

# Donor-Stabilized Monocarba-Bridged Bis(cyclopentadienyl)alanes

Wasim Haider, Volker Huch, Bernd Morgenstern, and André Schäfer\*<sup>[a]</sup>

Five monocarba-bridged bis(cyclopentadienyl)aluminum halide NHC and thione complexes and one monocarba-bridged bis(cyclopentadienyl)phosphanylalane NHC complex are reported. The former were synthesized by transmetalation of a C[1] magnesocenophane with the corresponding aluminum(III) chloride and aluminum(III) bromide donor adducts. The phosphanylalane complex was obtained by a subsequent functional-

ization of the corresponding bromoalane with lithium diphenylphosphide. All complexes were characterized in solution by multinuclear NMR spectroscopy and in the solid state by single crystal X-ray diffraction. Bonding energies of the NHC and thione ligands to the aluminum centres were estimated by DFT calculations.

## 1. Introduction

Alanes, more specifically trivalent aluminum compounds, are usually electron-deficient species and therefore possess Lewis acidic character and tend to form strong Lewis complexes with various  $\sigma$  donor ligands.<sup>[1]</sup> Such donor-stabilized alanes have been studied extensively and have attracted much attention for their applications, for instance in homogenous catalysis and in chemical vapor deposition processes.<sup>[2,3]</sup> Among such donor complexes of aluminum compounds, different mono-, bis- and tris(cyclopentadienyl)alane complexes with donors such as ethers, isonitriles, pyridines and carbenes have been reported (Figure 1).<sup>[4]</sup> In principle, the bonding of cyclopentadienyl substituents to an aluminum atom can vary between  $\sigma$  bonding and  $\pi$  complexation, thus hapticities of  $\eta^1$  to  $\eta^5$ , which is influenced by both electronic and steric factors of the ligands and the aluminum center.<sup>[5]</sup> Noteworthy, only few examples of bis(cyclopentadienyl) aluminum compounds with interlinked cyclopentadienyl moieties, which are structurally closely related to metallocenophanes, are known.<sup>[6]</sup> The first examples of this class of compounds, which was a dicarba-bridged system reported by Shapiro and coworkers, displayed different hapticities of the cyclopentadienyl groups of  $\eta^1$  and  $\eta^2$ , I, II, depending on the coordination environment of the aluminum atom.<sup>[6a]</sup> Our group recently reported a related disila-bridged systems with all  $\eta^1$   $\sigma$  bonded cyclopentadienyl groups, III,<sup>[6b]</sup> as well as an imine

substituted dicarba-bridged system with  $\eta^1$  and  $\eta^2$  bonded cyclopentadienyl groups, IV,<sup>[6c]</sup> and a bis(carba[2]aluminocenophane), possessing two  $\eta^5$  bonded cyclopentadienyl groups on each aluminum atom - the first neutral aluminum compound with such a bonding motif.<sup>[6c]</sup>

Moreover, nearly all bis(cyclopentadienyl)alanes possess either alkyl groups or halides as third substituents; none are pnictogenyl-functionalized.<sup>[5-7]</sup> This is surprising since pnictogenylalanes, such as phosphanylalanes, are well known compounds, especially in the form of donor-complexes, and have attracted much attention due to their very polar and reactive Al-Pn bonds.

With our groups continuous interest in main group cyclopentadienyl compounds, such as metallocenes and metallocenophanes, we have extended our study of bridged bis(cyclopentadienyl)alanes, and herein we present different monocarba-bridged bis(cyclopentadienyl)alane NHC and thione complexes with halide and phosphanyl substituents.

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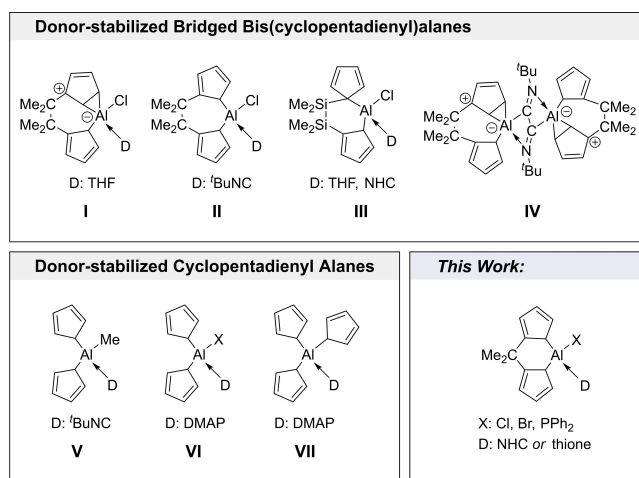


