Synthesis and Characterization of Aluminum Nitroxide Complexes

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ABSTRACT

We report the synthesis of aluminum complexes of pyridyl nitroxide (^RpyNO⁻) ligands. The dimeric complexes {(μ-pyNO⁻)Al(CH₃)₂}₂ (**1**) and {(μ-^{CH}₃pyNO⁻)Al(CH₃)₂}₂ (**2**) were prepared through the 1:1 reaction between the pyridyl hydroxylamine ligand precursors ^RpyNOH and trimethylaluminum. Both compounds were characterized by ¹H and ¹³C NMR spectroscopies. X-ray structural analysis revealed that **1** and **2** are isostructural, with the dimer structure resulting from an Al₂O₂ core. Reaction of pyNOH with two equivalents of trimethylaluminum yielded the aluminum complex (pyNO⁻)AlMe₂•AlMe₃ (**3**), which was also characterized by ¹H and ¹³C NMR spectroscopies and single-molecule X-ray diffraction. The electronic structure of the {(μ-pyNO⁻)Al(CH₃)₂}₂ and {(μ-^{CH}₃pyNO⁻)Al(CH₃)₂}₂ complexes were interrogated using UV-Vis

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4 electronic absorption spectroscopy and electrochemistry. The cyclic voltammograms of the
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6 complexes show two separate oxidation processes, the potentials of which are both dependent on
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8 the substitution pattern of the $^R\text{pyNO}^-$ ligands.
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10 11 12 KEYWORDS 13

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15 Aluminum, Redox-active ligand, Nitroxide ligand, Electrochemistry, Non-innocent ligand
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22 The synthesis of metal complexes of redox-active and non-innocent ligands has become an
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24 important area of research in recent years[1-3] and has expanded the tool-set for the metal-based
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26 manipulation of small molecules.[4] Aluminum is among the most abundant elements,
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28 comprising >8% of the earth's crust,[5] making it a readily available and inexpensive metal. The
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30 development of aluminum complexes that have novel reaction patterns aims to expand the utility
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32 of the metal by offering more sustainable systems for small molecule transformations. The
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34 Berben group has been investigating the coordination chemistry of redox-active ligands to
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36 aluminum, which has resulted in a series of complexes that have enabled ligand-facilitated
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38 reactivity and catalysis.[6] We have similarly been interested in the synthesis of aluminum
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40 complexes of redox-active ligands, and have prepared Al- α -diimine complexes across all three
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42 ligand oxidation states.[7, 8] Recently, we reported the preparation of a series of Al-nitroxide
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44 complexes of the type $(^R\text{pyNO}^-)_2\text{AlCl}$ ($^R\text{pyNO}^- = N\text{-tert-butyl-}N\text{-(2-pyridyl)nitroxyl}$, $R = \text{H}$,
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46 CH_3 , CF_3) and discussed the structural, spectroscopic, and computational aspects of the
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48 compounds.[9] We have continued this work and in the current contribution we report the
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50 reaction of the $^R\text{pyNOH}$ ($R = \text{H}$, CH_3) ligand-precursors with AlMe_3 . The spectroscopic and
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52 structural characterization of the resultant coordination complexes is also provided.
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MATERIALS AND METHODS

Physical Measurements. ^1H and ^{13}C NMR spectra were recorded at ambient temperature in C_6D_6 using a Varian 400 MHz spectrometer (399.78 MHz for ^1H , 100.52 MHz for ^{13}C). Chemical shifts were referenced to residual solvent. s = singlet, d = doublet, t = triplet, b = broad, m = multiplet. Elemental analyses were performed at Complete Analysis Laboratories on a CHN analyzer by Thermo Electron. Electrochemical measurements were performed in a glovebox under a dinitrogen atmosphere using a BASi Epsilon-EC Potentiostat/Galvanostat. A glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire plated with AgCl as a quasi-reference electrode were utilized. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were ~ 3 mM in analyte and 100 mM in $[n\text{-Pr}_4\text{N}][\text{BAR}^{\text{F}}]$ ($\text{BAR}^{\text{F}} = \text{B}(\text{3,5-CF}_3)_2\text{-C}_6\text{H}_3)_4^-$) in ~ 3 mL of THF. All data were collected in a positive-feedback IR compensation mode. Absorbance spectra were collected using an Agilent 8453 UV-vis spectroscopy system in anhydrous dichloromethane at ambient temperature and pressure.

