2.224(2), Al1–N2 = 2.199(2), Al1–N3 = 1.939(2), P1–N1 = 1.602(2), P2–N2 = 1.602(2), Al1–C1 = 1.982(2), Al1–C2 = 1.976(2), N1–Al1–N2 = 159.92(6), N1–Al1–N3 = 87.5(2), N1–Al1–C35 = 117.8(2), N1–Al1–N3 = 79.57(6), C1–Al1–C2 = 123.28(9).

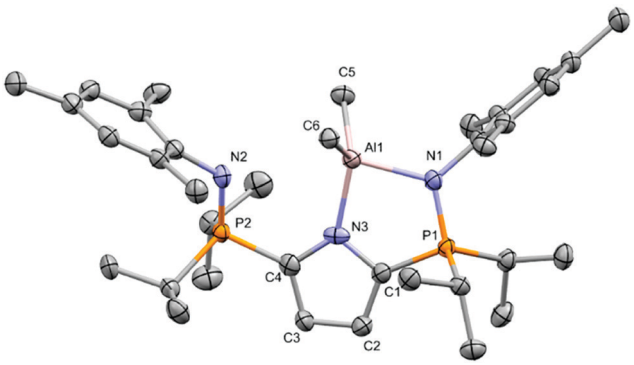


Fig. 4 X-ray crystal structure of $\mathbf{3}^{\mathbf{Mes}}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–N1 = 1.991(4), Al1–N3 = 1.944(4), P1–N1 = 1.621(4), P2–N2 = 1.575(5), Al1–C1 = 1.968(5), Al1–C2 = 1.969(5), N1–Al1–N3 = 87.5(2), N1–Al1–C1 = 109.80(2), N3–Al1–C1 = 117.9(2), N3–Al1–C2 = 119.1(2), C1–Al1–C2 = 112.6(2).

spectra, and are attributed to the $AlMe_2$ moieties ($\mathbf{3}^{\mathbf{Pipp}}$: δ −0.05, $\mathbf{3}^{\mathbf{Mes}}$: δ −0.35, $\mathbf{3}^{\mathbf{Dipp}}$: δ −0.33).

The solid-state structures of $\mathbf{3}^{\mathbf{Pipp}}$ and $\mathbf{3}^{\mathbf{Mes}}$ were elucidated by X-ray crystallography; high quality crystals of both complexes were grown from a 1 : 3 toluene:heptane mixture at −35 °C. Complex $\mathbf{3}^{\mathbf{Pipp}}$, like $\mathbf{1}^{\mathbf{Pipp}}$, exhibits distorted trigonal bipyramidal geometry (τ = 0.6107) with the pincer framework bound *via* a κ^3 coordination mode (Fig. 3). The metal centre also resides deep within the NNN-binding pocket, though in this case the difference between Al–$N_{pyrrole}$ and Al–$N_{phosphinimine}$ lengths is much more pronounced (Al1–N3 = 1.939(2) *vs.* Al1–N1 = 2.224(2), Al1–N2 = 2.199(2)). Although these lengths fall within the normal range for Al–N bonds in pentacoordinate organoaluminum complexes, they lie on the longer and shorter ends for distances to neutral and anionic nitrogen donors, respectively.[45–47] These long Al–$N_{phosphinimine}$ distances, in combination with relatively short P–N bonds (P1–N1 = 1.601(1), P2–N2 = 1.608(1)),[45,62–64] suggest that the phosphinimine donors may exhibit hemilability in solution, as has been observed for the rhodium complex $\mathbf{L}^{\mathbf{Pipp}}$Rh(CO), which demonstrates metal–ligand cooperative activation of various small molecules.[12–15]

As the steric bulk of the phosphinimine *N*-aryl group increases, the propensity for elongation of the Al–$N_{phosphinimine}$ bonds ultimately leads to κ^2 bonding between the ligand and aluminum, as observed in the solid-state structure of $\mathbf{3}^{\mathbf{Mes}}$ (Fig. 4). The geometry about the metal centre is tetrahedral and both Al–N bonds are similar in length (Al1–N1 = 1.991(4) Å, Al1–N3 = 1.944(4) Å). Although N2 lies only 0.481(3) Å out of the plane created by Al, N1, N3, P1 and P2, the distance to aluminum (3.098(3) Å) does not suggest a meaningful interaction exists between the two atoms. The P–N length (P2–N2 = 1.575(5) Å *vs.* 1.563(2) Å for $\mathbf{L}^{\mathbf{Mes}}$) in the free phosphinimine, which is significantly shorter than that observed in the coordinated group (P1–N1 = 1.621(4) Å), and closely matches systems that feature κ^2-bound $\mathbf{L}^{\mathbf{Pipp}}$,[13] is consistent with this finding. An X-ray diffraction study on poorly diffracting crystals of $\mathbf{3}^{\mathbf{Dipp}}$ established atom connectivity, showing that, as expected, the sterically demanding Dipp group also enforces κ^2-binding of the NNN-ligand. Since methyl complexes **3** exhibit apparent C_{2V} symmetry in solution between −75 °C and 20 °C, a fluxional process akin to that observed by Huang *et al.* in an aluminum methyl complex supported by a tridentate pyrrole-morpholine,[47] presumably exchanges the phosphinimine groups faster than the NMR timescale.

In an endeavour to access sterically and electronically unsaturated organoaluminum species complexes **3** were allowed to react with one equivalent of $B(C_6F_5)_3$ in pentane. Immediate formation of orange oils, which converted into voluminous beige solids upon prolonged exposure to reduced pressure, was observed. Upfield singlets (*ca.* δ −14) in the ^{11}B NMR spectra, broad ^{1}H NMR resonances at δ 1.28–1.29 (3H) and a narrow gap between *meta* and *para* C_6F_5 signals ($\Delta\delta_{mp}$ = 2.5 ppm)[65] in the ^{19}F NMR spectra are consistent with weakly coordinating $MeB(C_6F_5)_3^-$ anions generated *via* methide abstraction from $\mathbf{L}AlMe_2$ (Scheme 3). Analysis of ion pairs $[\mathbf{L}AlMe]^+[MeB(C_6F_5)_3]^-$ (**4**) by $^{31}P\{^1H\}$ NMR spectroscopy revealed a sharp singlet for each complex which resonates substantially further downfield (δ 46.4–61.9) than the neutral dimethyl precursors. Singlets integrating as 3H between δ −0.55 and δ −0.96 in the ^{1}H NMR spectra were assigned as the remaining Al–CH_3 groups. Despite exhaustive efforts, we were unable to obtain crystalline samples of complexes **4** suitable for analysis by X-ray diffraction. Nonetheless, the fact that these species showed no sign of decomposition in solution over 24 hours and contain weakly coordinating anions indicative of highly Lewis acidic metal centres,[66] bode well for future reactivity studies.