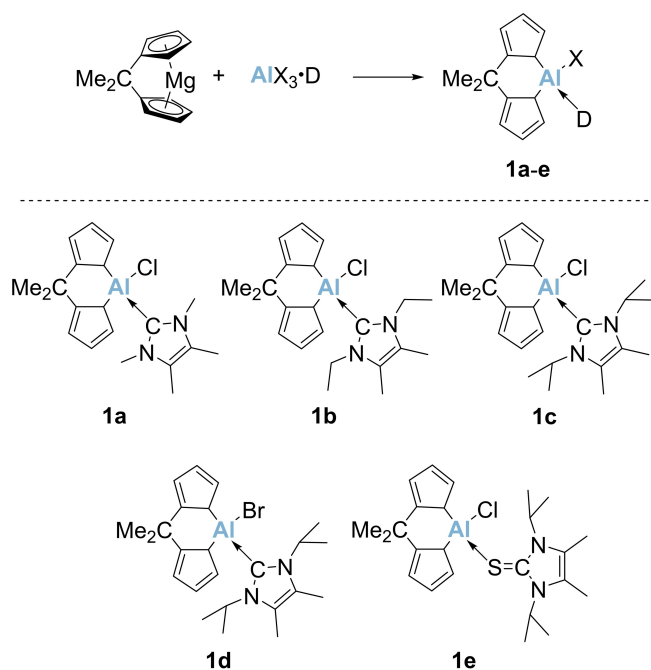
Figure 1. Selected examples of cyclopentadienyl-substituted aluminum donor complexes.

## 2. Results and Discussion

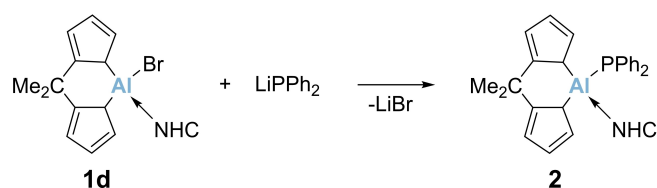
It has previously been shown that magnesocenes and magnesocenophanes are excellent Cp-transfer reagents in the synthesis of cyclopentadienyl alanes.<sup>[5a,6]</sup> Following this concept, the monocarba-bridged bis(cyclopentadienyl)alane NHC and thione complexes **1a–e** could be obtained by transmetalation of a corresponding C[1]magnesocenophane with *in-situ* generated aluminum(III) halide NHC and thione adducts (Scheme 1).

Complexes **1a–e** were obtained as air and moisture sensitive colorless solids and are stable at room temperature in the solid state and in solution for prolong periods of time. Different N-heterocyclic carbenes could be introduced, with 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene as the bulkiest example. In case of aluminum chloride adducts of even bulkier carbenes, such as 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIDipp) and a cyclic(amino)(alkyl)carbene (<sup>Me</sup>CAAC), no transmetalation reaction was observed at room temperature.

To investigate the possibility of functionalization of the aluminium halide moiety, in these bis(cyclopentadienyl)alanes, compound **1d** was treated with lithium diphenylphosphide in toluene. This resulted in a uniform reaction, yielding phosph-



