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Five-coordinate aluminum complexes of a PNP ligand

Jessica C. DeMott,[a] Chengyun Guo,[a] Bruce M. Foxman,[a] Dmitry V. Yandulov*[b,†] and Oleg V. Ozerov*[a,†]

[a] *Department of Chemistry, Brandeis University, Waltham, MA 02454, USA. E-mail: ozerov@brandeis.edu*
[b] *Department of Chemistry, Stanford University, Stanford, California, 94305-5080, USA.*
E-mail: yandulov@stanford.edu

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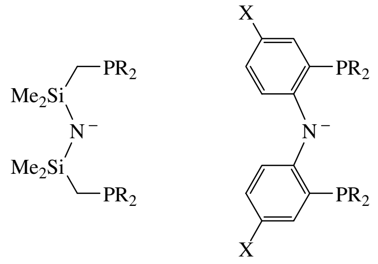
Experimental and computational studies demonstrate that the diarylamido-based PNP ligand is capable of supporting five-coordinate Al complexes.

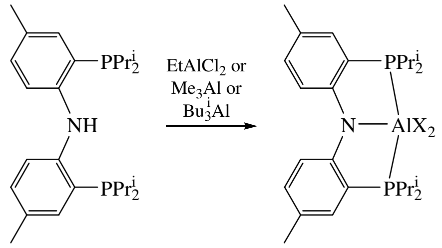
Hybrid amido/bis(phosphine) ligands were first introduced by Fryzuk and co-authors in the early 1980s in the form of the ^{Si}PNP system (Figure 1).[1–4] In the last few years, the chemistry of a new PNP pincer ligand system based on the diarylamine backbone has been described.[5–11] In comparison with ^{Si}PNP, the diarylamido-based PNP is more rigid, better prearranged for binding a metal center in the PNP cleft, and devoid of moisture sensitive Si–N bonds. The utilization of PNP (and, for the most part, ^{Si}PNP)[1–4] has been to date limited to the transition metal applications.[5] We surmised that the rigidity of the backbone and the relatively high donicity of the donor sites in PNP should make it a promising platform for investigations of hypercoordinate main group complexes. Here, we report an investigation of the chemistry of PNP complexes of aluminum.



^{Si}PNP PNP

Figure 1

Reaction of (PNP)K[‡] **2** with anhydrous AlCl$_3$ in THF resulted in the formation of (PNP)AlCl$_2$ **3** (^{31}P NMR evidence). While this approach allowed for the isolation of a small quantity of X-ray quality single crystals of **3**, high-yield isolation of **3** by this route was problematic owing to the difficulty in separating poorly soluble **3** from the KCl by-product. Liang and co-authors[12,13] have successfully used alkane elimination to prepare related amido/phosphine aluminum compounds. Conveniently, reaction of (PNP)H **1** with 1 equiv. of EtAlCl$_2$ in toluene overnight at 22 °C produced **3** (Scheme 1). The ^{1}H and ^{31}P NMR spectra of **3** were consistent with an apparent C_2 symmetry in solution. The X-ray diffraction study of **3** (Figure 2)[§] revealed that it displays C_2 symmetry in the solid state as well. In contrast, (PNP)PdCl is C_2-symmetric in the solid state but displays C_{2v} symmetry in solution on the NMR time scale (down to –70 °C) owing to the rapid flipping of the PNP backbone.[8] Ostensibly, the two Cl substituents in (PNP)AlCl$_2$ provide a strong enough impediment to the conformational freedom of the PNP ligand. The environment about Al in the X-ray structure of **3** is approximately trigonal-bipyramidal, with phosphines occupying the axial positions and



(PNP)H (**1**) (PNP)AlX$_2$

3 X = Cl
4 X = Me
5 X = Bu^i

Scheme 1

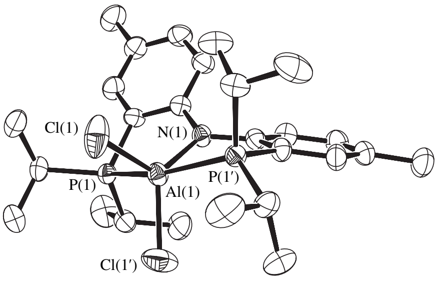


Figure 2 ORTEP drawing (50% probability ellipsoids) of **3** showing selected atom labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P(1)–Al(1) 2.4884(8), Cl(1)–Al(1) 2.1721(12), N(1)–Al(1) 1.915(4); P(1)–Al(1)–P(1′) 159.63(7), Cl(1)–Al(1)–Cl(1′) 113.53(10), N(1)–Al(1)–Cl(1) 123.23(5).

