Inorg. Chem. **1999,** *38,* 4467−4472 **4467**

The Reaction of $LiAlH_4$ with 1,4-Di-*tert*-butyl-1,4-diazabutadiene: Imine-Containing Aluminum Hydrides Stabilized by Lithium Coordination

Michael G. Gardiner,[†] Stacey M. Lawrence,[‡] and Colin L. Raston*,[§]

School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia, Faculty of Science and Technology, Griffith University, Nathan, Brisbane, Queensland 4111, Australia, and Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3168, Australia

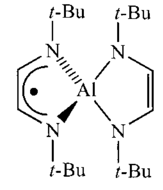
Received March 16, 1999

The reaction of 1,4-di-*tert*-butyl-1,4-diazabutadiene, **1**, with purified $LiAlH_4$ (free from Al metal) in diethyl ether has been investigated in detail, and a range of products have been isolated. The lithium diamidoaluminum dihydride $[Li\{N(t\text{-}Bu)CHCH_2N\text{-}t\text{-}Bu\}_2AlH_2]$, **2**, the dimeric diamidoaluminum hydride $[cis\text{-}\{[\mu\text{-}N(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu]AlH\}_2]$, **3**, or the heteroleptic lithium tetraamidoaluminum species $[(Et_2O)Li\{N(t\text{-}Bu)CH_2\}_2(CHN\text{-}t\text{-}Bu)_2Al]$, **4**, can be selectively obtained depending on the order of addition or stoichiometry of the reactants. We have rationalized these results in terms of the unstable adducts which are likely to be present in solution at low temperature. The X-ray crystal structures of **2** and the dimeric lithium aluminum hydride adduct $[\{[HN(t\text{-}Bu)CH(t\text{-}Bu)CHN\text{-}t\text{-}Bu]Li(\mu\text{-}H)_2AlH_2\}_2]$, **7**, are described.

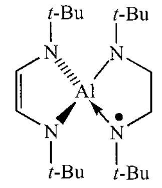
Introduction

In our recent series of papers,[1] we reported the reactions of aluminum hydrides with amines and imines in a detailed investigation aimed at a better level of understanding the course of these reactions and the intermediates involved in such metalation and addition reactions. We showed that the reaction of 1,4-di-*tert*-butyl-1,4-diazabutadiene with $LiAlH_4$ in the presence of Al metal led to reduction of the diazabutadiene, giving the homoleptic paramagnetic diazabutadiene complex $[Al(\{N(t\text{-}Bu)CH\}_2)_2]$, **5**.[2] In contrast to this result, the diazabutadiene reacted with $H_3Al{\cdot}NMe_3$ to give a partially hydrogenated paramagnetic complex, $[(HCN\text{-}t\text{-}Bu)_2Al\{N(t\text{-}Bu)CH_2\}_2]$, **6**, in which one of the ligands had been doubly reduced and the other ligand had had both imine functionalities hydrogenated.[2]

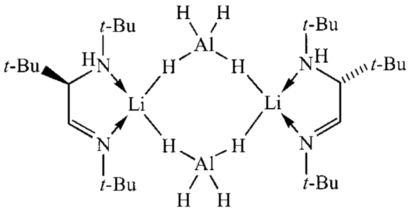
Herein we report the reaction of 1,4-di-*tert*-butyl-1,4-diazabutadiene with purified $LiAlH_4$ in diethyl ether in the absence of Al metal and show that the products feature again both addition to the imine functionalities and reduction of the diazabutadiene, and the reaction yielded three products dependent on the order of addition and stoichiometry of the reagents. We have rationalized the observation of these results in the context of our previously published results in this field.[3] We also report the crystal structure of one of these compounds and that of the previously reported dimeric lithium aluminum hydride adduct $[\{[HN(t\text{-}Bu)CH(t\text{-}Bu)CHN\text{-}t\text{-}Bu]Li(\mu\text{-}H)_2AlH_2\}_2]$, **7**,[4] which represent the first structurally characterized complexes of aluminum hydrides in the presence of reactive imine functionalities. Their stability is accredited to the coordination of the imine functionalities to the lithium centers, protecting them from hydroalumination.



5



6



7

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze/thaw degassed prior to use. 1,4-Di-*tert*-butyl-1,4-diazabutadiene was prepared according to the literature procedure.[5] $[\{[HN(t\text{-}Bu)CH(t\text{-}Bu)CHN\text{-}t\text{-}Bu]Li(\mu\text{-}H)_2AlH_2\}_2]$, **7**, was prepared according to our literature procedure.[4] $LiAlH_4$, obtained from Aldrich, was purified by recrystallization from diethyl ether and used as a standardized diethyl ether solution stored at −30 °C. All other reagents were obtained from Aldrich and used as received. ^1H NMR spectra were recorded on Varian Gemini-200 and Bruker AC-200 spectrometers in deuterated benzene and referenced to the residual ^1H resonances of the solvent (δ 7.15). ^{13}C NMR spectra

---

[†] The University of Sydney.

[‡] Griffith University.

[§] Monash University.

(1) (a) Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829. (b) Raston, C. L. *J. Organomet. Chem.* **1994**, *475*, 15. (c) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1.

(2) Cloke, F. G. N.; Dalby, C. I.; Henderson, M. J.; Hitchcock, P. B.; Kennard, C. H. L.; Lamb, R. N.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1394.

(3) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 1349.

(4) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4652.

(5) Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555.

10.1021/ic990298y CCC: $18.00

were recorded in deuterated benzene on Varian Gemini-200 and Bruker AC-200 spectrometers operating at 50 MHz and using broad-band proton decoupling and were referenced to the ^{13}C resonances of the deuterated solvent (δ 128.0). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, Canada, and the Chemical and MicroAnalytical Services Pty. Ltd., Melbourne, Australia. Melting points were determined in sealed glass capillaries under argon and are uncorrected. IR spectra were recorded as Nujol mulls on NaCl plates using a Perkin-Elmer 1725X Fourier transformed infrared spectrometer.