X-ray Structure Determination. X-ray diffraction data were collected on a Brüker APEX II CCD diffractometer employing graphite-monochromated Mo-K α radiation. Rotation frames were integrated using SAINT,[10] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[11] program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[12] The structures were solved by direct methods and refined by full-matrix least squares based on F^2 using SHELXL-97.[13] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. X-ray structures

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4 were rendered using Mercury as made available from the Cambridge Crystallographic Data
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10 **Preparation of Compounds.** All reactions and manipulations were performed under an inert
11 atmosphere (N₂) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II
12 drybox equipped with a molecular sieves 13X/Q5 Cu-0226S catalyst purifier system. Glassware
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14 was dried overnight at 150 °C before use. C₆D₆ was purchased from Sigma Aldrich and stored
15 over potassium metal prior to use. Tetrahydrofuran, methylene chloride, hexanes, pentane, and
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17 toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry
18 argon and dried using a commercial two-column solvent purification system comprising columns
19 packed with Q5 reactant and neutral alumina respectively (for hexanes, toluene, and pentane), or
20 two columns of neutral alumina (for THF and methylene chloride). The ligand precursors *N-tert*-
21 butyl-*N*-(2-pyridyl)hydroxylamine and *N-tert*-butyl-*N*-2-(5-methylpyridyl)-hydroxylamine were
22 prepared as previously reported.[14] [*n*-Pr₄N][BAr^F] was prepared according to literature
23 procedures.[15] All other reagents were purchased from commercial sources and used as
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42 **Synthesis of {(μ-pyNO⁻)Al(CH₃)₂}₂ (1):** *N-tert*-Butyl-*N*-(2-pyridyl)hydroxylamine (0.10 g,
43 0.60 mmol) was added to a flask equipped with a magnetic stir bar and was dissolved in toluene
44 (~25 mL). A 2.0 M solution of trimethylaluminum in heptane (0.30 mL, 0.60 mmol) was added
45 to the solution and the resulting mixture was stirred at room temperature. After 12 h, the reaction
46 was filtered over a Celite-padded frit and the volatiles were removed from the filtrate under
47 reduced pressure. The resultant oily solid was triturated with pentane (3 × 10 mL) and dried
48 under reduced pressure to give **1** as a yellow solid. Yield: 0.11 g, 0.25 mmol (83%). ¹H NMR
49 (C₆D₆): δ 7.45 (bs, 2H), 6.63 (t, *J* = 1.2 Hz, 2H), 6.44 (d, *J* = 8.8 Hz, 2H), 5.93 (t, *J* = 6.0 Hz,
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2H), 1.27 (s, 18H, C(CH₃)₃), -0.24 (s, 12H, Al-CH₃). ¹³C NMR (C₆D₆): δ 159.5, 143.0, 137.5, 115.5, 114.0, 62.6(C(CH₃)₃), 28.6 (C(CH₃)₃), -6.3 (AlCH₃). Anal. Calcd. for C₂₂H₃₈Al₂N₄O₂: C, 59.44; H, 8.62; N, 12.60. Found: C, 59.34; H, 8.46; N, 12.55. UV-vis spectrum (CH₂Cl₂), λ_{max} (ε_M): 284 (24,400), 355 (5430).

