that can undergo hydroalkoxylation with methylenecyclopropanes make this reaction a versatile process in organic synthesis.

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The First Molecular Main Group Metal Species Containing Interstitial Hydride[**]

David R. Armstrong, William Clegg, Robert P. Davies, Stephen T. Liddle, David J. Linton, Paul R. Raithby, Ronald Snaith, and Andrew E. H. Wheatley[*]

As part of an ongoing study[1] into the mechanism by which "mixed" organolithium/organoaluminum reagents promote conjugate addition to α,β-unsaturated ketones, we attempted to synthesize $Me_2(tBu)Al[N(2\text{-}Pyr)Ph]Li$ (2-Pyr = 2-pyridyl) by treating dimethyl(2-pyridylanilido)aluminum (**1**) with one equivalent of *t*BuLi. Remarkably, however, this reaction in toluene afforded in reasonable yield (over 40%) the ion-separated compound **2**, neither component of which contains any Al–N bonds. Rather, the anion is an unprecedented lithium bis(aluminate) while the cation, equally unprecedented, contains a hydride anion within a distorted $(Li^+)_8$ cubic cage. Treatment of the reaction mixture with THF results in removal of one Li^+ ion from this cage to give **3**.

$Me_2AlN(2\text{-}Pyr)Ph$ **1**

$[Li_8(H)\{N(2\text{-}Pyr)Ph\}_6]^+[Li(Me_2Al\textit{t}Bu_2)_2]^-$ **2**

$Li_7(H)[N(2\text{-}Pyr)Ph]_6$ **3**

Treatment of **1** in toluene at −78 °C with one equivalent of *t*BuLi gave a suspension which can be dissolved in further toluene, the resultant solution affording colorless crystals of **2** as the only isolable product. Superior yields were obtained by using 1.5 equivalents of *t*BuLi (see Experimental Section). X-ray crystallography[2] showed that in the solid state **2** is a remarkable mixed aggregate which incorporates both an unprecedented lithium bis(aluminate) anion and a hydride-containing lithium amide cation. The $[Li(Me_2Al\textit{t}Bu_2)_2]^-$ ion (Figure 1) contains two Al centers arranged such that two methyl substituents on each are tetrahedrally disposed about Li(5) to afford an $Al(\mu\text{-}C)_2Li(\mu\text{-}C)_2Al$ motif. This is one of the few examples of an alkali metal containing anion.[3] This molecular motif is related to the repeat unit of polymeric lithium tetra(alkyl)aluminates, and the mean Li–(μ-C) and Al–(μ-C) distances of 2.25 and 2.07 Å, respectively, are comparable to those of 2.30 and 2.02 Å in $LiAlEt_4$.[4]

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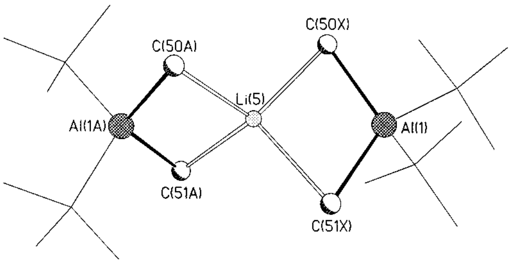

Figure 1. Molecular structure of the [Li(Me$_2$Al*t*Bu$_2$)$_2$]$^-$ anion of **2**; hydrogen atoms and minor disorder omitted for clarity.

The [Li$_8$(H){N(2-Pyr)Ph}$_6$]$^+$ part of **2** (Figure 2) is based on an unusual (Li$^+$)$_8$ cubic cage whose six faces are straddled by the N–C–N backbones of the six pyridylamide moieties. Each N atom coordinates to two Li$^+$ centers such that this dication adopts C_i symmetry (mean Li–N 2.047 Å). However, while six of the cations each interact with one amido group and two pyridyl N centers, Li(3) and Li(3A) bond only to three deprotonated N centers each (N(1), N(3), and N(5) for Li(3)). Because of the resulting distortions in the (Li$^+$)$_8$ core, the distances between nonbonding metal centers that involve the centers with tetragonally elongated geometry [Li(3) and Li(3A)] are longer (mean Li(3)$\cdots$Li 2.701 Å) than those which do not (mean Li$\cdots$Li 2.488 Å).