Conclusions

Synthesis of an array of group 13 complexes of monoanionic NNN-pincer ligands establishes these frameworks are effective at stabilizing a variety of main group species. Ligand denticity

is dependent upon the size of both the metal and the substituent bound to the phosphinimine nitrogen atom, which may provide the opportunity to leverage hemilability for metal–ligand cooperative processes. Ongoing efforts aim to garner a deep understanding of the capacity of these organoaluminum cations to participate in known and new chemical pathways.

Experimental

General procedures

All manipulations of air-sensitive materials and reagents were conducted using high-vacuum techniques under a purified argon atmosphere or in a glove box (MBraun Labmaster 130). Solvents (THF, toluene, benzene, pentane) were purified using an MBraun solvent purification system (MB-SPS), stored in PTFE-sealed glass vessels over sodium benzophenone ketyl, and vacuum transferred directly into reaction vessels. Deuterated solvents were purchased from Cambridge Isotopes, dried over sodium benzophenone ketyl (d_6-benzene) or CaH_2 (d_5-bromobenzene), degassed *via* at least three freeze–pump–thaw cycles, distilled under reduced pressure and stored under argon and over 4 Å molecular sieves in PTFE-sealed glass vessels. NMR spectra (^{1}H (300.13 MHz), ^{13}C{^{1}H} (75.47 MHz), ^{31}P{^{1}H} (121.48 MHz), ^{19}F (282.42 MHz), and ^{11}B (96.29 MHz)) were collected using a Bruker Avance II NMR spectrometer equipped with a variable-temperature unit, at ambient temperature. Chemical shifts are reported in parts per million (ppm) relative to $SiMe_4$ (^{1}H and ^{13}C), 85% H_3PO_4 (^{31}P), $BF_3{\cdot}Et_2O$ (^{11}B, ^{19}F). Residual H and C containing species were used as internal standards (d_6-benzene (δ 7.16; 128.1) and d_5-bromobenzene (δ 7.28, 7.00, 6.92; 130.9, 129.3, 126.1, 122.3)). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sp = septet, br = broad, m = multiplet, ov = overlapping), coupling constants (Hz), integration, assignment. ^{13}C NMR data are reported as follows: chemical shift, assignment. Assignment of resonances were supplemented by ^{1}H–^{1}H COSY, ^{13}C{^{1}H} APT, DEPT-135, DEPT-90, and ^{1}H–^{13}C{^{1}H} HSQC and HMBC experiments.

Elemental analyses (%CHN) were conducted at the University of Lethbridge on an Elementar Americas Vario MicroCube Analyzer (C, H, N, O, S capabilities) using bulk recrystallized compounds. Organoaluminum compounds produced elemental analysis data with consistently low carbon values, owing to the formation of aluminum carbides.[63,67–70] Compounds $\mathbf{L^{Pipp}}$, $\mathbf{NaL^{Pipp}}$ and 2,5-bis(diisopropylphosphino)-*N*-*H*-pyrrole were prepared according to previously reported literature methods, and analysis of these products agreed with reported spectral data.[13] $B(C_6F_5)_3$ was purchased from Boulder Scientific and dried by stirring a dichloromethane solution with Me_2SiHCl for no more than 20 minutes. The crude product was sublimed under dynamic vacuum at 80 °C.[71] All other materials were obtained in high purity (Sigma-Aldrich or Strem Chemicals) and used without further purification.

Synthesis and characterization

Synthesis of $\mathbf{L^{Mes}}$. Diphosphine 2,5-bis(diisopropylphosphino)-*N*-*H*-pyrrole (620.9 mg, 2.074 mmol) was added to a 50 mL round-bottomed flask equipped with a stir bar. Dry, degassed toluene (5 mL) was added forming an orange-brown solution. Under argon, mesityl azide (744.9 mg, 4.621 mmol) was added to this solution dropwise over 30 seconds resulting in vigorous bubbling. The reaction mixture was left to stir under argon for 16 h. Solvent was thereafter removed under reduced pressure yielding a beige solid. The solid was extracted with 8 mL of pentane and the solution cooled to −35 °C for 16 hours, whereupon the product was isolated as a beige solid. Yield: 1.0865 g (92.67%). Anal. Calcd (%) for $C_{34}H_{53}N_3P_2$: C, 72.18; H, 9.44; N, 7.43. Found: C, 72.47; H, 9.05; N, 7.21. ^{1}H NMR (d_6-benzene): δ 10.48 (br s, 1H, N*H*), 6.92 (s, 4H, *m*-Ar*H*), 6.27 (s, 2H, 3,4-pyrrole), 2.35 (s, 12H, *o*-Mes CH_3), 2.26 (s, 6H, *p*-Mes), 2.05 (dsp, $^3J_{HP}$ = 18.6 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*(CH$_3$)$_2$), 1.03 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, CH(CH_3)$_2$), 0.85 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 145.7 (s, 2C, Mes *ipso-C*), 131.2 (d, $^3J_{CP}$ = 6.2 Hz, 2C, Mes *ipso-C*), 129.0 (s, 2C, Mes *ipso-C*), 126.9 (s, 4C, Mes Ar-*C*), 125.2 (dd, $^1J_{CP}$ = 111.0 Hz, $^3J_{CP}$ = 4.9 Hz, 2C, 2,5-pyrrole), 114.8 (dd, $^2J_{CP}$ = 23.5 Hz, $^3J_{CP}$ = 11.8 Hz, 2C, 3,4-pyrrole), 28.4 (d, $^1J_{CP}$ = 64.9 Hz, 4C, P–*C*H(CH$_3$)$_2$), 21.3 (s, 4C, Mes *o*-*C*H$_3$), 20.7 (s, 2C, Mes *p*-*C*H$_3$), 16.2 (s, 4C, CH(*C*H$_3$)$_2$), 15.4 (d, $^2J_{CP}$ = 2.7 Hz, 4C, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 4.1 (s).