Synthesis of {(μ-^{CH₃}pyNO⁻)Al(CH₃)₂}₂ (2): *N-tert*-Butyl-*N*-2-(5-methylpyridyl)-hydroxylamine (0.11 g, 0.60 mmol) was added to a flask equipped with a magnetic stir bar and was dissolved in toluene (~25 mL). A 2.0 M solution of trimethylaluminum in heptane (0.30 mL, 0.60 mmol) was added to the solution and the resulting mixture was stirred at room temperature. After 12 h, the reaction was filtered over a Celite-padded frit and the volatiles were removed from the filtrate under reduced pressure. The resultant oily solid was triturated with pentane (3 × 10 mL) and dried under reduced pressure to give **2** as a yellow solid. Yield: 0.10 g, 0.21 mmol (70%). ¹H NMR (C₆D₆): δ 7.77 (bs, 2H), 6.57 (s, 4H), 1.52 (s, 6H, pyCH₃), 1.34 (s, 18H C(CH₃)₃), -0.18 (s, 12H, AlCH₃). ¹³C NMR (C₆D₆): δ 158.8, 143.3, 139.7, 114.6, 110.2, 63.3 (C(CH₃)₃), 28.7 (C(CH₃)₃), 17.0 (pyCH₃), -5.5 (AlCH₃). Anal. Calcd. for C₂₄H₄₂Al₂N₄O₂: C, 61.00; H, 8.96; N, 11.86. Found: C, 60.86; H, 9.04; N, 11.93. UV-vis spectrum (CH₂Cl₂), λ_{max} (ε_M): 285 (14,090), 355 (3344).

Synthesis of (pyNO⁻)Al(CH₃)₂•Al(CH₃)₃ (3): *N-tert*-Butyl-*N*-(2-pyridyl)hydroxylamine (0.10 g, 0.60 mmol) was added to a flask equipped with a magnetic stir bar and was dissolved in toluene (~25 mL). A 2.0 M solution of trimethylaluminum in heptane (0.60 mL, 1.20 mmol) was added to the stirring solution and the resulting mixture was stirred at room temperature. After 12 h, the reaction was filtered over a Celite-padded frit and the volatiles were removed from the filtrate under reduced pressure. The resultant oily solid was dissolved in hexane, filtered over a

Celite-padded frit, and dried under reduced pressure to give **3** as a colorless solid. Yield: 0.12g, 0.41 mmol (68%). ^1H NMR (C_6D_6): δ 6.97 (dm, 1H, $J = 5.6$ Hz), 6.57 (td, 1H, $J = 8.4$ Hz, $J = 1.6$ Hz), 6.34 (dm, 1H, $J = 8.4$ Hz), 5.94 (tm, 1H, $J = 5.6$ Hz) 1.06 (s, 9H $\text{C}(\text{CH}_3)_3$), -0.20 (s, 6H, AlCH_3), -0.27 (s, 9H, AlCH_3). ^{13}C NMR (C_6D_6): δ 161.6, 141.9, 140.8, 119.6, 116.5, 65.4 ($\text{C}(\text{CH}_3)_3$), 28.5 ($\text{C}(\text{CH}_3)_3$), -5.8 (AlCH_3), -7.0 (AlCH_3). Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{Al}_2\text{N}_2\text{O}$: C, 57.13; H, 9.59; N, 9.52. Found: C, 57.09; H, 9.65; N, 9.76. UV-vis spectrum (CH_2Cl_2), λ_{max} (ϵ_{M}): 284 (12,508), 351 (3025).

RESULTS AND DISCUSSION

Synthesis, Characterization, and Solid State Structures of Aluminum Complexes 1–3.

Reaction of one equivalent of a 2-(*t*-butyl-hydroxylamine)pyridine ($^{\text{R}}$ pyNOH) with AlMe_3 in toluene cleanly affords the $\{[\mu\text{-}O\text{-}\kappa^2\text{-}N_{\text{py}}, O\text{-}2\text{-}(^t\text{BuNO})\text{py}^{\text{R}}]\text{AlMe}_2\}_2$ complexes $\{(\mu\text{-pyNO}^-)\text{AlMe}_2\}_2$ (**1**) and $\{(\mu\text{-}^{\text{CH}_3}\text{pyNO}^-)\text{AlMe}_2\}_2$ (**2**), in 83% and 70% yield, respectively. The ^1H NMR spectra of the crude reaction products for both compounds indicate that the deprotonation reactions are occurring essentially quantitatively with no apparent side products. Compounds **1** and **2** were isolated as pale yellow solids that are indefinitely stable in the solid state when stored under an N_2 environment at -25 °C.

Scheme 1. Synthesis of the Al-pyridyl nitroxide complexes **1–3**.