Synthesis of [Li{N(*t*-Bu)CHCH$_2$N-*t*-Bu}$_2$AlH$_2$], 2. To a solution of 1,4-di-*tert*-butyl-1,4-diazabutadiene, **1** (1.00 g, 5.96 mmol), in diethyl ether (10 mL) at −50 °C was added dropwise a solution of LiAlH$_4$ (113 mg, 2.90 mmol) in diethyl ether (18 mL) at −50 °C over 10 min. The colorless solution was allowed to warm to room temperature to yield a pale yellow solution and a colorless crystalline precipitate. Diethyl ether (30 mL) was then added to dissolve all the solids, and the solution was stirred for 3 h. Filtering and concentrating the solution in vacuo and cooling to −30 °C yielded colorless prismatic crystals of **2** overnight. Subsequent cropping of the crystals yielded more product (0.82 g, 74% yield). Mp: 119−121 °C dec. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 1.04 (18H, s, Me), 1.26 (18H, s, Me), 3.57 (2H, dd, $^2J_{H-H}$ = 20.8 Hz, $^3J_{H-H}$ = 2.2 Hz, NCH$_2$), 4.35 (2H, d, $^2J_{H-H}$ = 20.8 Hz, NCH$_2$), 7.41 (2H, d, $^3J_{H-H}$ = 2.2 Hz, N═CH). ^{13}C NMR (50 MHz, C$_6$D$_6$): δ 30.4, 31.0 (Me), 53.3 (N*C*Me$_3$), 53.9 (NCH$_2$), 57.0 (N*C*Me$_3$), 172.9 (N═CH). IR, ν (cm^{-1}): 1661 (br, AlH). Anal. Found: C, 63.87; H, 11.84; N, 14.92. Calcd: C, 64.14; H, 11.84; N, 14.96.

Synthesis of [*cis*-{[μ-N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu]AlH}$_2$], 3. A solution of 1,4-di-*tert*-butyl-1,4-diazabutadiene, **1** (0.50 g, 2.98 mmol), in diethyl ether (10 mL) was added dropwise to a solution of LiAlH$_4$ (113 mg, 2.90 mmol) in diethyl ether (18 mL) at −50 °C over 10 min. The colorless solution was allowed to warm to room temperature to yield a colorless solution and a small amount of a white precipitate. The solution was filtered and the solvent removed in vacuo to give **3** as a white powder (0.56 g, 97% yield). The compound was physically and spectroscopically identical to samples prepared by our published procedure.[6]

Synthesis of [(Et$_2$O)Li{N(*t*-Bu)CH$_2$}$_2$(CHN-*t*-Bu)$_2$Al], 4. A solution of 1,4-di-*tert*-butyl-1,4-diazabutadiene, **1** (1.00 g, 5.96 mmol), in diethyl ether (10 mL) at −50 °C was added dropwise to a solution of LiAlH$_4$ (113 mg, 2.90 mmol) in diethyl ether (18 mL) at −50 °C over 10 min. The pale orange solution was allowed to warm to room temperature to yield a pale yellow solution and small amount of a white precipitate. The solvent was removed in vacuo to give **4** as a viscous white oil which became solid overnight. Compound **4** could be recrystallized in low yield from diethyl ether with difficulty (0.68 g, 63% yield). The complex is spectroscopically identical with the thermal decomposition product of compound **2**. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 0.83 (6H, t, $^3J_{H-H}$ = 7.0 Hz, Me), 1.44 (18H, s, Me), 1.42 (18H, s, Me), 3.38 (4H, s, NCH$_2$), 5.71 (2H, s, NCH). ^{13}C NMR (50 MHz, C$_6$D$_6$): δ 14.3 (CH$_2$*C*H$_3$), 30.8, 31.9 (2 × Me), 46.4 (OCH$_2$), 50.7, 50.8 (2 × N*C*Me$_3$), 64.8 (NCH$_2$), 111.6 (NCH).

Crystal Structure Determinations. Crystals of **2** and **7** suitable for X-ray structure determination were grown from diethyl ether solutions at −30 °C. The crystals were coated with oil and transferred directly to a nitrogen cold stream on the diffractometer for data collection at −100 °C. Crystals of **7** were very sensitive to loss of solvent. Unique diffractometer datasets were measured using Nicolet R3m/V and Rigaku AFC7r diffractometers (for **2** and **7**, respectively). Reflections with $I > 3.0\sigma(I)$ were considered "observed" and used in the full-matrix least-squares refinements, minimizing $\sum w\Delta^2$ after solution of the structures by direct methods. Conventional residuals on *F* at convergence are quoted. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[7] Computation used the teXsan 1.6[8] and SHELXS-86[9] program systems implemented on Silicon Graphics Indy computers. A summary of crystal, solution, and refinement data is given in Table 1. Non-hydrogen and important hydrogen atom coordinates are given in Tables 2 and 3. Molecular projections showing numbering schemes are given in Figures 1 and 2. Only one of the two crystallographically independent molecules of **7** is shown in Figure 2. Selected geometrical parameters are given in Tables 4 and 5 (for **2** and one of the crystallographically independent molecules of **7**). The flack parameters could not be determined for these data sets, and inverting the structures gave no change in the *R* factors. Thermal ellipsoids are drawn at the 20% probability level. For clarity, methyl hydrogens have been omitted; aluminum hydride atoms are shown with their isotropic temperature factor thermal ellipsoids, and others are shown as spheres of arbitrary radii. Anisotropic thermal parameters were refined for all non-hydrogen atoms in each structure. All aluminum hydride atoms were located and refined in *x*, *y*, *z* and U_{iso}; all others were calculated and constrained in *x*, *y*, *z* and U_{iso}.