Synthesis of $\mathbf{L^{Dipp}}$. Diphosphine 2,5-bis(diisopropylphosphino)-*N*-*H*-pyrrole (363.3 mg, 1.214 mmol) was added to a 50 mL round-bottomed flask equipped with a stir bar. Dry, degassed toluene (8 mL) was added forming an orange-brown solution. Under argon, 2,6-^{i}Pr$_2$C$_6$H$_3$N$_3$ (493.4 mg, 2.427 mmol) was added to this solution dropwise over 30 seconds resulting in vigorous bubbling. The reaction mixture was left to stir under argon for 20 h. Solvent was thereafter removed under reduced pressure yielding a light brown solid. The solid was extracted with 5 mL of pentane and the solution cooled to −35 °C for 16 hours. The desired product was isolated as a light brown solid. Yield: 701.7 mg (94.79%). Anal. Calcd (%) for for $C_{40}H_{65}N_3P_2$: C, 73.92; H, 10.08; N, 6.47. Found: C, 73.62; H, 10.06; N, 6.48. ^{1}H NMR (d_6-benzene): δ 10.32 (br s, 1H, N–H), 7.19 (m, 2H, *p*-Ar*H*), 7.03 (t, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-Ar*H*), 6.28 (s, 2H, 3,4-pyrrole), 3.60 (sp, $^3J_{HH}$ = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 2.18 (dsp, $^2J_{HP}$ = 23.4 Hz, $^3J_{HH}$ = 6.9 Hz, 4H, P–C*H*), 1.36 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.12 (dd, $^3J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 6.9 Hz, 12H, P–CH(CH_3)$_2$), 0.88 (dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 6.9 Hz, 12H, P–CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 145.2 (s, 2C, Dipp *ipso-C*), 142.2 (d, $^3J_{CP}$ = 6.0 Hz, 2C, Dipp *ipso-C*), 125.1 (d, $^1J_{CP}$ = 6.0 Hz, 2C, 2,5-pyrrole), 122.6 (s, 4C, Dipp Ar-*C*), 119.6 (s, 2C, 3,4-pyrrole), 115.2 (d, $^3J_{CP}$ = 12.0 Hz, 2C, Dipp Ar-*C*), 29.0 (s, 4C, *C*H(CH$_3$)$_2$), 28.9 (d, $^1J_{CP}$ = 63.4 Hz, 4C, P–*C*H(CH$_3$)$_2$), 23.6 (s, 4C, CH(*C*H$_3$)$_2$), 16.4 (s, 4C, CH(*C*H$_3$)$_2$), 15.4 (d, $^2J_{CP}$ = 1.5 Hz, 8C, P–CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 2.9 (s).

Synthesis of $\mathbf{NaL^{Mes}}$. $\mathbf{L^{Mes}}$ (360.1 mg, 0.6369 mmol) and NaH (15.2 mg, 0.661 mmol) were added to a 50 mL round-bottomed

flask equipped with a stir bar. The flask was cooled to −78 °C and THF (15 mL) was added under reduced pressure, forming a pale orange solution. The reaction mixture was gradually allowed to warm to ambient temperature, whereupon bubbling was observed. The reaction was stirred under argon for 2 h after which the solvent was removed to afford a light brown solid. Yield: 332.8 mg (91.53%). Anal. Calcd (%) for $C_{34}H_{52}N_3NaP_2$: C, 69.48; H, 8.92; N, 7.15. Found: C, 69.11; H, 8.89; N, 7.26. ^{1}H NMR (d_6-benzene): δ 6.94 (s, 4H, *m*-Ar*H*), 6.66 (d, $^3J_{HP}$ = 15.0 Hz, 2H, 3,4-pyrrole), 2.29 (ov s, 18H, *o*, *p*-Mes), 2.19 (dsp, $^2J_{HP}$ = 18.6 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*(CH$_3$)$_2$), 1.04 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 147.9 (s, 2C, Mes *ipso*-*C*), 132.5 (s, 4C, Mes *ipso*-*C*), 130.6 (s, 2C, Mes Ar-*C*), 128.8 (s, 4C, Mes Ar-*C*), 114.2 (dd, $^2J_{CP}$ = 27.2 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 3,4-pyrrole), 27.2 (d, $^1J_{CP}$ = 61.1 Hz, 4C, P–*C*H(CH$_3$)$_2$), 20.6 (s, 4C, Mes *o*-*C*H$_3$), 20.5 (s, 2C, Mes *p*-*C*H$_3$), 16.6 (s, 4C, CH(*C*H$_3$)$_2$), 15.5 (s, 4C, CH(*C*H$_3$)$_2$). One aromatic carbon (2,5-pyrrole) was not observed. ^{31}P{^{1}H} NMR (d_6-benzene): δ 19.2 (s).

Synthesis of Na$\mathbf{L^{Dipp}}$. $\mathbf{L^{Dipp}}$ (115.6 mg, 0.1779 mmol) and NaH (5.2 mg, 0.23 mmol) were combined in a 25 mL Teflon-sealed glass vessel equipped with a stir bar. The flask was cooled to −78 °C and THF (5 mL) was added under reduced pressure, forming a yellow-brown solution. The vessel was then sealed and heated to 100 °C for 42 h. Volatiles were removed under reduced pressure, after which the residue was reconstituted in 3 mL of toluene and filtered through a pad of Celite® pad. Removal of solvent gave the targeted compound as a tan solid. Yield: 0.1161 g (97.15%). Anal. Calcd (%) for $C_{40}H_{64}N_3NaP_2$: C, 71.50; H, 9.60; N, 6.25. Found: C, 71.83; H, 9.60; N, 6.63. ^{1}H NMR (d_6-benzene): δ 7.04 (d, $^3J_{HH}$ = 7.2 Hz, 4H, *m*-Ar*H*), 6.80 (t, $^3J_{HH}$ = 7.2 Hz, 2H, *p*-Ar*H*), 6.73 (br s, 2H, 3,4-pyrrole), 3.79 (sp, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 2.29 (dsp, $^1J_{HP}$ = 21.1 Hz, $^3J_{HH}$ = 7.0 Hz, 4H, P–C*H*), 1.27–1.06 (ov m, 48H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 148.4 (d, $^2J_{CP}$ = 3.8 Hz, 2C, Dipp *ipso*-*C*), 143.5 (d, $^3J_{CP}$ = 6.0 Hz, 4C, Dipp *ipso*-*C*), 129.5 (dd, $^1J_{CP}$ = 124.5 Hz, $^3J_{CP}$ = 18.8 Hz, 2C, 2,5-pyrrole), 122.5 (s, 4C, Dipp Ar-*C*), 118.3 (s, 2C, Dipp Ar-*C*), 115.8 (dd, $^2J_{CP}$ = 25.7 Hz, $^3J_{CP}$ = 12.0 Hz, 2C, 3,4-pyrrole), 28.5 (d, $^1J_{CP}$ = 64.1 Hz, 4C, P–*C*H(CH$_3$)$_2$), 28.0 (s, 4C, *C*H(CH$_3$)$_2$), 23.8 (s, 4C, CH(*C*H$_3$)$_2$), 17.2 (s, 4C, CH(*C*H$_3$)$_2$), 16.7 (d, $^2J_{CP}$= 3.0 Hz, 8C, P–CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 18.6 (s).