Complexes **1** and **2** were readily characterized by ¹H and ¹³C NMR spectroscopies. The ¹H NMR spectrum of **1** in C₆D₆ lacks the O–H signal of the ligand precursor, indicating that the deprotonation reaction between the hydroxylamine hydrogen and one of the basic Al–CH₃ moieties proceeds to completion. The remaining ligand resonances are readily assignable and in the expected chemical shift ranges, indicating that the complex is diamagnetic with an Al^{III} cation supported by a fully reduced hydroxylamine ligand. There are four unique aromatic resonances that all appear as multiplets and integrate with equal intensities and as well as a singlet assignable to the *t*-Bu protons at 1.28 ppm. The Al–CH₃ groups appear as a single resonance at –0.24 ppm.[16] The 3:2 integration ratio between the *t*-Bu group in the ligand backbone and the unreacted Al–CH₃ groups indicates addition of one ligand per aluminum ion

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4 and helps support the formulation of **1**. The ^1H NMR spectrum of **2** in C_6D_6 is similar to that of
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7 **1**, lacking the O–H signal of the ligand precursor and having a 3:2 ratio for the *t*-Bu protons (δ
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9 1.34 ppm) and Al–Me groups (δ –0.18 ppm).[16] In addition, there is a singlet at 1.52 ppm
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11 assignable to the methyl groups attached to the pyridine ring and two aromatic signals that
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13 integrate with a 2:1 ratio. The ^{13}C NMR spectra of **1** and **2** both have characteristic signals for
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15 the ligand *t*-Bu group, with resonances at ~28 ppm ($\text{C}(\text{CH}_3)_3$) and ~62 ppm ($\text{C}(\text{CH}_3)_3$) as well as
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17 five aromatic signals for the aromatic ring. Both **1** and **2** also have resonances assignable to the
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19 Al–CH₃ groups that resonate upfield at –6.3 ppm and –5.5 ppm, respectively.
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24 The structures of the complexes **1** and **2** were corroborated by X-ray crystallography. Single
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26 crystals of both compounds were grown from hexanes solutions at –25 °C. Crystallographic data
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28 is provided in Table 1 and the solid-state structures are represented in Figures 1 (for **1**) and 2 (for
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31 **2**).
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Table 1. Crystallographic Data for Complexes **1–3**.

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Formula	C ₂₂ H ₃₈ N ₄ O ₂ Al ₂	C ₂₄ H ₄₂ N ₄ O ₂ Al ₂	C ₁₄ H ₂₈ N ₂ OAl ₂
<i>a</i> (Å)	15.4855(4)	12.5111(7)	8.5369(13)
<i>b</i> (Å)	9.6921(3)	14.4715(8)	9.1411(13)
<i>c</i> (Å)	17.9445(5)	15.8403(8)	12.2948(19)
α (°)	90	90	93.166(5)
β (°)	109.9400(10)	103.133(2)	90.614(5)
γ (°)	90	90	112.238(4)
<i>V</i> (Å ³)	2531.78(12)	2792.9(3)	886.2(2)
<i>Z</i>	4	4	2
<i>FW</i> (g/mol)	444.52	472.58	294.34
<i>Space group</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>T</i> (K)	100(1)	100(1)	100(1)
λ (Å)	0.71073	0.71073	0.71073
<i>D</i> _{calc} (Mg·m ⁻³)	1.166	1.124	1.103
μ (mm ⁻¹)	0.139	0.129	0.160
<i>R</i> _I (I > 2σ(I))	0.0295	0.0286	0.0273
<i>wR</i> ₂ (all data)	0.0827	0.0830	0.0759
<i>T</i> _{max} / <i>T</i> _{min}	0.7456/0.7109	0.7456/0.7199	0.7456/0.7123
<i>GOF</i> (F ²)	1.023	1.029	1.053