Table 1. Crystallographic Data for Compounds **2** and **7**

Compound **2**	
empirical formula: C$_{20}$H$_{44}$N$_4$AlLi	space group: $P2_12_12_1$ (No. 19)
a = 10.127(2) Å	T = −100 °C
b = 12.721(3) Å	λ = 0.710 69 Å
c = 19.505(4) Å	ρ_{calcd} = 0.990 g cm^{-3}
V = 2512.8(9) Å^3	μ = 0.90 cm^{-1}
Z = 4	R^a = 0.062
fw 374.52	$R_w{}^b$ = 0.040
Compound **7**	
empirical formula: C$_{30}$H$_{73}$N$_4$Al$_2$Li$_2$O$_{0.5}$	space group: $P2_12_12_1$ (No. 19)
a = 15.708(3) Å	T = −100 °C
b = 35.58(1) Å	λ = 0.710 69 Å
c = 15.423(3) Å	ρ_{calcd} = 0.872 g cm^{-3}
V = 8619(3) Å^3	μ = 0.88 cm^{-1}
Z = 8	R^a = 0.076
fw 565.78	$R_w{}^b$ = 0.084

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Non-Hydrogen and Aluminum Hydride Atom Coordinates and Isotropic Thermal Parameters for **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Al1	−0.9721(2)	−0.1574(2)	−0.16745(10)	2.43(4)[a]
Li1	−0.8423(9)	−0.0067(7)	−0.0881(5)	2.0(2)[a]
N1	−1.0193(4)	−0.0164(3)	−0.1498(2)	2.00(9)[a]
N4	−0.8072(5)	0.1327(4)	−0.1433(2)	2.2(1)[a]
N5	−0.8151(5)	−0.1706(4)	−0.1165(2)	2.08(10)[a]
N8	−0.7980(5)	−0.0621(4)	0.0117(2)	2.3(1)[a]
C1	−1.1432(6)	0.0159(6))	−0.1150(3	3.0(1)[a]
C2	−0.9870(6)	0.0517(4)	−0.2080(3)	2.2(1)[a]
C3	−0.8830(6)	0.1334(5)	−0.1951(3)	2.2(1)[a]
C4	−0.7063(8)	0.2155(5)	−0.1358(4)	4.3(2)[a]
C5	−0.6851(7)	−0.1956(5)	−0.1491(3)	2.7(1)[a]
C6	−0.8338(6)	−0.2249(4)	−0.0513(3)	2.4(1)[a]
C7	−0.8069(6)	−0.1609(5)	0.0109(3)	2.5(1)[a]
C8	−0.7732(6)	−0.0061(5)	0.0780(3)	2.7(1)[a]
C11	−1.1521(6)	−0.0446(5)	−0.0473(3)	3.7(2)[a]
C12	−1.2649(6)	−0.0113(5)	−0.1569(3)	3.8(2)[a]
C13	−1.1435(7)	0.1332(5)	−0.0991(3)	4.4(2)[a]
C41	−0.7598(8)	0.2938(7)	−0.0865(5)	9.8(3)[a]
C42	−0.676(1)	0.2763(7)	−0.1993(4)	10.9(3)[a]
C43	−0.5870(8)	0.1682(8)	−0.1057(7)	14.7(4)[a]
C51	−0.6613(7)	−0.1199(5)	−0.2075(3)	3.5(2)[a]
C52	−0.5713(6)	−0.1830(5)	−0.0979(3)	3.4(2)[a]
C53	−0.6824(7)	−0.3085(5)	−0.1771(3)	3.8(2)[a]
C81	−0.8074(8)	−0.0701(5)	0.1413(3)	4.3(2)[a]
C82	−0.8573(7)	0.0925(5)	0.0772(3)	4.4(2)[a]
C83	−0.6287(7)	0.0228(6)	0.0786(4)	5.4(2)[a]
H1	−0.948(4)	−0.175(4)	−0.252(2)	2(1)
H2	−1.071(3)	−0.232(3)	−0.136(2)	0.7(8)

[a] Isotropic equivalent thermal parameters.

---

(6) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1996**, 4163.

(7) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: New York, 1974; Vol. 4.

(8) *teXsan*, Version 1.6; Molecular Structure Corp.: The Woodlands, TX, 1992.