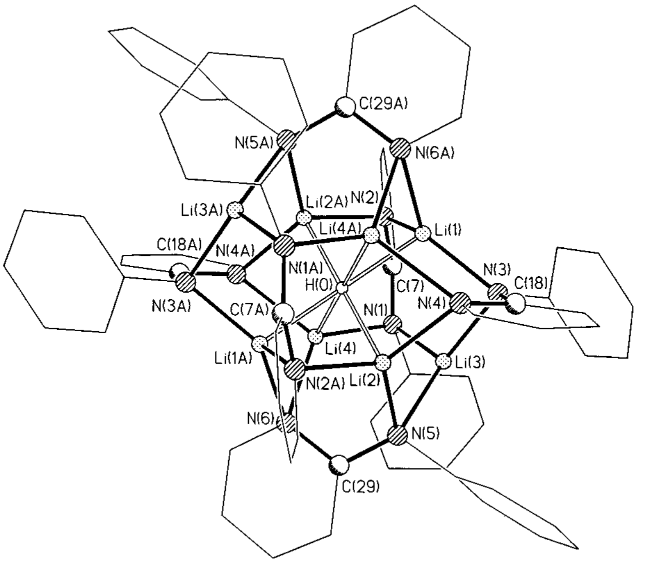

Figure 2. The hydride-containing [Li$_8$(H){N(2-Pyr)Ph}$_6$]$^+$ component of **2**; hydrogen atoms excluded for clarity.

The presence of the central hydride anion in the cation is consistent with its refinement from crystallographic data, with the Li–H distances, and with the ratio of [Li(Me$_2$Al*t*Bu$_2$)$_2$]$^-$ to [Li$_8${N(2-Pyr)Ph}$_6$]$^{2+}$. It is unprecedented in main group chemistry.[5] The different coordination of Li(3) and Li(3A) and the resulting extension of the Li$\cdots$Li distances involving them are in accord with the adoption by the hydride anion of an octahedral coordination sphere (mean Li–H(0) 2.015 Å) since neither Li(3) nor Li(3A) bonds with the interstitial ion (Li(3)$\cdots$H(0) 2.828(9) Å). Preliminary results from ab initio molecular orbital calculations (6-31G* basis set at the SCF level) on models of the cation of **2** lend support to these structural assignments. A viable and stable species resulted from the insertion of H$^-$ into the Li$_8$ cavity of a cube-based structure of type [Li$_8${N(H)CH$_2$NH$_2$}$_6$]$^{2+}$. Moreover, this optimized structure reproduces features seen in the structure of the cation of **2**: Two of the Li$^+$ ions are significantly extruded (Li$\cdots$H 3.45 Å), whilst the other six are bonded to the H$^-$ anion (Li–H 2.11 Å).

The solvent dependency of interstitial hydride formation is revealed by treatment of the reaction mixture with THF (see Experimental Section). The resultant solution yields a crystalline mixture of the lithium amide **3** and [Li(thf)$_4$]$^+$-[Li(Me$_2$Al*t*Bu$_2$)$_2$]$^-$ (**4**). X-ray crystallography[6] showed **3** to be the new hydride-containing cluster Li$_7$(H)[N(2-Pyr)Ph]$_6$ (Figure 3). The lithium amide monocation part of **3** adopts a similar motif to the cage dication component of **2**, except that one vertex of the cubic cage is absent. It is worth noting that the relative orientations of the organic ligands in **3** (resulting in the adoption of C_3 symmetry) are incompatible with its formation by the simple THF-induced extrusion of a metal ion from **2**. Owing to the absence of a single Li$^+$ ion, three of the six pyridyl N centers (N(3), N(3A), N(3B)) each interact with one (Li(1), Li(1A), Li(1B)) rather than two metal ions, while the lithium ion Li(3) *trans* to the vacant site bonds to three amido N centers (N(2), N(2A), N(2B)). Accordingly, there are now three distinct nonbonding Li$\cdots$Li distances in the (Li$^+$)$_7$ core (mean 2.565 Å); those involving the unique Li(3) are of intermediate length (2.586(8) Å). Atom Li(3) shows an extended Li$\cdots$H distance (2.49(3) Å). This relatively long interaction renders the interstitial hydride pseudo-seven-coordinate, Li(3) capping one face of a distorted octahedral coordination shell. The remaining metal–hydride interactions are comparable to those of **2** (mean Li–H(0) 2.06 Å).