Synthesis of $\mathbf{L^{Pipp}GaCl_2}$ ($\mathbf{1^{Pipp}}$). In a glove box Na$\mathbf{L^{Pipp}}$ (99.6 mg, 0.170 mmol) and $GaCl_3$ (30.1 mg, 0.171 mmol) were combined in a 20 mL scintillation vial equipped with a stir bar. Benzene (4 mL) was added to the vial, forming a yellow solution. The solution was stirred for 24 h, during which a large quantity of precipitate formed. The solution was filtered through a pad of Celite® and solvent removed under reduced pressure to afford an off-white solid. Yield: 97.6 mg (81.3%). Anal. Calcd (%) for $C_{34}H_{52}GaCl_2N_3P_2$: C, 57.89; H, 7.43; N, 5.96. Found: C, 57.57; H, 7.72; N, 6.08. ^{1}H NMR (d_6-benzene): δ 7.62 (dd, $^3J_{HH}$ = 8.4 Hz, $^5J_{HH}$ = 1.8 Hz, 4H, *o*-Ar*H*), 7.07 (d, $^3J_{HH}$ = 8.4 Hz, 4H, *m*-Ar*H*), 6.60 (dd, $^2J_{HP}$ = 2.4 Hz, $^3J_{HH}$ = 1.5 Hz, 2H, 3,4-pyrrole), 2.73 (sp, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$), 2.00 (dd, $^2J_{HP}$ = 23.1 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, P–C*H*), 1.16 (d, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.97 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 0.92 (dd, $^2J_{HP}$ = 3.3 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.87 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 143.3 (s, 2C, Pipp *ipso*-*C*), 143.0 (s, 2C, Pipp *ipso*-*C*), 130.0 (d, $^3J_{CP}$ = 6.0 Hz, 4C, Pipp Ar-*C*), 126.2 (s, 4C, Pipp Ar-*C*), 121.7 (dd, $^1J_{CP}$ = 125.3 Hz, $^3J_{CP}$ = 9.8 Hz, 2C, 2,5-pyrrole), 116.6 (dd, $^2J_{CP}$ = 10.6 Hz, $^3J_{CP}$ = 8.3 Hz, 2C, 3, 4-pyrrole), 33.6 (s, 2C, *C*H(CH$_3$)$_2$), 26.6 (d, $^1J_{CP}$ = 55.1 Hz, 4C, P–*C*H(CH$_3$)$_2$), 24.1 (s, 2C, CH(*C*H$_3$)$_2$), 15.7 (s, 2C, CH(*C*H$_3$)$_2$), 15.2 (s, 8C, P–CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 35.1 (s).

Synthesis of $\mathbf{L^{Mes}GaCl_2}$ ($\mathbf{1^{Mes}}$). In a glove box Na$\mathbf{L^{Mes}}$ (66.9 mg, 0.114 mmol) and $GaCl_3$ (20.2 mg, 0.115 mmol) were combined in a 20 mL scintillation vial equipped with a stir bar. Benzene (3 mL) was added to the vial, forming a yellow solution. The solution was stirred for 20 h, during which a large quantity of precipitate formed. The solution was filtered through a pad of Celite® and solvent removed under reduced pressure to afford a pale-yellow solid. Yield: 61.6 mg (76.6%). Anal. Calcd (%) for $C_{34}H_{52}GaCl_2N_3P_2$: C, 57.89; H, 7.43; N, 5.96. Found: C, 57.92; H, 7.79; N, 6.02. ^{1}H NMR (d_6-benzene): δ 6.85 (s, 4H, *m*-Ar*H*), 6.77 (d, $^2J_{HP}$ = 15.0 Hz, 2H, 3,4-pyrrole), 2.60 (s, 12H, *o*-Mes C*H*$_3$), 2.29–2.10 (ov m, 10H, *p*-Mes C*H*$_3$ and P–C*H*), 1.16 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 0.70 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 141.2 (d, $^2J_{CP}$ = 1.5 Hz, 2C, Mes *ipso*-*C*), 137.1 (d, $^3J_{CP}$ = 2.3 Hz, 4C, Mes *ipso*-*C*), 132.3 (d, $^5J_{CP}$ = 1.5 Hz, 2C, Mes *ipso*-*C*), 128.4 (s, 4C, Mes Ar-*C*), 121.7 (dd, $^1J_{CP}$ = 119.2 Hz, $^3J_{CP}$ = 9.8 Hz, 2C, 2,5-pyrrole), 119.0 (dd, $^2J_{CP}$ = 9.8 Hz, $^3J_{CP}$ = 3.0 Hz, 2C, 3,4-pyrrole), 27.6 (d, $^1J_{CP}$ = 55.1 Hz, 4C, P–*C*H(CH$_3$)$_2$), 21.4 (s, 4C, Mes *o*-*C*H$_3$), 20.8 (s, 2C, Mes *p*-*C*H$_3$), 17.8 (s, 4C, CH(*C*H$_3$)$_2$), 16.6 (s, 4C), CH(*C*H$_3$)$_2$. ^{31}P{^{1}H} NMR (d_6-benzene): δ 33.6 (s).

Synthesis of $\mathbf{L^{Dipp}GaCl_2}$ ($\mathbf{1^{Dipp}}$). In a glove box a mixture of Na$\mathbf{L^{Dipp}}$ (241.7 mg, 0.3597 mmol) and $GaCl_3$ (63.3 mg, 0.359 mmol) were combined with benzene (8 mL) in a 20 mL scintillation vial equipped with a stir bar. The yellow solution was allowed to stir for 24 h, during which a substantial amount of solid precipitated. The solution was filtered through a pad of Celite®, after which solvent was removed under reduced pressure to yield an off-white solid (284.0 mg, 87.32%). Anal. Calcd (%) for $C_{40}H_{64}GaCl_2N_3P_2$: C, 60.85; H, 8.17; N, 5.32. Found: C, 60.58; H, 7.99; N, 5.01. ^{1}H NMR (d_6-benzene): δ 7.14 (ov m, 6H, *m*-Ar*H*), 6.78 (d, $^3J_{HP}$ = 3.3 Hz, 2H, 3,4-pyrrole), 3.74 (sp, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 2.69 (dsp, $^2J_{HP}$ = 25.5 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, P–C*H*), 1.59 (br s, 12H, CH(C*H*$_3$)$_2$), 1.23 (ov m, 12H, CH(C*H*$_3$)$_2$), 1.15 (dd, $^3J_{HP}$ = 16.8 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.87 (dd, $^3J_{HP}$ = 16.1 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 147.3 (d, $^2J_{CP}$ = 5.4 Hz, 2C, Dipp *ipso*-*C*), 140.9 (d, $^3J_{CP}$ = 5.3 Hz, 4C, Dipp *ipso*-*C*), 128.1 (s, 4C, Dipp Ar-*C*), 124.7 (s, 2C, Dipp Ar-*C*), 123.9 (dd, $^1J_{CP}$ = 118.5 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 2,5-pyrrole), 122.1 (dd, $^2J_{CP}$ = 16.6 Hz, $^3J_{CP}$ = 9.8 Hz, 2C, 3,4-pyrrole), 29.0 (d, $^1J_{CP}$ = 55.8 Hz, 4C, P–*C*H(CH$_3$)$_2$), 28.0 (s, 4C, *C*H(CH$_3$)$_2$), 24.8 (br s, 8C, P–CH(*C*H$_3$)$_2$), 18.7 (s, 4C, CH(*C*H$_3$)$_2$), 17.0 (s, 4C, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 33.0 (s).