(9) *SHELXS-86: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

Table 3. Non-Hydrogen and Aluminum Hydride Atom Coordinates (Excluding Those of Solvent Molecules) and Isotropic Thermal Parameters for **7**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2	atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^2
Al1	−0.8766(1)	−0.24835(7)	−0.1532(1)	4.62(6)[a]	C73	−0.3707(5)	−0.1928(3)	−0.0967(5)	8.4(3)[a]
Al2	−0.6882(1)	−0.21193(6)	−0.3572(1)	3.85(5)[a]	C74	−0.4772(5)	−0.1843(3)	−0.2190(5)	8.4(3)[a]
Al3	−0.6001(1)	−0.02874(8)	−0.0166(1)	5.28(6)[a]	C81	−0.4966(6)	−0.3208(2)	−0.1318(8)	10.9(3)[a]
Al4	−0.3962(1)	−0.02974(6)	−0.2248(1)	3.84(5)[a]	C82	−0.6184(6)	−0.2999(3)	−0.0408(6)	9.0(3)[a]
Li1	−0.8912(7)	−0.2375(3)	−0.3579(7)	3.6(2)[a]	C83	−0.6373(7)	−0.3128(2)	−0.2007(6)	10.0(3)[a]
Li2	−0.6739(7)	−0.2247(3)	−0.1573(8)	5.0(3)[a]	C91	−0.6235(8)	−0.0995(2)	−0.3033(6)	12.9(4)[a]
Li3	−0.6048(7)	−0.0160(3)	−0.2128(7)	4.2(3)[a]	C92	−0.5970(6)	−0.0586(3)	−0.4203(7)	10.7(4)[a]
Li4	−0.3866(7)	−0.0321(3)	−0.0154(6)	3.5(2)[a]	C93	−0.7378(5)	−0.0872(2)	−0.4150(5)	7.4(2)[a]
N1	−0.9767(3)	−0.2151(1)	−0.4427(3)	4.3(1)[a]	C111	−1.0533(5)	−0.1694(2)	−0.5384(6)	7.9(3)[a]
N4	−0.9566(3)	−0.2877(1)	−0.3840(4)	4.6(1)[a]	C112	−0.9025(7)	−0.1862(3)	−0.5597(7)	14.8(4)[a]
N5	−0.6214(4)	−0.1961(1)	−0.0541(4)	5.7(2)[a]	C113	−0.9476(5)	−0.1509(2)	−0.4291(6)	8.4(3)[a]
N8	−0.5658(3)	−0.2566(2)	−0.1502(4)	5.7(2)[a]	C121	−0.7068(5)	0.1004(2)	−0.2640(6)	7.9(3)[a]
N9	−0.6840(4)	−0.0378(2)	−0.3058(4)	5.8(2)[a]	C122	−0.6210(5)	0.0601(2)	−0.3600(5)	7.2(2)[a]
N12	−0.6854(3)	0.0320(1)	−0.2340(3)	4.4(1)[a]	C123	−0.5687(5)	0.0750(2)	−0.2099(6)	7.0(2)[a]
N13	−0.3125(4)	−0.0535(1)	0.0816(3)	3.5(1)[a]	C131	−0.4136(6)	−0.0786(3)	0.1815(6)	9.5(3)[a]
N16	−0.3048(4)	0.0130(1)	−0.0073(3)	3.9(1)[a]	C132	−0.3399(7)	−0.1195(2)	0.0803(6)	10.7(3)[a]
C1	−0.9701(5)	−0.1807(2)	−0.4962(5)	6.1(2)[a]	C133	−0.2616(5)	−0.0926(2)	0.2094(5)	6.6(2)[a]
C2	−1.0374(4)	−0.2393(2)	−0.4576(4)	4.2(2)[a]	C151	−0.1476(4)	−0.0108(3)	−0.0235(5)	6.3(2)[a]
C3	−1.0405(4)	−0.2765(2)	−0.4191(4)	3.9(1)[a]	C152	−0.1756(4)	−0.0415(3)	−0.0923(5)	7.2(2)[a]
C4	−0.9096(5)	−0.3189(2)	−0.4331(5)	5.0(2)[a]	C153	−0.1170(5)	0.0268(3)	−0.0691(6)	9.9(3)[a]
C5	−0.6639(5)	−0.1714(2)	0.0076(5)	6.4(2)[a]	C154	−0.0736(4)	−0.0256(3)	0.0274(5)	7.3(2)[a]
C6	−0.5455(5)	−0.2076(2)	−0.0441(5)	5.1(2)[a]	C161	−0.3741(4)	0.0415(2)	0.1166(5)	6.0(2)[a]
C7	−0.5032(4)	−0.2346(2)	−0.1008(4)	5.4(2)[a]	C162	−0.4174(5)	0.0578(2)	−0.0369(6)	7.5(2)[a]
C8	−0.5771(5)	−0.2968(2)	−0.1303(5)	6.8(2)[a]	C163	−0.2790(5)	0.0821(2)	0.0230(5)	6.8(2)[a]
C9	−0.6658(5)	−0.0708(2)	−0.3618(5)	5.8(2)[a]	C211	−0.8429(5)	0.0105(3)	−0.2106(5)	7.9(2)[a]
C10	−0.7511(5)	−0.0173(2)	−0.3184(5)	5.3(2)[a]	C212	−0.8740(6)	0.0520(3)	−0.1711(7)	10.6(3)[a]
C11	−0.7635(4)	0.0186(2)	−0.2759(4)	4.3(2)[a]	C213	−0.9175(4)	−0.0055(3)	−0.2618(5)	7.3(2)[a]
C12	−0.6474(4)	0.0675(2)	−0.2658(5)	5.2(2)[a]	C214	−0.8200(4)	−0.0181(3)	−0.1337(5)	7.9(3)[a]
C13	−0.3296(5)	−0.0854(2)	0.1393(5)	5.1(2)[a]	H1a	−0.882(3)	−0.227(1)	−0.250(3)	3(1)
C14	−0.2441(4)	−0.0332(2)	0.0913(4)	3.1(1)[a]	H1b	−0.768(5)	−0.240(2)	−0.130(5)	12(1)
C15	−0.2264(4)	−0.0003(2)	0.0390(4)	3.4(1)[a]	H1c	−0.934(3)	−0.230(1)	−0.080(3)	5(1)
C16	−0.3439(4)	0.0487(2)	0.0247(5)	5.1(2)[a]	H1d	−0.887(3)	−0.293(1)	−0.159(3)	4(1)
C31	−1.1185(5)	−0.2752(3)	−0.3467(5)	7.0(2)[a]	H2a	−0.679(3)	−0.204(1)	−0.269(3)	2(1)
C32	−1.1966(5)	−0.2592(3)	−0.3859(5)	9.2(3)[a]	H2b	−0.772(3)	−0.228(1)	−0.386(3)	2(1)
C33	−1.0937(4)	−0.2513(2)	−0.2665(4)	5.6(2)[a]	H2c	−0.650(4)	−0.183(2)	−0.429(4)	9(1)
C34	−1.1378(7)	−0.3171(3)	−0.3180(7)	11.4(3)[a]	H2d	−0.607(4)	−0.246(2)	−0.359(4)	8(1)
C41	−0.8934(6)	−0.3033(3)	−0.5233(5)	8.0(3)[a]	H3a	−0.598(3)	−0.035(1)	−0.115(3)	5(1)
C42	−0.9555(5)	−0.3544(2)	−0.4360(7)	8.6(3)[a]	H3b	−0.504(3)	−0.033(1)	−0.013(3)	2(1)
C43	−0.8249(5)	−0.3242(2)	−0.3845(5)	6.7(2)[a]	H3c	−0.670(3)	−0.054(1)	0.041(3)	4(1)
C51	−0.7240(6)	−0.1936(3)	0.0615(6)	9.5(3)[a]	H3d	−0.614(5)	0.012(2)	−0.016(5)	10(1)
C52	−0.7143(6)	−0.1437(3)	−0.0499(6)	10.3(3)[a]	H4a	−0.399(3)	−0.048(1)	−0.132(3)	2(1)
C53	−0.5994(5)	−0.1502(2)	0.0668(5)	7.8(3)[a]	H4b	−0.479(3)	−0.013(1)	−0.244(3)	1.6(9)
C71	−0.4363(4)	−0.2091(3)	−0.1553(5)	6.7(2)[a]	H4c	−0.373(3)	−0.055(1)	−0.291(3)	3(1)
C72	−0.3820(6)	−0.2374(3)	−0.2151(6)	10.0(3)[a]	H4d	−0.352(4)	0.006(2)	−0.132(3)	6(1)

[a] Isotropic equivalent thermal parameters.