[†] Former students of the Higher Chemical College of the RAS (1992–1998).

[‡] (PNP)K **2** was produced *in situ* from (PNP)H **1** and KN(SiMe$_3$)$_2$. ^{31}P {^{1}H} NMR (THF) δ: –0.6.

[§] $C_{26}H_{40}AlCl_2NP_2$, M_r = 526.45, monoclinic, a = 11.5716(7), b = 9.3880(10), c = 12.9882(12) Å; β = 95.951(6)°, V = 1403.4(2) Å^3, space group $P2/n$, Z = 2, crystal size 0.22×0.36×0.50 mm, d_{calc} = 1.246 g cm^{-3}, $F(000)$ = 560, μ(MoKα) = 0.392 mm^{-1}, T = 294 K, 4449 data merged to 4261 unique (R_{int} = 0.015), final R, R_w indices [2066 data, $F > 1.96\sigma(F)$] 0.0558, 0.0595, S = 1.116.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 637714. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

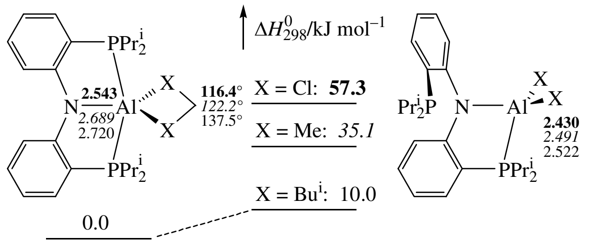


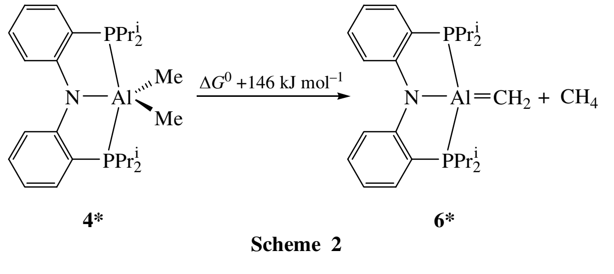
Figure 3 Computed relative enthalpies of 5- and 4-coordinate isomers of the model (PNP)AlX_2 compounds, X = Cl (**3***), Me (**4***), Bu^i (**5***), with selected geometrical parameters (Å, °).

resembles that in the structure of [κ^3-*P*,*N*,*P*-N(SiMe$_2$CHPPr$^i_2$)$_2$]-AlCl$_2$ reported by Fryzuk *et al.*[14]

Alkane elimination provided convenient access to dialkyl derivatives **4** and **5** (Scheme 1) *via* reactions of **1** in benzene with either AlMe$_3$ or AlBu$^i_3$, respectively. The reaction with AlMe$_3$ proceeded to completion in under 24 h at 22 °C while the reaction with AlBu$^i_3$ required 19 h at 90 °C for high-yield conversion. Both **4** and **5** possess C_2 symmetry at 22 °C in solution as judged by ^{1}H, ^{31}P and ^{13}C NMR. The characteristic ^{1}H NMR resonances of the α-Me in **4** (δ –0.06, t, $J_{\rm PH}$ 8 Hz) displayed coupling to two equivalent ^{31}P nuclei. The two hydrogens of the α-CH$_2$ group in **5** (δ 0.44 and 0.28) are diastereotopic and exhibit geminal coupling ($^2J_{\rm HH}$ 14 Hz). Coupling to the ^{31}P nuclei, albeit poorly resolved owing to the complexity of the multiplet, was evident for at least one of these hydrogens.

Unfortunately, we were not able to obtain X-ray quality crystals of **4** or **5**. To gain further insight into structural preferences of (PNP)AlX$_2$ in the series of X = Cl, Me and Bu^i, thermochemical parameters governing the $\kappa^3 \leftrightarrow \kappa^2$-(PNP) equilibrium were evaluated computationally for model compounds (Figure 3).¶ Consistent with the crystallographic data, (PNP)AlCl$_2$ **3*** is computed to favor the five-coordinate geometry decidedly, by $\Delta H^0_{\kappa^3\to\kappa^2}$ 57.3 kJ mol^{-1}. The endothermicity of the four-coordinate isomer is decreased by a better electron-donor X = Me (**4***), for which $\Delta H^0_{\kappa^3\to\kappa^2}$ 35.1 kJ mol^{-1}. With additional steric pressure from the X = Bu^i substituents (**5***), κ^3- and κ^2-(PNP) isomers become borderline isoenergetic with the five-coordinate geometry favored by only 10 kJ mol^{-1}. Greater electron-donation from the alkyl X groups renders P–Al bonds substantially longer (by > 0.14 Å) than those in (PNP)AlCl$_2$, while steric factors cause the X–Al–X angle to widen by 15° to accommodate X = Bu^i in the κ^3-(PNP) structure. Increasing accessibility of four-coordinate κ^2-(PNP)AlX$_2$ isomers on traversing the series of X = Cl, Me and Bu^i predicted here computationally echoes the behavior of [N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]AlX$_2$, X = Cl, Me, Et, CH$_2$Ph analogs studied experimentally.[14]