Synthesis of $\mathbf{L^{Pipp}InCl_2}$ ($\mathbf{2^{Pipp}}$). In a glove box 100.0 mg (0.1703 mmol) of Na$\mathbf{L^{Pipp}}$ and 37.7 mg (0.1704 mmol) of $InCl_3$

were added to a 20 mL scintillation vial equipped with a stir bar. The reagents were dissolved in benzene (4 mL), generating a yellow solution. The solution was allowed to stir for 24 h, over which period a large quantity of precipitate formed. The solution was filtered through a Celite® pad and then dried under vacuum to afford a colourless solid. Yield: 105.8 mg (82.1%). Anal. Calcd (%) for $C_{34}H_{52}InCl_2N_3P_2$: C, 54.42; H, 6.98; N, 5.60. Found: C, 54.35; H, 7.29; N, 5.99. ^{1}H NMR (d_6-benzene): δ 7.55 (d, $^3J_{HH}$ = 7.0 Hz, 4H, *o*-Ar*H*), 7.05 (d, $^3J_{HH}$ = 7.0 Hz, 4H, *m*-Ar*H*), 6.60 (d, $^3J_{HP}$ = 2.1 Hz, 2H, 3,4-pyrrole), 2.67 (sp, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$), 2.02 (dd, $^1J_{HP}$ = 23.1 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, P–C*H*), 1.11 (d, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 0.95 (d, $^3J_{HH}$ = 7.2 Hz, 6H, P–CH(C*H*$_3$)$_2$), 0.90 (dd, $^3J_{HP}$ = 4.4 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.85 (d, $^3J_{HH}$ = 7.2 Hz, 6H, P–CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 143.4 (d, $^2J_{CP}$ = 3.0 Hz, 2C, Pipp *ipso-C*), 143.3 (s, 2C, Pipp ipso-*C*), 128.8 (d, $^3J_{CP}$ = 6.0 Hz, 4C, Pipp Ar-*C*), 126.7 (s, 4C, Pipp Ar-*C*), 122.2 (dd, $^1J_{CP}$ = 126.8 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 2,5-pyrrole), 117.4 (dd, $^2J_{CP}$ = 10.6 Hz, $^3J_{CP}$ = 9.1 Hz, 2C, 3,4-pyrrole), 33.5 (s, 2C, *C*H(CH$_3$)$_2$), 25.9 (d, $^1J_{CP}$ = 55.8 Hz, 4C, P–*C*H(CH$_3$)$_2$), 24.0 (s, 4C, CH(*C*H$_3$)$_2$), 15.6 (s, 4C, P–CH(*C*H$_3$)$_2$), 15.2 (d, $^2J_{CP}$ = 3.0 Hz, 4C, P–CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 35.9 (s).

Synthesis of L^{Mes}InCl$_2$ (2^{Mes}). In a glovebox NaL^{Mes} (67.1 mg, 0.114 mmol) and InCl$_3$ (25.3 mg. 0.114 mmol) were combined in a 20 mL scintillation vial equipped with a stir bar. Benzene (3 mL) was added to the vial, forming a yellow solution. The solution was stirred for 24 h, during which a large quantity of precipitate formed. The solution was filtered through a pad of Celite®. Removal of solvent under vacuum gave the desired indium complex as an off-white solid in 75.2% yield (64.3 mg). Anal. Calcd (%) for $C_{34}H_{52}InCl_2N_3P_2$: C, 54.42; H, 6.98; N, 5.60. Found: C, 54.61; H, 7.25; N,: 5.94. ^{1}H NMR (d_6-benzene): δ 6.84 (s, 4H, *m-H*), 6.76 (d, $^3J_{HP}$ = 15.0 Hz, 2H, 3,4-pyrrole), 2.56 (s, 12H, *o*-Mes C*H*$_3$), 2.26–2.10 (ov m, 10H, *p*-Mes C*H*$_3$ and P–C*H*), 1.14 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 0.66 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 140.4 (d, $^2J_{CP}$ = 6.0 Hz, 2C, Mes *ipso-C*), 136.4 (d, $^3J_{CP}$ = 5.3 Hz, 4C, Mes *ipso-C*), 132.5 (d, $^4J_{CP}$ = 3.8 Hz, 4C, Mes Ar-*C*), 129.5 (s, 2C, Mes Ar-*C*), 121.9 (dd, $^1J_{CP}$ = 117.0 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 2,5-pyrrole), 119.4 (dd, $^2J_{CP}$ = 9.8 Hz, $^3J_{CP}$ = 8.3 Hz, 2C, 3,4-pyrrole), 27.2 (d, $^1J_{CP}$ = 56.6 Hz, 4C, P–*C*H(CH$_3$)$_2$), 21.1 (s, 4C, Mes *o-C*H$_3$), 20.8 (s, 2C, Mes *p-C*H$_3$), 17.2 (s, 4C, CH(*C*H$_3$)$_2$), 16.3 (s, 4C, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 34.1 (s).