Results and Discussion

Synthesis. The products obtained from the reaction of 1,4-di-*tert*-butyl-1,4-diazabutadiene, **1**, with purified $LiAlH_4$ in diethyl ether at −50 °C are outlined in Scheme 1. The products are based on both addition to the imine functionalities of **1**, giving 1,4-diazabutane-1,4-diyl (or ethylenediamide) species, and reduction of **1** to species containing 1,4-diazabut-2-ene-1,4-diyl moieties, so that the lithium diamidoaluminum dihydride [Li{N(*t*-Bu)CHCH$_2$N-*t*-Bu}$_2$AlH$_2$], **2**, the dimeric diamidoaluminum hydride [*cis*-{[*μ*-N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu]AlH}$_2$], **3**, and the heteroleptic lithium tetraamidoaluminum species [(Et$_2$O)Li{N(*t*-Bu)CH$_2$}$_2$(CHN-*t*-Bu)$_2$Al], **4**, were obtained selectively depending on the stoichiometry and order of addition of the reactants.

The outcomes of these reactions bear relevance to our prior studies on the reaction between the same substrate, **1**, and unpurified $LiAlH_4$ (or indeed the latter with the addition of elemental aluminum).[2] In that case, we found that the product obtained was the homoleptic paramagnetic diazabutadiene complex [Al({N(*t*-Bu)CH}$_2$)$_2$], **5**, which featured both singly and doubly reduced 1,4-diazabutadiene ligands chelating an Al(III) center.

We rationalize these latest results in terms of the initial adducts present in solution at low temperature prior to addition to the imine double bonds taking place as the first process at the reaction temperature of −50 °C. In the case of the addition of an ethereal solution of $LiAlH_4$ to an ethereal solution of **1** using an ideal stoichiometry of 2:1 (**1**:$LiAlH_4$), solvent-separated ion pairs are most likely present in solution, [Li(**1**)$_2$]$^+$[AlH$_4$]$^-$, which react to give the observed product **2** arising from addition to one imine of each of the diazabutadiene ligands. Accordingly, the reaction in a 1:1 stoichiometry yields **2** also (quantitatively in **1**). The hydroalumination of **1** to yield the product **2** must be rapid at the reaction temperature of −50 °C in order to observe the isolation of **2** when the reaction stoichiometry is 1:1 (vide infra; reactions carried out using the reverse order of addition of the reactants).

Interestingly, the reaction does not proceed beyond the formation of **2** by hydroalumination of the remaining imine functionalities of the 1,4-diaza-but-1-en-4-yl moieties to give the lithium tetraamidoaluminum species [Et$_2$O•Li{N(*t*-Bu)CH$_2$-CH$_2$N-*t*-Bu}$_2$Al], which we prepared previously by an independent route.[10] Complex **2** decomposes in benzene solution over a period of several weeks at room temperature (or 2 days

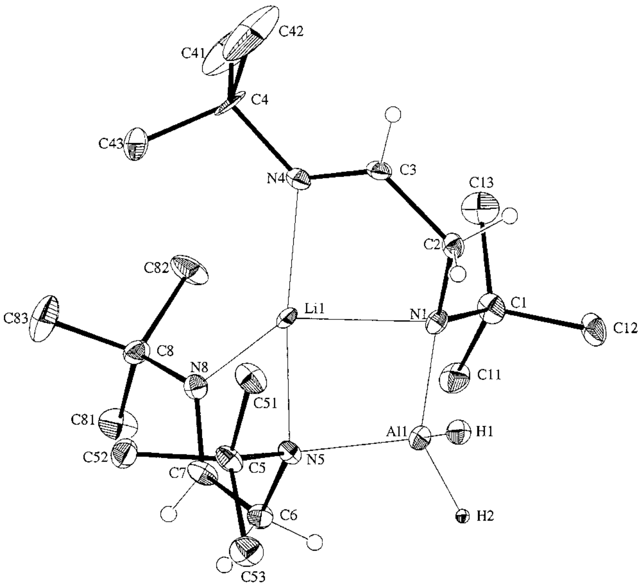


Figure 1. Molecular projection of [Li{N(*t*-Bu)CHCH$_2$N-*t*-Bu}$_2$AlH$_2$], **2**, showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, methyl hydrogen atoms are omitted.

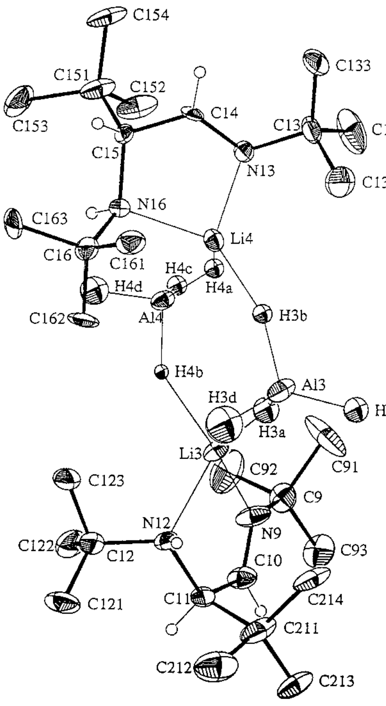


Figure 2. Molecular projection of [{[HN(*t*-Bu)CH(*t*-Bu)CHN-*t*-Bu]-Li(μ-H)$_2$AlH$_2$}$_2$], **7**, (molecule 2), showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, methyl hydrogen atoms are omitted.

in C_6D_6 at 100 °C in a sealed NMR tube experiment) to give a well-defined species which we propose to be the heteroleptic lithium tetraamidoaluminum species [Li{N(*t*-Bu)CH$_2$}$_2$(CHN-*t*-Bu)$_2$Al], **4**. This reactivity implies an overall rearrangement of the remaining unsaturated functionality of the 1,4-diaza-but-1-en-4-yl ligands, loss of H_2, and a displacement of the Li center from the N_4 coordination environment it held in **2** to the nonchelated position it occupies in the product **4**.