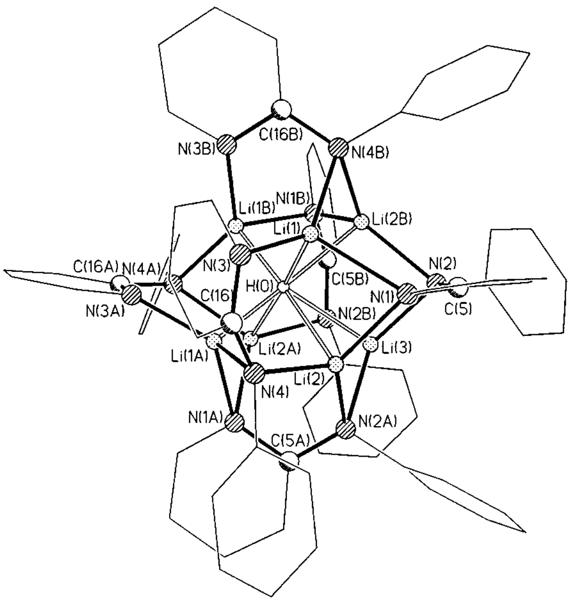

Figure 3. Molecular structure of **3**; hydrogen atoms omitted for clarity.

While there are several examples of transition metal clusters containing interstitial hydrido ligands,[5] we know of no molecular main group metal analogues. (The macrostructure of, for example, lithium hydride (Li–H 2.04 Å[7]) could be considered to contain metal-encapsulated hydride anions.) Hence, the structures of **2** and **3** are unprecedented. Probably the closest analogues are various O^{2-}-containing lithium species,[8] although these have traditionally been viewed as containing Li_2O, formed by the admission of moisture during the synthesis. More recently,[9] various dicationic $[Li_2Mg_2(amide)_4]^{2+}$ rings ("inverse crowns") have been shown to capture both O^{2-} and O_2^{2-}, and the compound $Li[(tBuCH_2O)_5Al_3H_5]\cdot OEt_2$ has been described as including molecular LiH that lies above the Al atoms of an Al_3O_3 chair.[10] Aside from the incorporation of hydride or other anions within molecular metal compounds, **2** and **3** are also unique in being based on polyhedral $(Li^+)_n/X$ frameworks ($n=8$, $X=H^-$ for **2**; $n=7$, $X=H^-$ for **3**). To our knowledge, all other reported alkali metalated organic compounds (amides, but also imides, alkoxides, enolates, alkyls, aryls, etc.) have structures based on rings.[9, 11]

In spite of the crystallographic evidence for interstitial hydride ions in **2** and **3**, the ^{1}H NMR spectra of neither compound afforded a signal attributable to hydride. These compounds are soluble only in polar solvents, and the identical signals of the aromatic groups (in spite of the various crystallographic symmetries of the amide anions in **2** and **3**) in the ^{1}H NMR spectra indicate that the cages of **2** and **3** are deaggregated in such media. It follows that the difficulty in observing the hydride ion in solution results from fragmentation of the cage, accompanied by liberation and reaction of H^-. This is consistent with the observation of significant effervescence on dissolution of **2** and **3**. Preliminary IR spectrocopic studies also point to the existence of interstitial hydride anion. The spectrum of **2** shows a band at 583 cm^{-1} (cf. 588 cm^{-1} for $(LiH)_\infty$[12]). The spectra of the parent amine [HN(2-Pyr)Ph] and of the lithium amide [LiN(2-Pyr)Ph], which show essentially the same fingerprint bands as **2**, both lack this signal.

We are attempting to elucidate the mechanism by which these compounds are formed. Preliminary experiments suggest that the formation of hydride-containing amidolithium polyhedral clusters requires the presence of a pyridylamide or similar heterocyclic anion and an excess of an organolithium compound that can undergo β elimination of LiH.[13] On the last count, for example, reactions of **1** with *n*BuLi or *s*BuLi followed by recrystallization from THF gave **3** and analogues of **4**, that is, $[Li(thf)_4]^+[Li(Me_2AlR_2)_2]^-$ (R = *n*Bu, *s*Bu); in contrast, **1** reacts with MeLi to afford only the expected lithium aluminate $Li[AlMe_3\{N(2\text{-}Pyr)Ph\}]$.