**Scheme 1.** Synthesis of monocarba-bridged bis(cyclopentadienyl)alane NHC and thione complexes **1a–e**.

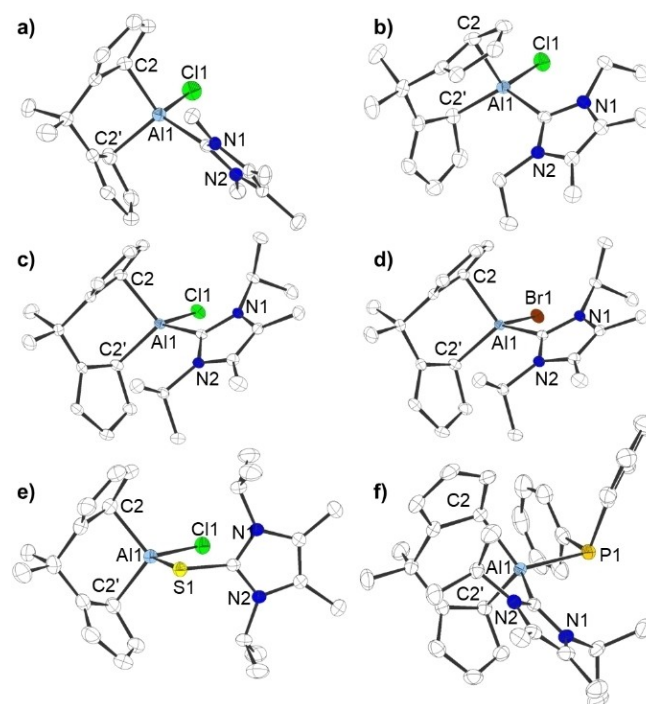


**Scheme 2.** Synthesis of phosphanylalane **2** (NHC: 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene).

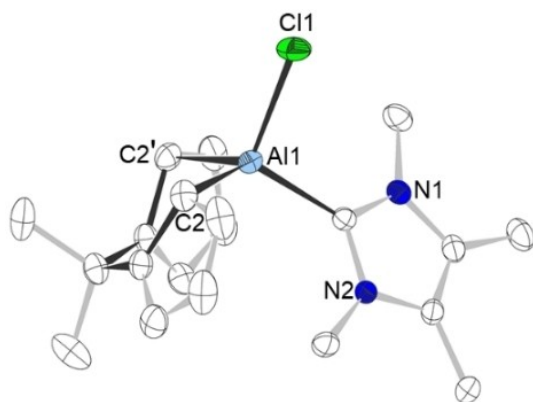
nylthane **2** in 65% isolated yield, as a colorless crystalline solid (Scheme 2).

Crystals of compounds **1a–e** and **2** suitable for single crystal X-ray diffraction could be obtained from saturated toluene solutions at 253 K and allowed for structural characterization of these species (Figure 2). In all complexes, **1a–e** and **2**, the ligand adopts a butterfly-like arrangement and binds to the aluminum center in an  $\eta^1 \sigma$ , 2,2'-type fashion, forming a six membered ring in chair conformation, with the halide or phosphorous atom in the axial and the NHC or thione ligand in equatorial position (Figure 3). This six membered ring conformation is believed to be the energetically most favorable conformation, and a similar arrangement was observed before in case of disila-bridged bis(cyclopentadienyl)alanes.<sup>[6b]</sup>

In compounds **1a–e** and **2**, the aluminum atom is tetrahedral coordinated with  $\sigma$  bonded cyclopentadienyl rings. Accordingly, longer and shorter C–C bonds are found within the Cp-rings, correlating to single and double bonds (C=C: 134.7–138.0 pm; C–C: 142.9–148.0 pm). The two Al–C<sup>Cp</sup> bonds are exhibiting slight differences in lengths, by 2–4 pm (Table 1). This is in accordance with the Al–C<sup>Cp</sup> bond lengths in the previously reported disila- and dicarba-bridged systems, II,III, and in unbridged donor stabilized cyclopentadienylalanes, V–VII, which average between 200.9 pm and 208.0 pm.<sup>[4,6a,b]</sup> The steric demand of the coordinated NHC ligands has only a minimal influence on the Al–C<sup>NHC</sup> bond lengths, with small elongation of the Al–Cl bonds observed from **1a** (202.3 pm) to **1b** (203.2 pm) to **1c** (204.0 pm). A slightly longer Al–C<sup>NHC</sup> bond



**Figure 2.** Molecular structures of a) **1a**, b) **1b**, c) **1c**, d) **1d**, e) **1e**, f) **2**, in the crystal (displacement ellipsoids for 50% probability level; H-atoms omitted for clarity). Selected bond lengths: Al–D: **1a**: 202.28(12) pm; **1b**: 203.17(13) pm; **1c**: 203.98(12) pm; **1d**: 203.66(14) pm; **1e**: 228.87(6), 2: 206.18(13) pm; Al–X: **1a** (X=Cl): 216.96(5) pm, **1b** (X=Cl): 217.12(5) pm, **1c** (X=Cl): 218.71(5) pm, **1d**: (X=Br) 235.42(5) pm, **1e** (X=Cl): 216.14(6), **2** (X=P): 240.18(5) pm.