Table 4. Selected Structural Parameters for **2**

Bond Distances (Å)

Li1−N1	2.16(1)	Al1−H1	1.67(5)	N4−C4	1.474(9)
Li1−N4	2.11(1)	Al1−H2	1.51(5)	N5−C5	1.50(1)
Li1−N5	2.18(1)	N1−C1	1.485(9)	N5−C6	1.460(8)
Li1−N8	2.12(1)	N1−C2	1.464(8)	C6−C7	1.49(1)
Al1−N1	1.888(6)	C2−C3	1.50(1)	N8−C7	1.259(9)
Al1−N5	1.882(7)	N4−C3	1.269(8)	N8−C8	1.498(9)

Bond Angles (deg)

N1−Al1−N5	101.7(3)	N5−C6−C7	115.4(7)
N1−Al1−H1	110(2)	C6−C7−N8	124.7(7)
N1−Al1−H2	110(1)	C7−N8−C8	119.8(7)
N5−Al1−H1	112(1)	Al1−N1−Li1	86.9(4)
N5−Al1−H2	106(1)	C1−N1−Li1	115.5(6)
H1−Al1−H2	114(2)	C1−N1−Al1	124.1(3)
N1−Li1−N4	84.4(5)	C2−N1−Li1	102.3(5)
N5−Li1−N8	83.6(5)	C2−N1−Al1	111.3(4)
N1−Li1−N5	84.7(5)	C3−N4−Li1	108.1(7)
N1−Li1−N8	131.9(7)	C4−N4−Li1	131.9(6)
N4−Li1−N5	131.0(7)	Al1−N5−Li1	86.7(4)
N4−Li1−N8	135.6(7)	C5−N5−Li1	115.1(6)
C1−N1−C2	112.3(6)	C5−N5−Al1	122.6(4)
N1−C2−C3	115.9(6)	C6−N5−Li1	102.4(6)
C2−C3−N4	123.6(7)	C6−N5−Al1	113.1(5)
C3−N4−C4	119.6(7)	C7−N8−Li1	102.4(6)
C5−N5−C6	112.6(6)	C8−N8−Li1	132.1(6)

Table 5. Selected Structural Parameters for **7** (Molecule 2)

Bond Distances (Å)

Li3−N9	2.05(2)	Al3−H3b	1.59(8)	C10−C11	1.45(1)
Li3−N12	2.15(2)	Al3−H3c	1.67)9)	N12−C11	1.47(1)
Li4−N13	2.04(2)	Al3−H3d	1.5(1)	N12−C12	1.48(1)
Li4−N16	2.06(2)	Al4−H4a	1.46(7)	N13−C13	1.50(1)
Li3−H3a	1.66(9)	Al4−H4b	1.46(7)	N13−C14	1.30(1)
Li3−H4b	2.04(7)	Al4−H4c	1.42(8)	C14−C15	1.45(1)
Li4−H3b	1.89(8)	Al4−H4d	1.4(1)	N16−C15	1.50(1)
Li4−H4a	1.90(8)	N9−C9	1.49(1)	N16−C16	1.49(1)
Al3−H3a	1.53(9)	N9−C10	1.30(1)		

Bond Angles (deg)

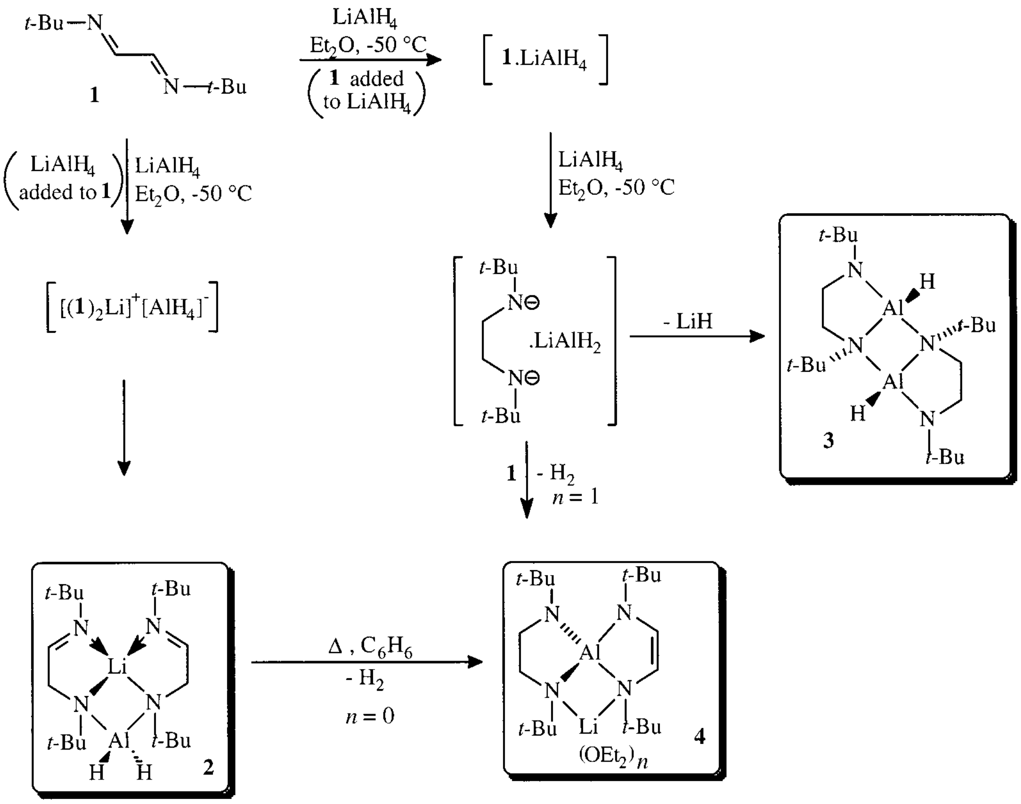
H3a−Al3−H3b	104(4)	N16−Li4−H4a	110(2)
H3a−Al3−H3c	117(4)	H3b−Li4−H4a	96(3)
H3a−Al3−H3d	98(5)	Al3−H3a−Li3	147
H3b−Al3−H3c	114(4)	Al4−H3b−Li4	149
H3b−Al3−H3d	103(5)	Al3−H4a−Li4	138
H3c−Al3−H3d	115(6)	Al4−H4b−Li3	143
H4a−Al4−H4b	109(4)	C9−N9−C10	120(1)
H4a−Al4−H4c	113(3)	N9−C10−C11	122(1)
H4a−Al4−H4d	111(4)	C10−C11−N12	111.8(10)
H4b−Al4−H4c	110(4)	C11−N12−C12	117.8(9)
H4b−Al4−H4d	94(4)	C13−N13−C14	120.7(9)
H4c−Al4−H4d	116(4)	N13−C14−C15	122.9(9)
N9−Li3−N12	80.6(8)	C14−C15−N16	111.3(8)
N9−Li3−H3a	121(3)	C15−N16−C16	116.7(9)
N9−Li3−H4b	116(2)	C9−N9−Li3	126.0(10)
N12−Li3−H3a	119(3)	C10−N9−Li3	112.7(10)
N12−Li3−H4b	119(2)	C11−N12−Li3	107.6(9)
H3a−Li3−H4b	100(3)	C12−N12−Li3	119.4(9)
N13−Li4−N16	83.8(7)	C13−N13−Li4	128.9(9)
N13−Li4−H3b	112(2)	C14−N13−Li4	110.3(8)
N13−Li4−H4a	129(1)	C15−N16−Li4	107.1(8)
N16−Li4−H3b	127(2)	C16−N16−Li4	115.2(8)