Figure 1. Solid state structure of $\{(\mu\text{-pyNO}^-)\text{Al}(\text{CH}_3)_2\}_2$ (**1**). Ellipsoids are projected at 30% probability and H atoms are omitted for clarity. Selected bond distances (Å): N(4)–O(2), 1.4348(11); Al(2)–C(21), 1.9858(13); Al(2)–C(22), 1.9722(13); Al(2)–O(1), 1.8890(8); Al(2)–N(1), 2.0840(10); N(2)–O(1), 1.4334(11); Al(1)–C(19), 1.9905(12); Al(1)–C(20), 1.9752(12); Al(1)–O(2), 1.9054(8); Al(1)–N(3), 2.0806(10); Al(1)–O(1), 1.9973(8); Al(2)–O(2), 1.9813(8). Selected bond angles (°): C(21)–Al(2)–C(22), 116.65(6); O(1)–Al(2)–C(21), 124.61(5); O(1)–Al(2)–C(22), 118.67(5); O(1)–Al(2)–N(1), 76.59(4); O(1)–Al(2)–O(2), 70.33(3); N(1)–Al(2)–C(21), 93.51(5); N(1)–Al(2)–C(22), 97.93(5); N(1)–Al(2)–O(2), 144.51(4); O(2)–Al(2)–C(21), 94.77(5); O(2)–Al(2)–C(22), 108.83(4); C(19)–Al(1)–C(20), 114.84(6); O(2)–Al(1)–C(19), 132.61(5); O(2)–Al(1)–C(20), 112.52(5); O(2)–Al(1)–N(3), 76.33(4); O(2)–Al(1)–O(1), 69.66(3); N(3)–Al(1)–C(19), 93.71(4); N(3)–Al(1)–C(20),

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4 100.49(4); N(3)–Al(1)–O(1), 139.84(4); O(1)–Al(1)–C(19), 93.88(4); O(1)–Al(1)–C(20),
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6 111.70(4).
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38 **Figure 2.** Solid state structure of $\{(\mu\text{-CH}_3\text{pyNO}^-)\text{Al}(\text{CH}_3)_2\}_2$ (**2**). Ellipsoids are projected at 30%
39 probability and H atoms are omitted for clarity. Selected bond distances (Å): N(2)–O(1),
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41 1.4362(10); Al(1)–C(11), 1.9909(11); Al(1)–C(12), 1.9768(10); Al(1)–O(1), 1.8998(7);
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43 1.4362(10); Al(1)–C(11), 1.9909(11); Al(1)–C(12), 1.9768(10); Al(1)–O(1), 1.8998(7);
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45 Al(1)–N(1), 2.0993(9); Al(1)–O(1B), 1.9829(7). Selected bond angles (°): C(11)–Al(1)–C(12),
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47 114.35(5); O(1)–Al(1)–C(11), 126.83(4); O(1)–Al(1)–C(12), 118.81(4); O(1)–Al(1)–N(1),
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49 76.59(3); O(1)–Al(1)–O(1B), 69.74(3); N(1)–Al(1)–C(11), 92.87(4); N(1)–Al(1)–C(12),
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51 101.29(4); N(1)–Al(1)–O(1B), 142.76(3); O(1B)–Al(1)–C(11), 94.72(4); O(1B)–Al(1)–C(12),
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53 108.48(4).
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Both **1** and **2** are near C_2 -symmetric and the overall geometries of the complexes are quite similar. The complexes are dimeric and feature Al_2O_2 diamondoid cores formed through dative bonding between the oxygen atom of one ($^R\text{pyNO}^-$)AlMe₂ unit with the aluminum atom of the other. The core is both puckered and asymmetric, with the Al–O distances within each ($^R\text{pyNO}^-$)AlMe₂ unit being shorter (Al–O_{ave} = 1.90 Å) relative to the Al---O dative interactions (Al–O_{ave} = 1.99 Å). A similar asymmetry was observed in solid state structures of the aluminum amidate complexes {Me₂Al[μ-*t*-BuNC(R)]}₂ (R = Ph, 4-*t*-Bu-C₆H₄, 2,6-F₂-C₆H₄, Me, CF₃; 4-CF₃-C₆H₄) prepared by Lin et al.[17, 18] In all cases, the aluminum cations are five-coordinate in **1** and **2** with geometries best described as slightly distorted square pyramids, as supported by the structural τ_5 parameters in the range of 0.03-0.08.[19] At 1.90 Å and 2.09 Å, respectively, the average Al–O and Al–N bond distances in **1** and **2** are longer than those observed in our previously reported ($^R\text{pyNO}^-$)₂AlCl complexes (Al–O_{ave} = 1.79 Å; Al–N_{ave} = 1.96 Å).[9] The Al–C distances in **1** and **2** are in the range of 1.9722(13)–1.9909(11) Å, and compare well to other structurally characterized 5-coordinate aluminum complexes with Al–CH₃ moieties.[20] The average N–O distance in **1** and **2** is 1.43 Å, which is comparable to the corresponding distances observed in the ($^R\text{pyNO}^-$)₂AlCl complexes (N–O_{ave} = 1.40 Å).[9] The N–O bond distance in **1** and **2** are indicative of N–O single bonds[21] and support the fully reduced oxidation state assignment of the $^R\text{pyNO}^-$ ligands.