The PNP ligand has been used as a robust scaffold to support unusual group 4 alkylidenes, some of which were formed *via* α-abstraction reactions from PNP-supported metal polyalkyl precursors.[10,15] Here, one of our goals was to probe whether analogous chemistry is at all possible for the PNP-supported Al dialkyls such as **4** and **5**. We saw no evidence of thermal reactivity of either **4** or **5** and, therefore, turned to computational methods. The transformation of **4*** into putative **6*** was found to be strongly endoergic (Scheme 2). The 146 kJ mol^{-1} difference is great enough that it is highly unlikely that such a reaction can be made thermodynamically favorable for (PNP)Al(alkyl)$_2$ through variation of the nature of the alkyl.



4* **6***

Scheme 2

In summary, experimental and computational studies demonstrate that the PNP ligand is capable of supporting five-coordinate Al complexes. In (PNP)AlX$_2$ complexes, the preference for the five-coordinate form decreases with increasing size and donicity of X. Computational studies predict that α-abstraction reactions in (PNP)Al(alkyl)$_2$ to produce the hitherto unknown Al alkylidenes are decidedly unfavorable thermodynamically.

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¶ Using Gaussian 03[16] according to the scheme: ONIOM[17] (B3PW91[18,19]/[6-311+G(2d,p)]:UFF{iPr})//ONIOM (B3PW91/[Al, Cl, P: SDD+polarization(d)[20]; H, C, N: 6-31G(d,p)]:UFF{iPr})/. Metric parameters of (PNP)AlCl$_2$ are reproduced to within 0.05 Å/3°, or 2.6% of the X-ray values.

(PNP)AlCl$_2$ **3**. (PNP)H **1** (333 mg, 0.779 mmol) and EtAlCl$_2$ (779 µl of 1 M solution in hexanes, 0.779 mmol) were dissolved in 20 ml of toluene. The solution was stirred overnight. Solid **3** was filtered off, washed with Et$_2$O and dried *in vacuo*. Yield, 223 mg (55%). ^{1}H NMR (CDCl$_3$) δ: 7.48 (s, 2H, Ar–*H*), 7.39 (m, 2H, Ar–*H*), 7.28 (d, 2H, Ar–*H*, *J* 8 Hz), 2.85 (m, 2H, C*H*Me$_2$), 2.60 (m, 2H, C*H*Me$_2$), 2.56 (s, 6H, Ar–*Me*), 1.70 (dd, 6H, CH*Me*$_2$, *J* 17 Hz, *J* 7 Hz), 1.59 (dd, 6H, CH*Me*$_2$, *J* 15 Hz, *J* 7 Hz), 1.40 (m, 12H, CH*Me*$_2$). Low solubility precluded collection of quality ^{13}C NMR data. ^{31}P{^{1}H} NMR (CDCl$_3$) δ: –22.9 (br. s). Found (%): C, 59.34; H, 7.56. Calc. for $C_{26}H_{40}P_2NAlCl_2$ (%): C, 59.32; H, 7.65.

(PNP)AlMe$_2$ **4**. (PNP)H **1** (211 mg, 0.494 mmol) and AlMe$_3$ (0.25 ml, 0.49 mmol) were dissolved in 4 ml of benzene. The solution was stirred for 24 h. The volatiles were removed under vacuum, the solid redissolved in C$_6$D$_6$ and then filtered through a pad of Celite. Recrystallization from Et$_2$O yielded 50% of analytically pure **4**. ^{1}H NMR (C$_6$D$_6$) δ: 7.26 (m, 2H, Ar–*H*), 6.94 (s, 2H, Ar–*H*), 6.89 (d, 2H, Ar–*H*, *J* 8 Hz), 2.17 (s, 6H, Ar–*Me*), 2.10 (m, 2H, C*H*Me$_2$), 1.81 (m, 2H, C*H*Me$_2$), 1.40–1.18 (m, 18H, CH*Me*$_2$), 0.88 (m, 6H, CH*Me*$_2$), –0.06 (t, 6H, AlMe$_2$, $J_{\rm PH}$ 8 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ: 158.4 (br. s, C–Ar), 144.1 (s, C–Ar), 133.4 (s, C–Ar), 132.2 (s, C–Ar), 120.9 (s, C–Ar), 119.2 (s, C–Ar), 23.6 (br. s, *C*HMe$_2$), 21.2 (br. s, *C*HMe$_2$), 20.4 (s, Ar–*Me*), 19.9 (two overlapping peaks, CH*Me*$_2$), 19.8 (d, CH*Me*$_2$, *J* 13 Hz), 17.2 (CH*Me*$_2$), –3.1 (br. s, Al*Me*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ: –17.4 (s). Found (%): C, 69.22; H, 9.51. Calc. for $C_{26}H_{40}P_2NAl(CH_3)_2$ (%): C, 69.25; H, 9.55.