**Figure 3.** Molecular structure of **1a** in the crystal, highlighting its six-membered ring chair conformation (displacement ellipsoids for 50% probability level; H-atoms omitted for clarity).

Compounds	Al-X <sup>[a]</sup> bond length [pm]	Al-D bond length [pm]	Al-C <sup>cp</sup> bond length [pm]	$\delta$ <sup>27</sup> Al [ppm]	E(Al-D) <sup>[b]</sup> [kJ mol <sup>-1</sup> ]
<b>1a</b>	217.0	202.3	201.7 204.7	125	-233.8
<b>1b</b>	217.1	203.2	204.7 202.3	126	-239.2
<b>1c</b>	218.7	204.0	203.9 201.9	127	-244.9
<b>1d</b>	235.4	203.7	203.3 201.3	124	-244.4
<b>1e</b>	216.1	228.9	203.7	134	-176.5
<b>2</b>	240.4	206.2	202.7 206.3	138	-222.8

[a] X = Cl (**1a–c, e**), X = Br (**1d**), X = P (**2**). [b] Calculated at B3LYP-D3/def2-TZVP.<sup>[8]</sup>

of 206.2 pm is observed in case of phosphanylalane **2** (Table 1), which is in-line with the electron donating character of the phosphanyl group. In addition, the Al–P bond length of 240.4 pm is in agreement with an Al–P single bond, which is also depicted by the strong pyramidalization of the phosphorous atom ( $\Sigma\angle P$ : 307.8°).

It has previously been observed for the dicarba- and disila-bridged bis(cyclopentadienyl) systems, I–III, that the aluminum atom undergoes a rapid [1,5] sigmatropic rearrangement in solution at room temperature.<sup>[6a,b]</sup> It is unclear whether this is also the case for compounds **1a–e** and **2**, since the <sup>1</sup>H NMR spectra display four signals for the cyclopentadienyl protons and the <sup>13</sup>C NMR spectra display five signals for ring carbon atoms of the Cp groups, which is in-line with the 2,2'-type coordination observed in the solid state. Interestingly, relatively upfield shifted signals for the Cp carbon atoms bonded to the aluminum atoms are detected in the <sup>13</sup>C NMR spectra ( $\delta^{13}C = 59.2$ – $68.9$ ), possibly indicating that **1a–e** and **2**, possess a static structure in solution, unlike previously reported bis(cyclopentadienyl) systems, I–III.

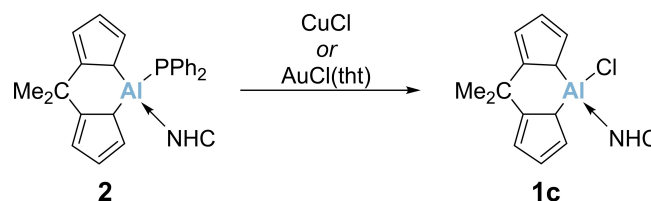
In order to investigate how strongly the NHC and thione ligands are coordinated to the aluminum atoms in **1a–e** and **2**, DFT calculation at the B3LYP-D3/def2-TZVP<sup>[8]</sup> level of theory were executed. Notably, a slight increase in bonding energy is observed, when going from complex **1a** with the sterically less demanding N-methyl substituted carbene to complexes **1b** and **1c** with the sterically more demanding N-ethyl and N-isopropyl substituted carbenes (Table 1). This is most likely related to attractive dispersion forces, as has been recognized before for main group metallocene NHC complexes.<sup>[9]</sup> Furthermore, the bond strength of the Al–C<sup>NHC</sup> bond in bromoalane **1d** is about the same than in chloroalane **1c**, indicating that the halide substituent has little influence on the carbene coordination. In addition, the substitution of the electron withdrawing groups (Cl, Br) in **1c,d** with an electron donating group (PPh<sub>2</sub>) in **2** led to a decrease in the bonding energy by ca. 22 kJ mol<sup>-1</sup> (Table 1). Since the thione ligand in complex **1e** is a significantly weaker donor than the carbene ligand in complex **1c**, a lower complexation energy of 176.5 kJ mol<sup>-1</sup> ( $\Delta E = 61.2$  kJ mol<sup>-1</sup>) is predicted.