Synthesis of L^{Dipp}InCl$_2$ (2^{Dipp}). In a glove box NaL^{Dipp} (154.9 mg, 0.2305 mmol) and InCl$_3$ (51.3 mg, 0.232 mmol) were combined with 10 mL of benzene in a 20 mL scintillation vial equipped with a stir bar. The yellow solution was stirred for 24 h and then filtered through a pad of Celite®. The solvent was removed under vacuum giving 0.1637 g (85.12%) of a colourless solid. Anal. Calcd (%) for $C_{40}H_{64}InCl_2N_3P_2$: C, 57.56; H, 7.73; N, 5.03. Found: C, 57.83; H, 7.77; N, 4.89. ^{1}H NMR (d_6-benzene): δ 7.17 (br s, 4H, *m*-Ar*H*), 7.11 (br s, 2H, *p*-Ar*H*), 6.79 (d, $^3J_{HP}$ = 3.1 Hz, 2H, 3,4-pyrrole), 3.84 (sp, $^3J_{HH}$ = 6.6 Hz, 4H, C*H*(CH$_3$)$_2$), 2.41 (dsp, $^3J_{HP}$ = 24.6 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, P–C*H*), 1.59 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.25 (br d, $^3J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.20 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.66 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 12.6 Hz, 12H, P–CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 147.4 (d, $^2J_{CP}$ = 5.3 Hz, 2C, Dipp *ipso-C*), 139.5 (s, 4C, Dipp *ipso-C*), 127.9 (s, 4C, Dipp Ar-*C*), 124.4 (s, 2C, Dipp Ar-*C*), 122.1 (dd, $^1J_{CP}$ = 125.1 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 2,5-pyrrole), 119.9 (dd, $^2J_{CP}$ = 17.4 Hz, $^3J_{CP}$ = 9.8 Hz, 2C, 3,4-pyrrole), 28.2 (d, 2C, *C*H(CH$_3$)$_2$), 27.6 (d, 2C, *C*H(CH$_3$)$_2$), 27.2 (d, $^1J_{CP}$ = 55.1 Hz, 4C, P–*C*H(CH$_3$)$_2$), 24.8 (s, 8C, P–CH(*C*H$_3$)$_2$), 17.9 (s, 4C, CH(*C*H$_3$)$_2$), 16.4 (s, 4C, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 33.3 (s).

Synthesis of L^{Pipp}AlMe$_2$ (3^{Pipp}). In a glove box L^{Pipp} (294.8 mg, 0.5214 mmol) was dissolved in 4 mL of pentane in a 20 mL scintillation vial equipped with a stir bar. AlMe$_3$ (115 μL, 4.6 M in hexanes, 0.53 mmol) was added dropwise to the yellow solution, immediately causing a change in colour to dark orange-red, along with vigorous bubbling. The solution was stirred for 18 h, when a large quantity of beige precipitate was observed. THF (~0.2 mL) was added to the mixture which was then stirred for 15 min. The volatiles were removed under reduced pressure leaving a light brown solid. Yield: 306.4 mg (94.51%). Anal. Calcd (%) for $C_{36}H_{58}AlN_3P_2$: C, 69.54; H, 9.40; N, 6.76. Found: C, 65.72; H, 9.26; N, 6.29. ^{1}H NMR (d_6-benzene): δ 7.35 (d, $^3J_{HH}$ = 6.6 Hz, 4H, *o*-Ar*H*), 7.10 (d, $^3J_{HH}$ = 6.6 Hz, 4H, *m*-Ar*H*), 6.58 (d, $^3J_{HP}$ = 2.1 Hz, 2H, 3,4-pyrrole), 2.76 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.12 (dsp, $^2J_{HP}$ = 20.1 Hz, $^3J_{HH}$ = 6.0 Hz, 4H, P–C*H*), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.99 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Pipp CH(C*H*$_3$)$_2$), 0.93 (d, $^3J_{HH}$ = 6.0 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.90 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Pipp CH(C*H*$_3$)$_2$), −0.07 (s, 6H, Al–C*H*$_3$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 146.4 (s, 2C, Pipp *ipso-C*), 141.1 (s, 2C, Pipp *ipso-C*), 127.5 (d, 4C, Pipp Ar-*C*), 126.4 (s, 4C, Pipp Ar-*C*), 124.5 (dd, $^1J_{CP}$ = 133.6 Hz, $^3J_{CP}$ = 11.3 Hz, 2C, 2,5-pyrrole), 115.7 (d, $^2J_{CP}$ = 20.4 Hz, $^3J_{CP}$ = 11.3 Hz, 2C, 3,4-pyrrole), 33.6 (s, 2C, *C*H(CH$_3$)$_2$), 26.0 (d, $^1J_{CP}$ = 53.6 Hz, 4C, P–*C*H(CH$_3$)$_2$), 24.2 (s, 4C, CH(*C*H$_3$)$_2$), 16.1 (s, 4C, P–CH(*C*H$_3$)$_2$), 15.6 (s, 4C, P–CH(*C*H$_3$)$_2$), −5.9 (s, 2C, Al–*C*H$_3$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 35.0 (s).

Synthesis of L^{Mes}AlMe$_2$ (3^{Mes}). In a glove box L^{Mes} (91.1 mg, 0.161 mmol) was suspended in 4 mL of pentane in a 20 mL scintillation vial equipped with a stir bar. AlMe$_3$ (40 μL, 4.6 M in hexanes, 0.18 mmol) was added dropwise causing all solid to dissolve and immediately changing the colour to dark orange-red. Vigorous bubbling was observed. The solution was stirred for 18 h during which a beige precipitate formed. THF (~0.2 mL) was added and the mixture stirred for 15 min. Solvent was removed under reduced pressure leaving an off-white solid. Yield: 93.6 mg (93.4%). Anal. Calcd (%) for $C_{36}H_{58}AlN_3P_2$: C, 69.54; H, 9.40; N, 6.76. Found: C, 66.24; H, 9.25; N, 6.57. ^{1}H NMR (d_6-benzene): δ 6.88 (s, 4H, *m*-Ar*H*), 6.76 (br s, 2H, 3,4-pyrrole), 2.45 (s, 12H, *o*-Mes C*H*$_3$), 2.20–2.08 (ov m, 10H, *p*-Mes C*H*$_3$ and P–C*H*), 1.05 (dd, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.86 (dd, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), −0.35 (s, 6H, Al–C*H*$_3$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 142.8 (d, $^3J_{CP}$ = 3.8 Hz, 4C, Mes *ipso-C*), 134.6 (d, $^2J_{CP}$ = 5.3 Hz, 2C, Mes *ipso-C*), 130.2 (d, $^5J_{CP}$ = 3.0 Hz, 2C, Mes *ipso-C*), 129.4 (d, $^4J_{CP}$ = 2.2 Hz, 4C, Mes Ar-*C*), 128.2 (dd, $^1J_{CP}$ = 120.0 Hz, ^{3}J$_{CP}$ = 10.9 Hz, 2C, 2,5-pyrrole), 118.5

(dd, $^2J_{CP}$ = 19.2 Hz, $^3J_{CP}$ = 10.4 Hz, 2C, 3,4-pyrrole), 28.2 (d, $^1J_{CP}$ = 57.3 Hz, 4C, P–*C*H(CH$_3$)$_2$), 21.2 (s, 4C, Mes *o*-*C*H$_3$), 20.7 (s, 2C, Mes *p*-*C*H$_3$), 17.9 (s, 4C, CH(*C*H$_3$)$_2$), 16.9 (s, 4C, CH(*C*H$_3$)$_2$), −4.2 (s, 2C, Al–*C*H$_3$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 28.5 (s).