Our attempts to prepare the (pyNO[−])₂AlMe complex through the 2:1 reaction of pyNOH and AlMe₃ were not successful. Instead we isolated complex **1**, indicating that only one of the deprotonation reactions between the pyNOH ligands and AlMe₃ is occurring. This is in contrast to the 2:1 reaction between pyNOH and AlMe₂Cl, which gives (pyNO[−])₂AlCl.[9] Increasing the number of equivalents of pyNOH to three relative to trimethylaluminum still yielded **1** as the

only metal containing product. However, reaction of pyNOH with two equivalents of AlMe₃ in toluene at room temperature gives the monomeric, dinuclear aluminum complex [$\kappa^2\text{-}N_{py}, O\text{-}2\text{-}(t\text{-}BuNO)py^R]$ AlMe₂-AlMe₃ ((pyNO[−])AlMe₂•AlMe₃, **3**) (Scheme 1). Compound **3** was isolated as a colorless solid that is stable in the solid state when stored under an N₂ environment at −25 °C.

Complex **3** was readily characterized by ¹H and ¹³C NMR spectroscopies, which support a diamagnetic complex with a fully reduced nitroxide ligand. As with **1** and **2**, the ¹H NMR spectrum of **3** in C₆D₆ lacks the O–H signal of the ligand precursor, indicating that the deprotonation reaction between the hydroxylamine hydrogen and one of the basic Al–CH₃ moieties was complete. The aromatic region in the ¹H NMR spectra of **3** is similar to that of **1**, with the exception of the most downfield resonance which is shifted upfield in **3** by ~0.5 ppm relative to the same signal in **1**. A singlet assignable to the *t*-Bu protons in **3** comes at 1.06 ppm. The most significant difference in the ¹H NMR spectra of **3** relative to **1** is the presence of two resonances for the Al–CH₃ groups of **3** corresponding to the Al(CH₃)₂ fragment and Al(CH₃)₃ Lewis acid. Both of these groups resonate below 0 ppm (−0.20 and −0.27 ppm, respectively) and integrate in a 2:3 integration ratio. The ¹³C NMR spectra of **3** is very similar to that of **1**, with the exception of an extra resonance assignable to the Al–CH₃ groups of Al(CH₃)₃ in **3**, which comes at −7.0 ppm.

Single crystals of **3** were grown from a hexanes solution at −25 °C. Crystallographic data is provided in Table 1 and the solid-state structure is represented in Figure 3. The extra equivalent of AlMe₃ inhibits formation of the dimeric structure observed for **1** and instead **3** exists as a single (pyNO[−])AlMe₂ unit coordinated to an equivalent of AlMe₃ through the nitroxide oxygen. Both of the aluminum ions in **3** are four-coordinate and according to the τ_4 parameter introduced

by Houser[22] the geometries of both exist between the tetrahedral and trigonal pyramidal geometries ($\tau_4 = 0.90$ (for Al(1)), $\tau_4 = 0.92$ (for Al(2))).

Figure 3. Solid state structure of (pyNO)Al(CH₃)₂•Al(CH₃)₃ (**3**). Ellipsoids are projected at 30% probability and H atoms are omitted for clarity. Selected bond distances (Å): N(2)–O(1), 1.4659(10); Al(1)–C(10), 1.9539(12); Al(1)–C(11), 1.9457(12); Al(1)–O(1), 1.8628(8); Al(1)–N(1), 1.9660(10); Al(2)–C(12), 1.9824(12); Al(2)–C(13), 1.9890(12); Al(2)–C(14), 1.9899(12); Al(2)–O(1), 1.9357(8). Selected bond angles (°): C(10)–Al(1)–C(11), 116.99(5); O(1)–Al(1)–C(10), 115.15(4); O(1)–Al(1)–C(11), 116.51(5); O(1)–Al(1)–N(1), 82.24(4); N(1)–Al(1)–C(10), 114.10(5); N(1)–Al(1)–C(11), 106.26(5); C(12)–Al(2)–C(13), 113.59(5); C(12)–Al(2)–C(14), 111.27(5); C(13)–Al(2)–C(14), 116.27(5); O(1)–Al(2)–C(12), 111.20(4); O(1)–Al(2)–C(13), 100.50(4); O(1)–Al(2)–C(14), 102.85(4).

