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Ni complexes of an alane/tris(phosphine) ligand built around a strongly Lewis acidic tris(*N*-pyrrolyl)aluminum<sup>†</sup>

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Syntheses of a new tripodal alane/tris(phosphine) ligand (AlP<sub>3</sub>) based on 2-(diisopropylphosphino)pyrrole, and AlP<sub>3</sub>-supported Ni complexes are reported. The central tris(pyrrolyl)aluminum moiety acts as a stronger Lewis acid towards Ni than other related group 13 element-centered tripodal ligands, as demonstrated by the binding of H<sub>2</sub> to Ni and the ease of reduction.

Z-Type ligand is a term that arose to describe the binding of typical  $\sigma$ -Lewis acids to transition metal centers functioning as Lewis bases.<sup>1</sup> Such  $M \rightarrow Z$  complexes have attracted considerable attention because of the potential for the modulation of the properties of the transition metal center *via* changes in the nature of the Z-Lewis acid, including for applications in catalysis.<sup>2-7</sup> Z-Ligands are often incorporated into polydentate chelates.<sup>1,2</sup> The ZL<sub>3</sub> type, combining a central Z site with three outer neutral donors, has been commonly explored (**A**, **B**, **C**, Fig. 1).<sup>8-15</sup> The known ZL<sub>3</sub> ligands typically position the Z and the L sites in a 1,2-relationship to each other. 1,2-Disposition on an aromatic ring such as in **B** provides significant rigidity and preorganization to the structure that is geometrically well set up for binding a transition metal.

We surmised that using a 1,2-pyrrolediyl connection presents an attractive alternative to 1,2-benzenediyl in **B**. Both are flat aromatic connectors, but *N*-pyrrolyl is a very electronwithdrawing substituent compared to a *C*-aryl,<sup>16</sup> introducing intrinsic electronic asymmetry. We note that the pyrrole backbone has not been widely used in ligand construction,<sup>17–21</sup> in contrast to the benzene ring connectors which are ubiquitous in many ligand types far beyond ZL<sub>3</sub>. A reliable synthesis of a 2-phosphinopyrrole precursor should permit a more active exploration of these options. The only known derivative is 2-diphenylphosphinopyrrole,<sup>22–25</sup> which was most recently used by Tonks *et al.*<sup>26,27</sup> and Johnson *et al.*<sup>28</sup> Its synthesis is not highyielding and may not be easily adaptable to other phosphino variations.<sup>29</sup> In this work, we wish to report two synthetic pathways leading to 2-(diisopropylphosphino)pyrrole (**4**, Scheme 1), as well as the straightforward use of **4** in the construction of a new AlP<sub>3</sub> ligand (Scheme 2) and AlP<sub>3</sub> complexes.<sup>30</sup> The AlP<sub>3</sub> ligand combines a central Z-type alane site with three outer phosphine donors. We were attracted to exploring AlP<sub>3</sub> because the pyrrolyl substituents on Al should render it more electronpoor than the *C*-aryl substituents on boron in **B** or the dialkylamido substituents on Al in **C**. Coupled with the absence of the extra amine donor such as in **C**, we expected that the alane site in AlP<sub>3</sub> should be considerably more Lewis acidic<sup>31</sup> than other common ZL<sub>3</sub> systems with a central group 13 Lewis acid.

*N*-Boc protected 2-bromopyrole (1) was prepared according to a published procedure.<sup>32</sup> Lithium/bromine exchange presumably generated the unobserved 2 *in situ*, which was allowed to react with  $ClP^{i}Pr_{2}$ , resulting in the formation of crude 3 (Method A, Scheme 1). Deprotection of the Boc group produced 4 in good yield, but in sub-optimal purity, which can be traced to the 87% purity of 1. Purification of 4 can be accomplished *via* the synthesis of the lithio derivative 5, which was isolated in a 60% yield. Air-free hydrolysis of 5 then gave 4 of >98% purity (47% yield based on <sup>i</sup>Pr<sub>2</sub>PCl). An alternative synthesis (Method B)



в

[M] = Ni, B1

 $R = Ph or^{i}Pi$ 

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NR<sup>i</sup>Pr<sub>2</sub>

С

[M] = Ni, E = Al, C1

[M] = Ni, E = Ga, C2

[M] = Ni, E = In, C3 [M] = Ni, E = 3H, C4

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Scheme 1 Synthesis of phosphinopyrrole.



generates the presumed intermediate 2 *via* deprotonation of **6**<sup>33</sup> with LiTMP,<sup>23</sup> followed by phosphination and Boc-deprotection. Distillation of the crude product, followed by recrystallization from isooctane yielded **4** in high purity and 75% yield.