Experimental Section

2: Trimethylaluminum (0.5 mL, 2.0 M in toluene, 1.0 mmol) was added to 2-pyridylaniline (0.17 g, 1.0 mmol) in toluene (2 mL) at −78 °C under N_2. The resultant yellow solution was stirred at this temperature until effervescence subsided and then at room temperature for 1 h. *tert*-Butyllithium (0.88 mL, 1.7 M in hexanes, 1.5 mmol) was added at −78 °C, and the mixture was warmed to room temperature, giving a yellow suspension. The addition of toluene (5 mL) followed by filtration gave a yellow solution. Storage at room temperature for 2 d afforded colorless crystals of **2**. Yield 42% (based on *t*BuLi consumed), m.p. 268–270 °C. Elemental analysis calcd for $C_{86}H_{103}Al_2Li_9N_{12}$: C 72.68, H 7.25, N 11.83, Li 4.44; found: C 72.07, H 7.34, N 12.69, Li 3.99; ^{1}H NMR (500 MHz, $[D_8]$THF): $\delta = 7.48$ (dd, 6H, 6-Pyr), 6.85 (dd, 12H, 3-Ph), 6.79 (ddd, 6H, 4-Pyr), 6.75 (d, 12H, 2-Ph), 6.51 (d, 6H, 3-Pyr), 6.35 (t, 6H, 4-Ph), 5.69 (dd, 6H, 5-Pyr), 0.67–0.55 (m, 36H, *t*Bu), −1.46 (sext., ^2J(H,Al) = 5.9 Hz, 12H, Me).

Cosyntheses of **3** and **4**: As for **1**, but with dissolution at room temperature by the addition of THF (0.2 mL). Filtration and storage of the orange solution at 5 °C for 2 d afforded a colorless cocrystalline mixture of **3** and **4**, m.p. 307–311 °C. Elemental analysis calcd for **3** ($C_{66}H_{55}Li_7N_{12}$): C 73.32, H 5.69, N 13.55, Li 3.71; found (for manually separated **3**): C 74.44, H 5.17, N 15.79, Li 4.61; ^{1}H NMR (500 MHz, $[D_8]$THF): $\delta = 7.58$ (d, 6H, 6-Pyr), 6.95 (dd, 12H, 3-Ph), 6.90 (ddd, 6H, 4-Pyr), 6.86 (d, 12H, 2-Ph), 6.61 (d, 6H, 3-Pyr), 6.46 (t, 6H, 4-Ph), 5.80 (dd, 6H, 5-Pyr), 3.59 (m, 1H, 0.25 THF), 1.75 (m, 1H, 0.25 THF), 0.77–0.66 (m, 1.5H, 0.2 *t*Bu), (sext., ^2J(H,Al) = 5.6 Hz, 0.5H, 0.2 Me).

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[2] a) Crystal data for **2**: $C_{86}H_{102}Al_2Li_9N_{12}$, $M_r = 1420.2$, orthorhombic, space group *Pbcn*, $a = 19.546(4)$, $b = 16.098(1)$, $c = 26.168(6)$ Å, $V = 8234(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.146$ g cm^{-3}; $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, $\mu = 0.698$ mm^{-1}; $T = 180$ K. A total of 6434 reflections (5111 unique reflections, $R_{int} = 0.0439$, $\theta < 55.02°$) were collected on a Stoe Siemens four-circle diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 values of all data (G. M. Sheldrick, SHELXTL manual, Bruker AXS Inc., Madison, WI, USA, 1998, version 5.1) to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2476$, conventional $R = 0.0792$ for F values of 3583 reflections with $F_o^2 > 2\sigma(F_o^2)$, and $S = 1.033$ for 541 parameters. Twofold disorder was resolved and refined for methyl groups attached to Al. Max./min. residual electron density: $0.35/-0.42$ e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-118874 (**2**) and -118873 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[6] Crystal data for **3**: $C_{66}H_{55}Li_7N_{12}$, $M_r = 1064.8$, rhombohedral, space group $R\bar{3}$, $a = 14.383(2)$ Å, $\alpha = 85.822(3)°$ (primitive axes), $V = 2952.8(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.198$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.071$ mm^{-1}; $T = 160$ K. A total of 12479 relections

(3475 unique reflections, $R_{\text{int}} = 0.1492$, $\theta < 25.0°$) were collected on a Bruker SMART CCD diffractometer. The structure was solved and refined as for **2**:[2a] $wR2 = 0.1147$, conventional $R = 0.0494$ for F values of 1407 reflections with $F_o^2 > 2\sigma(F_o^2)$, and $S = 0.802$ for 259 parameters. Isotropic H atoms bonded to C were constrained. Max./min. residual electron density: $0.15/-0.16$ e Å^{-3}.[2b]

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First and Highly Diastereoselective Synthesis of Palladepanes[**]