At 1.4659(10) Å, the N(2)–O(1) distance in **3** is slightly longer than the similar distances observed in **1** and **2** and is indicative of a N–O single bond.[21] The Al–O (1.8628(8) Å) and

Al–N (1.9660(10) Å) bond distances observed for the (pyNO[−])AlMe₂ unit of **3** are comparable to those observed in **1** and **2**, although they are slightly shorter in the former. The Al(2)–O(1) bond distance of 1.9357(8) Å is longer than the Al–O for the (pyNO[−])AlMe₂ unit, as expected for the dative interaction. At 1.9539(12) Å and 1.9457(12) Å, the Al–C bond distances observed for the (pyNO[−])AlMe₂ unit of **3** are comparable to other distances observed for structurally characterized complexes with a AlMe₂ unit coordinated by a bidentate ligand. For example, the series of (ketiminate)AlMe₂ complexes prepared by Ma et al. have an Al–C_{ave} of 1.95 Å[23] while the anilido-oxazolate aluminum complexes prepared by Chen et al. have an average Al–C bond length of 1.96 Å.[24] Finally, the [Me₂Al{(NCOC₆H₄)₂CH}] complex prepared by Dauer and Stalke has Al–C distances of 1.951(2) Å and 1.959(2) Å.[25] At 1.99 Å, the average Al–C bond distance for the AlMe₃ group in **3** compares well to other structurally characterized complexes with a Lewis base–AlMe₃ unit. For example, the Me₂Al[OC(CH₃)₂CH₂NH₂]AlMe₃ complex reported by Lewiński had an average Al–C distance of 1.98 Å for the AlMe₃ moiety.[26] The pyridineenolato-aluminum complex prepared by Lee et al.[27] and the nitric oxide complex [MeAl(ONNMeO)]AlMe₃ prepared by Smith et al.[28] both have average Al–C distances of 1.96 Å for the AlMe₃ groups.

Electronic Structure of the Aluminum Complexes **1** and **2**.

The absorption spectra of compounds **1** and **2** were collected in dichloromethane (Figure 4). The spectra for both compounds appear similar, with a dominant feature at ~285 nm ($\epsilon_M \sim 12,000\text{--}15,000$) and a smaller feature at ~355 nm ($\epsilon_M \sim 3000\text{--}5000$). Both spectra look similar to those of the (R₂pyNO)₂AlCl complexes,[9] although there is slight (~5 nm) bathochromic shift in both features for the complexes herein. We propose that the features in the UV-vis of **1** and **2** arise from transitions from ligand-based orbitals to primarily pyridine based π^* orbitals, as was

proposed for the (^RpyNO)₂AlCl complexes. Although the visual appearance of the solutions of **1** (yellow) and **3** (colorless) is different, the absorbance spectra are very similar suggesting that the different Lewis-base interactions of the (pyNO[−])AlMe₂ unit between the complexes does not significantly alter the ligand-based electronic transitions.

Figure 4. UV-vis spectra of 1×10^{-4} M solutions of **1–3** in CH₂Cl₂.