The tripodal ligand AlP<sub>3</sub> (7) was synthesized *via* protolysis of AlMe<sub>3</sub> with 3 equiv. of pyrrolylphosphine (4) at 80 °C for 1 h in toluene. After all the volatiles were removed under vacuum, AlP<sub>3</sub> was obtained as an orange oil of >95% purity (NMR evidence). Attempts to purify AlP<sub>3</sub> (7) further were hampered by its high lipophilicity and sensitivity towards water and other protic sources, but the crude material could be used effectively in the next step. Thermolysis of 7 with Ni(COD)<sub>2</sub> at 100 °C for 4 h in toluene led to the formation of (AlP<sub>3</sub>)Ni (8, Scheme 2), which was isolated in the form of analytically pure dark-green crystals in 75% yield after filtration and recrystallization. Both 7 and 8 displayed apparent  $C_{3v}$  symmetry in their NMR spectra at ambient temperature, although the signals of 8 appeared broadened.



Fig. 2 ORTEP drawing (50% thermal ellipsoids) of **8** showing selected atom labeling. Hydrogen atoms and isopropyl groups were omitted for clarity. Selected bond distances (Å) and angles (°): Ni1–P1, 2.2217(13); Ni1–P2 2.2227(13); Ni1–P3 2.2197(17); Ni1–Al1, 2.2695(16); Al–N1, 1.8591(19); Al–N2, 1.8545(16); Al–N3 1.8483(19); P1–Ni1–P2, 117.61(5); P1–Ni1–Al1, 86.18(4); P2–Ni1–Al1, 84.18(3); P3–Ni1–P1, 118.91(2); P3–Ni1–P2 120.89(4); P3–Ni1–Al1 83.60(2); N1–Al1–Ni1, 106.55(5); N2–Al1–Ni1, 104.57(6); N2–Al1–N1, 112.91(7); N3–Al1–Ni1, 107.39(4); N3–Al1–N1, 113.03(6), N3–Al1–N2, 111.73(7).

Single crystals suitable for an X-ray study were obtained via vapor diffusion of pentane into a toluene solution of (AlP<sub>3</sub>)Ni. An XRD study revealed an approximately  $C_3$ -symmetric structure for 8 in the solid state (Fig. 2). The Ni centre is only slightly displaced from the plane defined by the three phosphorus atoms ( $\Sigma P$ -Ni-P = 357.4°), while the geometry of the Al center is decidedly tetrahedral with an average Ni-Al-N angle of 112.6°. The Ni-Al distance in 8 (2.2695(16) Å) can be contrasted with the much longer Ni-Al distance in Lu's C1 (ca. 2.45 Å)<sup>14</sup> and the sum of the corresponding covalent radii per Alvarez et al. (also 2.45 Å).<sup>34</sup> Furthermore, the Ni–Al distance in 8 is only ca. 0.1 Å longer than the Ni-B distance in **B1**,<sup>12</sup> in spite of a 0.37 Å larger covalent radius for Al vs. B.<sup>34</sup> These data suggest a strong Ni–Al interaction. It is best viewed as  $\sigma$ -donation from a zerovalent Ni to the Al Lewis acid. The presence of this interaction renders the Ni center divalent because two electrons of the original  $d^{10}$  configuration at Ni are being used for Ni  $\rightarrow$  Al bonding.35 The semantics and the nuanced theoretical underpinnings of the nomenclature pertaining to the oxidation state and  $d^n$  configuration assignments in M  $\rightarrow$  Z complexes have been debated and analysed elsewhere.<sup>1-3,14,36-38</sup>

Further evidence of the strong Ni  $\rightarrow$  Al donation can be deduced from the electrochemical study of (AlP<sub>3</sub>)Ni (8). Cyclic voltammogram of 8 (Fig. S30, ESI<sup>†</sup>) displayed two quasireversible waves with  $E_{1/2}$  values of -0.49 V and -1.65 V vs. the Fc/Fc<sup>+</sup> couple. We assign these two redox events as oxidation and reduction of 8, respectively. The contrast with the complexes by Lu et al. is instructive. Reversible oxidation was reported for C1 (-0.74 V), C2 (-0.57), and the Lewis-acid free complex C4 (-1.02 V), indicating that 8 is more difficult to oxidize than any of these (Fig. 3). A reversible reduction for C1 was not reported, but the Ga analog C2 displayed a reversible reduction at -2.48 V.14,15 The overall analysis by Lu et al. suggested that Ga is more electron-withdrawing than Al with respect to Ni in their compound series.<sup>15</sup> Thus, the much greater ease of reduction of 8 is striking. The larger difference in the potentials for the reduction events between 8 and C2  $(\Delta E_{1/2} = 0.83 \text{ V})$ , compared to a modest difference in potentials for the oxidation event ( $\Delta E_{1/2} = 0.08$  V) is likely a reflection of