Synthesis of $L^{Dipp}AlMe_2$ (3^{Dipp}). In a glove box L^{Dipp} (166.8 mg, 0.2566 mmol) was suspended in 4 mL of pentane in a 20 mL scintillation vial equipped with a stir bar. To this mixture AlMe$_3$ (60 μL, 4.6 M in hexanes, 0.28 mmol) was added dropwise resulting in complete dissolution of all solid, a change in colour to dark orange and vigorous bubbling. The solution was stirred for 18 h whereupon ∼0.2 mL of THF was added. After 15 min of stirring the solvent was removed under vacuum providing a golden brown solid. Yield: 163.7 mg (92.5%). Anal. Calcd (%) for $C_{42}H_{70}AlN_3P_2$: C, 71.46; H, 9.99; N: 5.95. Found: C, 68.03; H, 10.10; N: 6.39. ^{1}H NMR (d_6-benzene): δ 7.17 (d, $^3J_{HH}$ = 6.6 Hz, 4H, *m*-Ar*H*), 7.08 (d, $^3J_{HH}$ = 6.6 Hz, 2H, *p*-Ar*H*), 6.96 (d, $^3J_{HP}$ = 2.1 Hz, 2H, 3,4-pyrrole), 3.63 (sp, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 2.49 (dsp, $^2J_{HP}$ = 11.6 Hz, $^3J_{HH}$ = 6.6 Hz, 4H, P–C*H*), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.91 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 3.0 Hz, 12H, CH(C*H*$_3$)$_2$), −0.33 (s, 6H, Al–C*H*$_3$). ^{13}C{^{1}H} NMR (d_6-benzene): δ 144.5 (s, 2C, Dipp Ar-*C*) 141.0 (d, $^2J_{CP}$ = 2.3 Hz, 2C, Dipp *ipso*-*C*), 129.8 (dd, $^1J_{CP}$ = 109.4 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 2,5-pyrrole), 123.8 (d, $^4J_{CP}$ = 1.5 Hz, 4C, Dipp Ar-*C*), 122.2 (d, $^3J_{CP}$ = 2.3 Hz, 4C, Dipp *ipso*-*C*), 121.7 (dd, $^2J_{CP}$ = 17.4 Hz, $^3J_{CP}$ = 10.6 Hz, 2C, 3,4-pyrrole), 28.9 (br s, 4C, P–*C*H(CH$_3$)$_2$), 28.1 (s, 4C, Dipp *C*H(CH$_3$)$_2$), 24.9 (s, 8C, Dipp CH(*C*H$_3$)$_2$), 16.9 (s, 8C, P–CH(*C*H$_3$)$_2$), −4.9 (s, 2C, Al–*C*H$_3$). ^{31}P{^{1}H} NMR (d_6-benzene): δ 23.6 (s).

Synthesis of $[L^{Pipp}AlMe]^+[MeB(C_6F_5)_3]^-$ (4^{Pipp}). In a glove box $L^{Pipp}AlMe_2$ (113.6 mg, 0.1827 mmol) and 93.5 mg (0.1823 mmol) of B(C$_6$F$_5$)$_3$ were added to a 20 mL scintillation vial equipped with a stir bar. Pentane (5 mL) was added which dissolved the B(C$_6$F$_5$)$_3$ creating a colourless solution. The mixture was stirred for 24 h during which period an orange-brown oil formed. Removal of volatiles under reduced pressure gave a voluminous beige solid. Yield: 188.9 mg (91.3%). Anal. Calcd (%) for $C_{54}H_{58}AlBF_{15}N_3P_2$: C, 57.21; H, 5.16; N, 3.71. Found: C, 50.86; H, 5.39; N, 3.29. ^{1}H NMR (d_5-bromobenzene): δ 7.10 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *o*-Ar*H*), 6.85 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-Ar*H*), 6.77 (br s, 2H, 3,4-pyrrole), 2.67 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.21 (m, 4H, P–C*H*(CH$_3$)$_2$), 1.29 (br s, 3H, B–C*H*$_3$), 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.88–0.79 (ov m, 24H, P–CH(C*H*$_3$)$_2$), −0.66 (s, 3H, Al–C*H*$_3$). ^{11}B{^{1}H} NMR (d_5-bromobenzene): δ −14.0 (br s). ^{13}C{^{1}H} NMR (d_5-bromobenzene): δ 146.7 (s, 2C, Pipp *ipso*-*C*), 138.9 (s, 2C, Pipp *ipso*-*C*), 128.6 (s, 4C, Pipp Ar-*C*), 128.3 (dd, $^1J_{CP}$ = 46.0 Hz, $^3J_{CP}$ = 22.6 Hz, 2C, 2,5-pyrrole), 125.7 (d, $^3J_{CP}$ = 5.3 Hz, 4C, Pipp Ar-*C*), 115.7 (dd, $^2J_{CP}$ = 17.0 Hz, $^3J_{CP}$ = 8.7 Hz, 2C, 3,4-pyrrole), 33.7 (s, 2C, *C*H(CH$_3$)$_2$), 25.9 (d, $^1J_{CP}$= 52.8 Hz, 4C, P–*C*H(CH$_3$)$_2$), 24.1 (s, 4C, CH(*C*H$_3$)$_2$), 15.4 (s, 8C, P–CH(*C*H$_3$)$_2$), −12.6 (br s, Al–*C*H$_3$). MeB(C$_6$F$_5$)$_3^-$ resonances are not reported. ^{19}F{^{1}H} NMR (d_5-bromobenzene): δ −130.4 (d, $^3J_{FF}$ = 19.8 Hz, 6F, *o*-F), −162.6 (t, $^3J_{FF}$ = 19.8 Hz, 3F, *p*-F), −165.1 (t, $^3J_{FF}$ = 19.8 Hz, 6F, *m*-F). ^{31}P{^{1}H} NMR (d_5-bromobenzene) δ 61.9 (s).