The cyclic voltammograms of **1** and **2** were collected in THF (Figures 5 and 6, Table 2). The CVs of both **1** and **2** exhibit two features, which we assign as sequential one-electron oxidation processes corresponding to the N–O[−]/N–O[•] couples of each ^RpyNO[−] ligand in the dimer. We do not observe the other two oxidation processes corresponding to the N–O[•]/N=O⁺ couples in the electrochemical window. In both complexes, the first oxidation process is irreversible with the return reduction features essentially absent. The second oxidation is quasi-reversible with diminished return reduction waves for both **1** and **2**. The electrochemistry of **3** in THF is

identical to that of **1** (see Appendix A, Figure A7), which we attribute to dissociation of AlMe_3 from the $(\text{pyNO}^-)\text{AlMe}_2$ moiety in THF solution and subsequent dimerization.[29]

Figure 5. Cyclic voltammogram of compound **1** recorded in 0.1 M $[n\text{-Pr}_4\text{N}][\text{BAR}^{\text{F}}]$ THF solution.

Table 2. Electrochemical Potentials (V vs Fc/Fc^+) for Complexes **1** and **2**.

	$\text{pyNO}^-\text{pyNO}^-/\text{pyNO}^0\text{pyNO}^-$		$\text{pyNO}^0\text{pyNO}^-/\text{pyNO}^0\text{pyNO}^0$		ΔE_{pa}
	E_{pa}	E_{pc}	E_{pa}	E_{pc}	
1	0.07	----	0.78	0.56	0.71
2	0.03	----	0.58	0.43	0.55

Figure 6. Cyclic voltammogram of compound **2** recorded in 0.1 M [*n*-Pr₄N][BAR^F] THF solution.

There is a dependence of the redox potentials for both features in the CVs for **1** and **2** with changing substituent on the pyridine ring. Complex **2** has more negative potentials, as expected from the electron-donating CH₃ group. A similar dependence was seen for both the ^RpyNOH ligand precursors[14] and our previously prepared (^RpyNO⁻)AlCl complexes.[9] Relative to free ligand, the potentials for the redox events observed for **1** and **2** are shifted to more positive values, suggesting that the Lewis acidic AlMe₂ fragment stabilizes the reduced form of the ligand. For example, the first oxidation in **1** occurs at ~0.07 V while the pyNOH/pyNO⁰ couple for free ligand comes at $E_{1/2} = -0.39$ V (versus vs Fc/Fc⁺).[14] Similarly, the first oxidation in **2** occurs ~0.03 V, while the pyNOH/pyNO⁰ couple for free ligand comes at $E_{1/2} = -0.45$ V (versus

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4 vs Fc/Fc^+).[14] A similar stabilization was seen in the $(^R\text{pyNO}^-)\text{AlCl}$ complexes, although the
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6 effect in that case was more pronounced.
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9 10 CONCLUSIONS

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13 The aluminum-pyridyl nitroxide complexes **1–3** were synthesized from the reactions of
14 trimethylaluminum and pyridyl hydroxylamine ligand precursors $^R\text{pyNOH}$. All three complexes
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16 were identified by X-ray crystallography as well as ^1H and ^{13}C NMR spectroscopies. The
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18 electrochemical characterization of complexes **1** and **2** display two redox events, the potentials of
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20 which vary systematically with substitution pattern of the pyridine ring. The complexes prepared
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22 herein complement our previously prepared $(^R\text{pyNO})_2\text{AlCl}$ complexes and further demonstrate
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24 that pyridyl nitroxide ligands can be coordinated to an Al^{III} ion to afford aluminum complexes
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26 supporting redox-active ligands. We are currently investigating the reaction of the pyridyl
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28 hydroxylamines with other aluminum starting materials. We are also investigating the reaction of
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30 compound **1** with Lewis-acid groups to prepare complexes of the type $((\text{pyNO}^-)\text{AlMe}_2 \cdot \text{Lewis}$
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32 Acid to investigate how the Lewis base/Lewis acid interaction affect the electronic structure of
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34 the Al-nitroxide complexes.
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43 44 ACKNOWLEDGMENTS

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Appendix A. Supporting Information. CCDC 1431794-1431796 contains the supplementary crystallographic data for **1**, **2**, and **3**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk. Additional supplementary data (^1H and ^{13}C NMR spectra of **1–3**, CV of **3**) associated with this article can be found in the online version.

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9 not retained, as evidenced by a shift and broadening of the AlMe₃ signal.
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Aluminum complexes of pyridyl nitroxide ligands have been prepared and characterized spectroscopically and structurally. Electrochemical analysis of the complexes shows multi-electron redox properties of the complexes with redox potentials dependent on the ligand substitution pattern.