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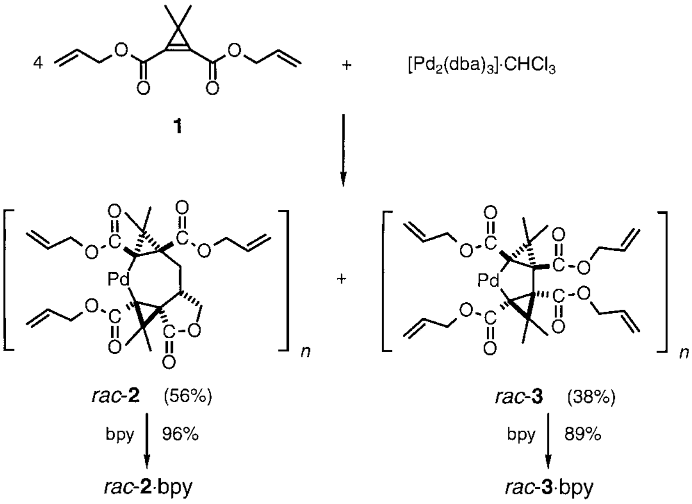
Jan W. Bats, and Michael Bolte

Although many palladium-catalyzed reactions are supposed to proceed via palladacyclo[n]alkanes,[1] such species have, with one singular exception, never been isolated or detected for compounds with more than five ring atoms! The high tendency of such intermediates to form the corresponding cyclo[$n-1$]alkanes by a fast reductive elemination is probably responsible for this observation. The exception mentioned above is a diphosphane complex of a nine-membered palladacycloalkane derivative that was formed in the reaction of 3,3-dimethylcyclopropene with a Pd^0 precursor.[2] Here we report the first synthetic approach to palladacycloheptane derivatives.

Since several of our efforts to achieve an intermolecular "mixed" oxidative cyclization between a cyclopropene and another unsaturated organic molecule at a Pd^0 center failed, we prepared **1**, which offered a terminal double bond as an intramolecular reaction partner at an appropriate distance. In the reaction of **1** with [Pd$_2$(dba)$_3$]·CHCl$_3$, two products were formed. The minor product could be identified as the palladatricyclo[4.1.0.0^{2,4}]heptane (PTH) derivative *rac*-**3** (Scheme 1). We had observed this mode of reaction many times before for cyclopropene-1,2-dicarboxylates.[3] The major product turned out to be the seven-membered palladacycloalkane derivative *rac*-**2**. As reported before for the PTHs, the palladacycloalkanes *rac*-**2** and *rac*-**3**, which would be coordinatively unsaturated, are stabilized by the formation of coordination polymers. The PTHs that possess no olefinic side chains are readily dissolved in coordinating solvents like acetone or acetonitrile, and complexes with two molecules of these easily exchangable solvents were obtained.[3b,c] In contrast, the ^{1}H NMR spectra of *rac*-**2** and *rac*-**3** in these solvents showed that they are still aggregated (probably through intermolecular coordination of the olefin moieties). As PTHs are known to form stable complexes with bidentate ligands,[3a,d,e] the 2,2′-bipyridyl (bpy) ligand was used to prepare the monomeric complexes *rac*-**2**·bpy (Table 1) and *rac*-**3**·bpy from *rac*-**2** and *rac*-**3**.



Scheme 1. Cyclization of cyclopropene **1**. bpy = 2,2′-bipyridyl, dba = dibenzylideneacetone.

An X-ray crystal structure analysis was carried out for *rac*-**2**·bpy (Figure 1).[4] Thus the connectivity as well as the stereochemical assignment was proven unambiguously. We could not detect the other diastereomer of *rac*-**2** possessing a *cis* arrangement of the two three-membered rings annelated to the central seven-membered ring. The high yields of *rac*-**2** and *rac*-**3** (sum 94%) clearly showed that other processes which one could have feared to occur with the allyl ester moieties of the molecules (formation of π-allyl–Pd$^{\text{II}}$ species with the stoichiometric amount of Pd^0, like in the Tsuji–Trost reaction)[5] were of no significance under these conditions.

We then tested whether the double bond of the allyl ester is capable of directing the regioselectivity of the cyclization. The cyclopropene **4** bearing methyl and allyl ester moieties led to the maximum number of constitutional isomers one could expect. As PTHs the three isomers *rac*-**7**, *rac*-**8**, and *rac*-**9** were formed (Scheme 2). While *rac*-**8** could easily be assigned by its

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