In the 1:1 stoichiometric reaction in which an ethereal solution of **1** is added to an ethereal solution of $LiAlH_4$, an initial adduct of 1:1 stoichiometry is most probably formed (possibly having a dimeric structure analogous to our previously reported related $LiAlH_4$ adducts having the structural motif [{L$_2$Li(μ-H)$_2$AlH$_2$}$_2$], where L_2 represents an N,N-bidentate ligand).[3] Addition to the imine functionalities then would give a lithium diamidoaluminum dihydride of unknown structure, {LiH[N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu]AlH}$_n$, which we have shown in previous studies to be unstable with respect to elimination of LiH to yield the observed cis isomer of the dimeric diamidoaluminum hydride, [*cis*-{[μ-

---

(10) Gardiner, M. G.; Raston, C. L.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1997**, *36*, 2795.

Scheme 1



N(*t*-Bu)CH_2CH_2N-*t*-Bu]AlH}$_2$], **3**.[6] A product with the same NMR spectroscopic features as those of the thermal decomposition product of **2** is obtained from the reaction carried out using the same order of addition but a stoichiometry of 2:1 (**1**:$LiAlH_4$). We account for this reactivity by proposing that the thermally unstable lithium diamidoaluminum dihydride {LiH[N(*t*-Bu)CH_2-CH_2N-*t*-Bu]AlH}$_n$ must be formed at the reaction temperature of −50 °C. This species then reacts with the second stoichiometric quantity of **1** by the elimination of molecular hydrogen, with concomitant 2-electron reduction of **1** to yield the heteroleptic lithium tetraamidoaluminum species [(Et_2O)Li{N(*t*-Bu)-CH_2}$_2$(CHN-*t*-Bu)$_2$Al], **4**. The formation of **4** must occur prior to the thermal decomposition of {LiH[N(*t*-Bu)CH_2CH_2N-*t*-Bu]-AlH}$_n$ to give **3**, since isolated samples of complex **3** do not react further with an equivalent of **1**.

Compounds **2**−**4** were isolated as air- and moisture-sensitive crystalline solids and were characterized using ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy, and microanalysis (accurate microanalysis for **4** could not be obtained due to its poor crystallinity). The X-ray crystal structure was determined for compound **2**. Compound **3** is physically and spectroscopically identical to samples prepared previously by independent methods,[6] and its characterization will not be discussed here. The NMR spectroscopic features of compounds **2** and **4** are in accordance with the proposed structures; for **4**, fluxionality is observed in solution at room temperature, giving rise to equivalence of the *t*-Bu substituents and methylene and vinylic groups within each of the {N(*t*-Bu)CH_2CH_2N-*t*-Bu} and {N(*t*-Bu)CHCHN-*t*-Bu} dianions. Such fluxional motion of the lithium cations was previously noted by us and other groups in related lithium tetraamidoaluminum complexes.[11]

X-ray Structure Commentary. The X-ray structure determinations of **2** and **7** represent the first examples of aluminum hydride derivatives in which an imine functionality is present. The stability of the complexes can be attributed to the coordination of the imine functionalities to the lithium centers in the complexes. Hydroalumination of imines is believed to occur through coordination of the imine nitrogen to the aluminum center followed by addition to the C=N double bond.[12] The lithium centers in complexes **2** and **7** compete with this process, rendering the compounds stable with respect to hydroalumination in the solid state and also relatively stable in solution at room temperature.

(a) Structure of 2. Complex **2** crystallizes as prismatic crystals in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell, the asymmetric unit comprising one discrete monomeric molecule, Figure 1. In the lithium diamidoaluminum dihydride, the *N*-aluminated 1,4-diaza-but-1-ene ligands chelate the lithium cation with the metalated amido nitrogen centers bridging the aluminum dihydride unit, achieving 4-fold, distorted tetrahedral coordination for both the aluminum and lithium centers which have {μ-N(amido)$_2$}H_2 and {μ-N(amido)$_2$}N(imine)$_2$ coordination environments, respectively. The molecule possesses noncrystallographic C_2 symmetry, the molecular symmetry axis passing through the lithium and aluminum centers. The chemical features of the structure are closely related to the recently reported bis(diethyl ether) adduct of the lithium dipnictidoaluminum dihydrides [(Et_2O)$_2$Li{μ-E($SiMe_3$)$_2$}$_2AlH_2$] (E = P, As).[13]

The terminal Li−N(imine) distances of 2.11(1) and 2.12(1) Å are similar to those in [Li(1,4-di-*tert*-butyl-1,4-diazabutadi-

---

[11] (a) Veith, M.; Zimmer, M.; Müller-Becker, S. *Angew. Chem.* **1993**, *105*, 1771; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1731. (b) Maseras, F.; Lledós, A. *J. Chem. Soc., Chem. Commun.* **1995**, 443.