Synthesis of $[L^{Mes}AlMe]^+[MeB(C_6F_5)_3]^-$ (4^{Mes}). In a glove box $L^{Mes}AlMe_2$ (102.9 mg, 0.1655 mmol) and B(C$_6$F$_5$)$_3$ (84.8 mg) (0.1653 mmol) were combined with 5 mL of pentane in a 20 mL scintillation vial equipped with a stir bar. The mixture was stirred for 24 h during which an orange oil formed. The solvent was removed under vacuum yielding 175.2 mg (94.9%) of 4^{Mes} as a light orange solid. Anal. Calcd (%) for $C_{54}H_{58}AlBF_{15}N_3P_2$: C, 57.21; H, 5.16; N, 3.71. Found: C, 54.76; H, 4.99; N, 3.80. ^{1}H NMR (d_5-bromobenzene): δ 6.83 (d, $^3J_{HP}$ = 12.6 Hz, 2H, 3,4-pyrrole), 6.71 (s, 4H, *m*-*H*), 2.26 (sp, 4H, $^3J_{HH}$ = 6.9 Hz, P–C*H*(CH$_3$)$_2$), 2.10 (s, 12H, Mes *o*-C*H*$_3$), 2.08 (s, 6H, Mes *p*-C*H*$_3$), 1.28 (br s, 3H, B–C*H*$_3$), 0.86 (dd, $^3J_{HP}$ = 17.4 Hz, $^3J_{HH}$ = 6.9 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.72 (dd, $^3J_{HP}$ = 17.7 Hz, $^3J_{HH}$ = 6.9 Hz, 12H, P–CH(C*H*$_3$)$_2$), −0.86 (s, 3H, Al–C*H*$_3$). ^{11}B{^{1}H} NMR (d_5-bromobenzene): δ −14.0 (br s). ^{13}C{^{1}H} NMR (d_6-benzene): δ 140.7 (s, 4C, Mes *ipso*-*C*), 136.7 (s, 2C, Mes *ipso*-*C*), 134.6 (d, $^3J_{CP}$ = 3.0 Hz, 2C, Mes *ipso*-*C*), 127.8 (s, 4C, Mes Ar-*C*), 124.4 (dd, $^1J_{CP}$ = 109.6 Hz, $^3J_{CP}$ = 9.8 Hz, 2C, 2,5-pyrrole), 115.1 (dd, $^2J_{CP}$ = 22.8 Hz, $^3J_{CP}$ = 9.8 Hz, 2C, 3,4-pyrrole) 25.4 (d, $^1J_{CP}$ = 58.0 Hz, 4C, P–*C*H(CH$_3$)$_2$), 20.7 (s, 4C, Mes *o*-*C*H$_3$), 19.5 (s, 2C, Mes *p*-*C*H$_3$), 16.1 (s, 4C, P–CH(*C*H$_3$)$_2$), 15.2 (d, $^2J_{CP}$ = 9.0 Hz, 4C, P–CH(*C*H$_3$)$_2$), −10.7 (br s, Al–*C*H$_3$). MeB(C$_6$F$_5$)$_3^-$ resonances are not reported. ^{19}F{^{1}H} NMR (d_5-bromobenzene): δ −130.9 (d, $^3J_{FF}$ = 19.8 Hz, 6F, *o*-F), −162.3 (t, $^3J_{FF}$ = 19.8 Hz, 3F, *p*-F), −164.8 (t, $^3J_{FF}$ = 19.8 Hz, 6F, *m*-F). ^{31}P{^{1}H} NMR (d_5-bromobenzene): δ 53.2 (s).

Synthesis of $[L^{Dipp}AlMe]^+[MeB(C_6F_5)_3]^-$ (4^{Dipp}). In a glove box $L^{Dipp}AlMe_2$ (41.2 mg, 0.0584 mmol), B(C$_6$F$_5$)$_3$ (29.9 mg, 0.0583 mmol) and 5 mL of pentane were combined in a 20 mL scintillation vial equipped with a stir bar. After 24 h of stirring an orange-brown oil had formed. The solvent was removed under reduced pressure to afford a beige solid. Yield: 68.2 mg (94.7%). Anal. Calcd (%) for $C_{60}H_{70}AlBF_{15}N_3P_2$: C, 59.17; H, 5.79; N, 3.45. Found: C, 55.18; H, 5.85; N: 3.76. ^{1}H NMR (d_5-bromobenzene): δ 7.01 (ov m, 6H, Dipp-*H*), 6.94 (br s, 2H, 3,4-pyrrole), 2.86 (sp, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 2.20 (br sp, 4H, $^3J_{HH}$ = 7.2 Hz, P–C*H*(CH$_3$)$_2$), 1.29 (br s, 3H, B–C*H*$_3$), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 0.94 (dd, $^3J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, P–CH(C*H*$_3$)$_2$), 0.73 (dd, $^3J_{HP}$ = 18.6 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), −0.96 (s, 3H, Al–C*H*$_3$). ^{11}B{^{1}H} NMR (d_5-bromobenzene): δ −13.9 (br s). ^{13}C{^{1}H} NMR (d_6-benzene): δ 145.8 (d, $^2J_{CP}$ = 4.8 Hz, 2C, Dipp *ipso*-*C*), 137.7 (d, $^3J_{CP}$ = 3.0 Hz, 4C, Dipp *ipso*-*C*), 128.2 (s, 2C, Dipp Ar-*C*), 125.4 (s, 4C, Dipp Ar-*C*), 122.8 (d, $^3J_{CP}$ = 9.8 Hz, 2C, 2,5-pyrrole), 114.5 (br s, 2C, 3, 4-pyrrole), 29.7 (s, 2C, *C*H(CH$_3$)$_2$), 25.8 (s, 2C, *C*H(CH$_3$)$_2$), 25.5 (d, $^1J_{CH}$ = 66.4, 4C, P–*C*H(CH$_3$)$_2$), 24.5 (s, 8C, *C*H(CH$_3$)$_2$), 16.3 (br s, 4C, P–CH(*C*H$_3$)$_2$), 15.5 (br s, 4C, P–CH(*C*H$_3$)$_2$), −12.9 (br s, Al–*C*H$_3$). MeB(C$_6$F$_5$)$_3^-$ resonances are not reported. ^{19}F{^{1}H} NMR (d_5-bromobenzene): δ −130.3 (d, $^3J_{FF}$ = 19.8 Hz, 6F, *o*-F), −162.6 (t, $^3J_{FF}$ = 19.8 Hz, 3F, *p*-F), −165.1 (t, $^3J_{FF}$ = 19.8 Hz, 6F, *m*-F). ^{31}P{^{1}H} NMR (d_5-bromobenzene): δ 46.4 (s).

Conflicts of interest

The authors declare no competing financial interests.

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