Phosphanylalanes, such as complex **2**, exhibiting a polar Al–P single bond, have attracted much attention in the past for their reactivities, which include coordination of transition metal fragments to the phosphorous atom and insertion reactions into the aluminum phosphorous bond.<sup>[10,11]</sup> In this regard, it is noteworthy that phosphanylalanes with cyclopentadienyl groups bonded the aluminum atom are, to the best of our knowledge, unknown, which encouraged us to investigate the reactivity of phosphanylalane **2** towards different transition metals compounds (Scheme 3).

Interestingly, the steric demand of the *ansa*-ligand system in conjunction with the coordinated NHC seems to make the phosphorous atom relatively inaccessible. Treatment of phosphanylalane **2** with W(CO)<sub>5</sub>(thf) in thf at room temperature led to a complex mixture of products, from which the desired tungsten complex could not be isolated. The reaction of phosphanylalane **2** with sterically less demanding transition metal compounds like CuCl and AuCl(tht) led to a cleavage of the Al–P bond and formation of chloroalane **1c** as the major product.

### 3. Conclusions

In this contribution, we have expanded our investigation towards donor complexes of bridged bis(cyclopentadienyl) alanes, and we present six new donor complexes of mono-carba-bridged bis(cyclopentadienyl)alanes, **1a–e**, **2**. These com-



**Scheme 3.** Reactions of phosphanylalane **2** with CuCl and AuCl(tht) (NHC: 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene).

pounds, which are structurally derived from metallocenophanes of aluminum, were characterized in solution and in the solid state, supported by DFT calculations. The Al–P bond in phosphanylalane **2** was found to be a reactive side in the molecule and is easily cleaved by treatment with CuCl or AuCl (tht).

## Experimental Section

All manipulations were carried out under an argon inert gas atmosphere (argon 5.0), using either Schlenk line techniques or a glovebox. Aluminum trichloride and aluminum tribromide were purchased from Sigma Aldrich and used as received. The other starting materials, Me<sub>2</sub>C[1]magnesocenophane<sup>[12]</sup>, lithium diphenylphosphide (obtained as a yellow highly air-sensitive solid from the reaction of *n*-butyllithium and diphenylphosphane)<sup>[13]</sup>, NHCs<sup>[14]</sup> and thione<sup>[14]</sup> were synthesized following literature established procedures. NMR spectra were recorded on a Bruker Avance III 400 spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced using the solvent signals<sup>[15]</sup> ( $\delta^1\text{H}(\text{C}_6\text{HD}_5) = 7.16$ ;  $\delta^{13}\text{C}(\text{C}_6\text{D}_6) = 128.06$ ). <sup>27</sup>Al and <sup>31</sup>P NMR spectra were referenced using external standards ( $\delta^{27}\text{Al}(\text{AlCl}_3 \text{ in } \text{D}_2\text{O}) = 0$ ) ( $\delta^{31}\text{P}(85\% \text{ H}_3\text{PO}_4 \text{ in } \text{D}_2\text{O}) = 0$ ). Elemental analysis was performed on an Elementar vario MICROcube®. Single crystal X-ray diffraction analysis were carried out at low temperatures on Bruker AXS X8 Apex CCD and Bruker AXS D8 Venture diffractometers. Structure solution and refinement was performed using SHELX<sup>[16]</sup>.

### Synthesis of Bis(cyclopentadienyl)alanes 1 a-e

The aluminum trihalide donor adducts used in the synthesis of **1 a-e** were generated *in situ*. The corresponding aluminum trihalide (**1 a**: 0.69 g/5.13 mmol AlCl<sub>3</sub>; **1 b**: 0.69 g/5.13 mmol AlCl<sub>3</sub>; **1 c**: 2.06 g/15.4 mmol AlCl<sub>3</sub>; **1 d**: 3.0 g/11.2 mmol AlBr<sub>3</sub>; **1 e**: 2.06 g/15.4 mmol AlCl<sub>3</sub>) and the corresponding NHC or thione (**1 a**: 0.64 g/5.13 mmol NHC; **1 b**: 0.78 g/5.13 mmol NHC; **1 c**: 2.78 g/15.4 mmol NHC; **1 d**: 2.03 g/11.2 mmol NHC; **1 e**: 3.27 g/15.4 mmol thione) were suspended in 10 mL of toluene and stirred for 15–20 min until all components were completely dissolved. The resulting solution was then used directly in the synthesis of **1 a-e**. To a suspension of Me<sub>2</sub>C[1]magnesocenophane (**1 a,b**: 1.0 g/5.13 mmol; **1 c**: 3.0 g/15.4 mmol; **1 d**: 2.18 g/11.2 mmol; **1 e**: 3.0 g/15.4 mmol) in 50 mL of toluene was slowly added a toluene solution of the corresponding aluminium trihalide donor adduct and the mixture was stirred at room temperature overnight. After filtration, the filtrate was concentrated to approximately 20 mL and stored at 253 K overnight. The colourless crystalline precipitate was collected, washed with small portions of cold toluene and dried *in vacuo*.