[12] (a) Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560. (b) Coxon, J. M.; Luibrand, R. T. *Tetrahedron Lett.* **1993**, *34*, 7093, 7097.

[13] Janik, J. F.; Wells, R. L.; White, P. S. *Organometallics* **1998**, *17*, 2361.

ene)$_2$],[14] 2.134(7)−2.148(6) Å, and [{LiO{4-Me-2,6-[N(*i*-Pr)-CH]$_2$C$_6$H$_2$}}$_3$],[15] 2.12 Å, but longer than those observed in the dimeric lithium amides [*trans*-{Li[*μ*-N(SiMe$_3$)C(Ph)CHC(Ph)-NSiMe$_3$]}$_2$],[16] 1.95(1) Å, and [*cis*-{Li[*μ*-N(*t*-Bu)C(*t*-Bu)HCHN-*t*-Bu]}$_2$],[17] 1.977(6) Å, which is in accordance with the coordination numbers of the lithium atoms being only 3 in the latter cases. The lithium coordinated imine C═N bond distances measure 1.259(9) and 1.269(8) Å. The bridging Li−N(amido) distances measure 2.16(1) and 2.18(1) Å and are relatively long. The N−Li−N ligand bite angles (84.4(5) and 83.6(5)°) and the N−Li−N angles of the four-membered LiAlN$_2$ ring (84.7(5)°) represent the largest distortions of the geometry about the lithium center from ideal tetrahedral coordination, though the remaining exocyclic N−Li−N angles are also much larger than ideal, at 131.0(7)−135.6(7)°.

The bridging Al−N(amido) distances measure 1.888(6) and 1.882(7) Å, and the Al−H distances are 1.51(5) and 1.67(5) Å. The coordination geometry at the aluminum center is only slightly distorted from ideal tetrahedral coordination, the largest distortions being observed for the cyclic N−Al−N (101.7(3)°) and exocyclic H−Al−H (114(2)°) angles. Other bond lengths and angles within the molecule are unexceptional and do not require comment.

(b) Structure of 7. Complex **7** crystallizes as prismatic crystals in the orthorhombic space group $P2_12_12_1$ with eight dimeric molecules of **7** and four molecules of noncoordinating diethyl ether in the unit cell, the asymmetric unit containing two dimeric molecules of **7** and one molecule of diethyl ether, Figure 2. The crystallographically independent molecules are enantiomers (arising from a nonstereospecific addition to the imine of the 1,4-diazabut-1-ene) and show no significant difference in geometry beyond minor packing effects. The 1,4-diazabut-1-enes chelate in a cis manner with respect to each other and the central Li$_2$Al$_2$H$_4$ ring. The chirality at the *C* centers are the same within each dimer. The molecules possess noncrystallographic C_2 symmetry, the axes passing through the centers of the hydride-bridged ring cores of the molecules. The geometry description will thus be based on both molecules combined. In the dimeric lithium aluminum tetrahydride species, the lithium cations are chelated by the 1,4-diazabut-1-ene units, and the [Al(*μ*-H)$_2$H$_2$]$^-$ units bridge the lithium centers through two monohydride bridges forming a central Li$_2$Al$_2$H$_4$ ring, which deviates significantly from planarity. The lithium and aluminum centers both share 4-fold, distorted tetrahedral coordination and have N(imine)N(amine)H$_2$ and (*μ*-H)$_2$H$_2$ coordination environments, respectively.

The terminal Li−N(imine) distances cover a small spread, 2.04(2)−2.06(2) Å, with the lithium-coordinated C═N imine bond distances measuring 1.27(1)−1.31(1) Å. However, the terminal Li−N(amine) distances are quite varied, 2.05(2)−2.15(2) Å. The N−Li−N ligand bite angles measure 80.6(8)−84.3(9)°, and the H−Li−H angles, 95(3)−109(5)°.

The Al−H distances of the isotropically refined hydrides vary from 1.39(8) to 1.8(1) Å. The Li−H distances are also spread over a considerable range, 1.6(1)−2.04(7) Å. These geometries concerning the refined hydride positions compare well with those of a related dimeric ethylenediamine adduct of LiAlH$_4$, [{[HN(*t*-Bu)CH(*t*-Bu)CH$_2$N(H)(*t*-Bu)]Li(*μ*-H)$_2$AlH$_2$}$_2$], in which the hydrides were better refined.[3] The coordination geometries at the aluminum centers are somewhat distorted from ideal tetrahedral coordination, the H−Al−H angles ranging from 94(4) to 119(4)°, with no trends in being observed between the chemically inequivalent angles. Other bond lengths and angles within the molecules are unexceptional and do not require comment.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council. We thank G. D. Fallon for collection of one of the X-ray datasets.

Supporting Information Available: Tables of X-ray crystallographic data and full listings of atomic coordinates, thermal parameters, and bond distances and angles for **2** and **7** and a molecular projection of compound **7** (molecule 1). This material is available free of charge via the Internet at http://pubs.acs.org.

IC990298Y

---

(14) Gardiner, M. G.; Hanson, G. R.; Henderson, M. J.; Lee, F. C.; Raston, C. L. *Inorg. Chem.* **1994**, *33*, 2456.

(15) Korobov, M. S.; Minkin, V. I.; Nivorozhkin, L. E.; Kompan, O. E.; Struchkov, Y. T. *Zh. Obshch. Khim.* **1989**, *59*, 429.

(16) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699.

(17) Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4206.