Fig. 3 Comparison of selected properties of **8** and its HD and CO adducts with literature examples.

that the Ni  $\rightarrow$  Al interaction is much more influential on the LUMO than on the HOMO of an (L<sub>3</sub>Z)Ni molecule.<sup>14</sup>

Lu et al. investigated the binding of H<sub>2</sub> to Ni in their series of compounds C1-C3, including demonstrating that catalysis of olefin and CO<sub>2</sub> hydrogenation was possible.<sup>5,15</sup> Notably, they observed little to no binding of H<sub>2</sub> to C1 at RT, and only to the Ga and In analogs C2 and C3.<sup>39</sup> Binding of H<sub>2</sub> to B1 was also not detected.<sup>40</sup> In contrast, the dark-green solution of 8 in  $C_6D_6$ turned pale green immediately when it was exposed to 1 atm H<sub>2</sub>. NMR spectroscopy indicated the formation of a new complex 8-H<sub>2</sub>, with a broad resonance at -2.1 ppm in the <sup>1</sup>H NMR spectrum, and new, considerably shifted resonances in the  ${}^{31}P{}^{1}H{}$  (24.3 ppm vs. 13.0 ppm for 8) and  ${}^{27}Al$  NMR spectra (138.0 ppm vs. 104.4 ppm for 8). Variable temperature NMR experiments showed that below -20 °C, the resonance for the Ni-bound  $H_2$  shifted to *ca.* -2.5 ppm, the signal for free  $H_2$ appeared, and no trace of 8 was evident. This suggests that 8-H<sub>2</sub> constitutes ca. 90% of the mixture at RT and is in rapid equilibrium with 8 and free H2. At temperatures below -20 °C, however, the formation of 8-H<sub>2</sub> is complete under 1 atm of H<sub>2</sub>. Collecting NMR spectra at temperatures down to -75 °C did not allow for an unambiguous  $T_{1\min}$  value, but the lowest obtained values of <25 ms were consistent with a classical dihydrogen complex.41 This was corroborated by the  $J_{\text{H-D}}$  = 35 Hz determined for **8-HD** isotopomer prepared from **8** and HD gas.<sup>42</sup> This value can be compared against those for the HD adducts of C2 (34 Hz) and C3 (32 Hz) analysed by Lu et al. (Fig. 3).<sup>39,43</sup> The slightly higher value in 8-HD suggests less back-donation to HD from Ni and is consistent with the notion

of a more electron-poor Ni center in **8-HD**. However, all these values are near the upper limit for HD complexes, and are similar to that observed by Peters *et al.* in the closely related **D-HD** (Fig. 3).<sup>40</sup>

Exposure of a  $C_6D_6$  solution of 8 to 1 atm of CO resulted in complete conversion to the new complex 8-CO (Fig. 3). Its  $\nu$ (CO) value can be used to compare the capacity of the Ni center for  $\pi$ -back-donation in the three locally isoelectronic systems C1-CO,<sup>44</sup> 8-CO, and D-CO<sup>40</sup> (Fig. 3). The  $\nu$ (CO) values for these three complexes lie in between the values for complexes E-CO and F-CO (Fig. 3), which possess the more traditional, fourcoordinate geometries about zerovalent Ni (E-CO, tetrahedral)<sup>45</sup> and low-spin divalent Ni (**F-CO**, square-planar).<sup>46</sup> The values for C1-CO and 8-CO are closer to the value of the zerovalent E-CO, whereas the value for D-CO is closer to F-CO. However, it must be noted that the difference between 8-CO and D-CO (74  $\text{cm}^{-1}$ ) is similar to the differences between 8-CO and E-CO (70  $\text{cm}^{-1}$ ), or **D-CO** and **F-CO** (60 cm<sup>-1</sup>). Thus, the triad of **C1/8/D** can be viewed as part of a continuum of possible structures in which Ni is rendered to be more electron-poor by the donation to a progressively stronger Lewis acid: base-stabilized tris(amido)alane in C1, tris(pyrrolyl)alane in 8, and formally triarylsilylium cation in D.

All in all, our observations indicate with that the central Lewis acid in  $AlP_3$  (7) is considerably stronger than the Z fragments in other common group 13-centered ZL<sub>3</sub> ligands. The greater degree to which the alane site in 8 withdraws electron density from Ni is consistent with the short Al–Ni distance, ease of reduction of (AlP<sub>3</sub>)Ni (8), and the ability of Ni in 8 to bind H<sub>2</sub>.

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## Conflicts of interest

There are no conflicts to declare.

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