(PNP)Al(Bu^i)$_2$ **5**. (PNP)H **1** (116 mg, 0.270 mmol) and Al(Bu^i)$_3$ (270 µl, 1 M solution in hexanes, 0.270 mmol) were dissolved in benzene and the solution heated at 90 °C for 19 h. The volatiles were removed *in vacuo* and the residual pale yellow solid was recrystallized from Et$_2$O to give 83.3 mg (54%) of **5**. ^{1}H NMR (C$_6$D$_6$) δ: 7.19 (dd, 2H, Ar–*H*, *J* 8 Hz, *J* 4 Hz), 6.92 (s, 2H, Ar–*H*), 6.86 (d, 2H, Ar–*H*, *J* 8 Hz), 2.21 (m, 2H, PC*H*Me$_2$), 2.15 (s, 6H, Ar–*Me*), 2.04 (m, 2H, AlCH$_2$C*H*Me$_2$), 1.88 (m, 2H, PC*H*Me$_2$), 1.32 (d, 6H, AlCH$_2$CH*Me*$_2$, *J* 6 Hz), 1.22 (d, 6H, AlCH$_2$CH*Me*$_2$, *J* 6 Hz), 1.20 (dd, 6H, PCH*Me*$_2$, *J* 12 Hz, *J* 6 Hz), 1.16 (dd, 6H, PCH*Me*$_2$, *J* 15 Hz, *J* 7 Hz), 1.07 (dd, 6H, PCH*Me*$_2$, *J* 15 Hz, *J* 7 Hz), 0.87 (t, 6H, PCH*Me*$_2$, *J* 5 Hz), 0.44 (d, 2H, AlC*H*$_2$CHMe$_2$, *J* 14 Hz, *J* 4 Hz), 0.28 (m, 2H, AlC*H*$_2$CHMe$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): 7.19 (d, 2H, Ar–*H*, *J* 8 Hz), 6.92 (s, 2H, Ar–*H*), 6.86 (d, 2H, Ar–*H*, *J* 8 Hz), 2.21 (sept., 2H, PC*H*Me$_2$, *J* 4 Hz), 2.15 (s, 6H, Ar–*Me*), 2.04 (m, 2H, AlCH$_2$C*H*Me$_2$), 1.88 (sept., 2H, PC*H*Me$_2$, *J* 7 Hz), 1.32 (d, 6H, AlCH$_2$CH*Me*$_2$, *J* 6 Hz), 1.22 (d, 6H, AlCH$_2$CH*Me*$_2$, *J* 6 Hz), 1.20 (d, 6H, PCH*Me*$_2$, *J* 6 Hz), 1.16 (d, 6H, PCH*Me*$_2$, *J* 7 Hz), 1.07 (d, 6H, PCH*Me*$_2$, *J* 7 Hz), 0.87 (d, 6H, PCH*Me*$_2$, *J* 6 Hz), 0.44 (dd, 2H, AlC*H*$_2$CHMe$_2$, *J* 14 Hz, *J* 4 Hz), 0.28 (dd, 2H, AlC*H*$_2$CHMe$_2$, *J* 14 Hz, *J* 10 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ: 158.3 (m, Ar–*C*), 132.6 (s, Ar–*C*), 131.9 (s, Ar–*C*), 127.5 (br. s, Ar–*C*), 121.3 (s, Ar–*C*), 118.2 (m, Ar–*C*), 29.7 (s), 28.1 (t, *J* 6 Hz), 27.7 (s), 23.3 (s), 20.5 (s, Ar–*Me*), 19.4 (br. s), 19.3 (m, two overlapping peaks), 18.4 (m), 16.0 (t, *J* 3 Hz), 15.7 (t, *J* 3 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ: –18.0.

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