**1 a**: Yield: 41% (0.73 g). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 6.91$  (d,  $J = 4.4$  Hz, 2H), 6.31 (dd,  $J = 2.5, 1.5$  Hz, 2H), 6.23 (dd,  $J = 4.5, 2.4$  Hz, 2H), 4.91 (s, 2H), 2.69 (s, 6H), 1.90 (s, 3H), 1.76 (s, 3H), 0.98 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 157.6, 127.5, 125.9, 121.9, 115.3, 65.7, 39.1, 34.0, 34.0, 27.5, 7.8$ ; <sup>27</sup>Al{<sup>1</sup>H} NMR (104.26 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta = 125$ ; Elemental analysis for C<sub>30</sub>H<sub>26</sub>AlClN<sub>2</sub>: calculated: 67.31% C, 7.34% H, 7.85% N; found: 66.64% C, 7.14% H, 7.83% N.

**1 b**: Yield: 20% (0.39 g). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 6.90$  (d,  $J = 4.6$  Hz, 2H), 6.32 (dd,  $J = 4.6, 2.3$  Hz, 2H), 6.17 (dd,  $J = 2.3, 1.3$  Hz, 2H), 5.04 (s, 2H), 3.20 (q,  $J = 7.2$  Hz, 4H), 1.91 (s, 3H), 1.78 (s, 3H), 1.12 (s, 6H), 0.87 (t,  $J = 7.1$  Hz, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 158.6, 129.3, 126.1, 122.4, 111.6, 68.9, 42.8, 39.2, 34.0, 28.0, 16.5, 8.0$ ; <sup>27</sup>Al{<sup>1</sup>H} NMR (104.26 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta = 126$ ;

Elemental analysis for C<sub>22</sub>H<sub>30</sub>AlClN<sub>2</sub>: calculated: 68.65% C, 7.86% H, 7.28% N; found: 68.22% C, 7.85% H, 6.87% N.

**1 c**: Yield: 70% (4.45 g). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 6.88$  (d,  $J = 4.5$  Hz, 2H), 6.37 (dd,  $J = 2.4, 1.5$  Hz, 2H), 6.26 (dd,  $J = 4.5, 2.4$  Hz, 2H), 4.86 (s, 2H), 3.67 (m, 2H), 1.89 (s, 3H), 1.72 (s, 3H), 1.36 (s, 6H), 1.03 (d,  $J = 6.9$  Hz, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 158.6, 128.5, 126.9, 122.2, 116.5, 64.0, 52.6, 39.1, 22.3, 10.1$ ; <sup>27</sup>Al{<sup>1</sup>H} NMR (104.26 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 127$ ; Elemental analysis for C<sub>24</sub>H<sub>34</sub>AlClN<sub>2</sub>: calculated: 69.80% C, 8.30% H, 6.53% N; found: 69.37% C, 8.28% H, 7.28% N.

**1 d**: Yield: 56% (2.87 g). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 6.90$  (dt,  $J = 4.5, 1.5$  Hz, 2H), 6.38 (dd,  $J = 2.5, 1.5$  Hz, 2H), 6.26 (dd,  $J = 4.5, 2.4$  Hz, 2H), 4.89 (s, 2H), 3.67 (sept,  $J = 6.9$  Hz, 2H), 1.87 (s, 3H), 1.70 (s, 3H), 1.34 (s, 6H), 1.02 (d,  $J = 6.9$  Hz, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 158.6, 128.8, 127.1, 122.4, 117.0, 64.2, 52.7, 39.1, 35.1, 27.1, 22.3, 10.0$ ; <sup>27</sup>Al{<sup>1</sup>H} NMR (104.26 MHz, C<sub>6</sub>D<sub>6</sub>, 294 K):  $\delta = 124$ ; Elemental analysis for C<sub>24</sub>H<sub>34</sub>AlBrN<sub>2</sub>: calculated: 63.02% C, 7.49% H, 6.12% N; found: 63.15% C, 7.59% H, 6.42% N.

**1 e**: Yield: 39% (2.64 g). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 6.90$  (dt,  $J = 3.3, 1.6$  Hz, 2H), 6.72 (t,  $J = 2.1, 2$ Hz), 6.62 (dd,  $J = 4.5, 2.5$  Hz, 2H), 5.47 (m, 2H), 4.84 (s, 2H), 2.01 (s, 3H), 1.76 (s, 3H), 1.32 (s, 6H), 1.03 (d,  $J = 7.1$  Hz, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 155.8, 146.4, 126.8, 125.5, 122.2, 117.3, 64.0, 51.3, 39.2, 33.2, 27.2, 20.5, 9.6$ ; <sup>27</sup>Al{<sup>1</sup>H} NMR (104.26 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K):  $\delta = 134$ ; Elemental analysis for C<sub>24</sub>H<sub>34</sub>AlClSN<sub>2</sub>: calculated: 64.77% C, 7.70% H, 6.29% N; found: 64.52% C, 7.67% H, 5.92% N.

### Synthesis of Phosphanylalane 2

Compound **1 d** (500 mg/1.09 mmol) and lithium diphenyl phosphide (209 mg/1.09 mmol) were charged into a Schlenk flask. 20 mL of toluene were added, and the mixture was stirred overnight at room temperature. After filtration, the solution was concentrated to approximately 20 mL and stored at 253 K overnight, resulting in the crystallization of **2**. Isolation of the precipitate and drying *in vacuo* yielded the product as a colourless crystalline solid.

Yield: 65% (0.40 g). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 7.82$ –7.75 (m, 4H), 7.16–7.08 (m, 4H), 7.03–6.97 (m, 2H), 6.78 (dt,  $J = 4.4, 1.3$  Hz, 2H), 6.39 (dd,  $J = 2.3, 1.5$  Hz, 2H), 6.31 (dd,  $J = 4.5, 2.4$  Hz, 2H), 4.61 (s, 2H), 3.98 (m, 2H), 1.87 (s, 3H), 1.47 (s, 3H), 1.30 (s, 6H), 1.12 (d,  $J = 6.9$  Hz, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 160.3, 142.1$  (d,  $J = 22.6$  Hz), 134.1 (d,  $J = 15.7$  Hz), 129.0, 128.7 (d,  $J = 5.9$  Hz), 128.6, 127.1, 126.2, 121.9, 116.3, 59.2, 52.5 (d,  $J = 12.3$  Hz), 38.9, 35.0, 27.1, 22.7, 10.2; <sup>27</sup>Al{<sup>1</sup>H} NMR (104.26 MHz, C<sub>6</sub>D<sub>6</sub>, 294 K):  $\delta = 138$ ; <sup>31</sup>P{<sup>1</sup>H} NMR (161.97 MHz, C<sub>6</sub>D<sub>6</sub>, 294 K)  $\delta = -51.1$ ; Elemental analysis for C<sub>36</sub>H<sub>44</sub>AlPN<sub>2</sub>: calculated: 76.84% C, 7.88% H, 4.98% N; found: 75.57% C, 7.99% H, 4.85% N.

### Reaction of Phosphanylalane 2 and CuCl

Phosphanylalane **2** (300 mg/0.32 mmol) and CuCl (32 mg, 0.32 mmol) were dissolved in 5 mL of thf. The mixture was stirred overnight at room temperature. A dark precipitate, presumable Cu<sup>0</sup>, was filtrated off and all volatiles were removed *in vacuo* to afford a colourless solid. Multinuclear NMR spectroscopy indicated the solid to be chloroalane **1 c**.

### Reaction of Phosphanylalane 2 and AuCl(tht)

Phosphanylalane **2** (100 mg/0.17 mmol) and AuCl(tht) (57 mg, 0.17 mmol) were dissolved in 5 mL of thf. The mixture was stirred overnight at room temperature. A dark precipitate, presumable Au<sup>0</sup>,

was filtrated off and all volatiles were removed *in vacuo* to afford a colourless solid. Multinuclear NMR spectroscopy indicated the solid to be chloroalane 1c.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** aluminum · cyclopentadienylalanes · phosphanylalanes · NHCs · metallocenophanes

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