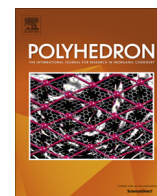




Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of aluminum nitroxide complexes

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ARTICLE INFO

Article history:

Received 20 October 2015

Accepted 1 December 2015

Available online xxxx

Keywords:

Aluminum

Redox-active ligand

Nitroxide ligand

Electrochemistry

Non-innocent ligand

ABSTRACT

We report the synthesis of aluminum complexes of pyridyl nitroxide (^RpyNO⁻) ligands. The dimeric complexes $\{(\mu\text{-pyNO}^-)\text{Al}(\text{CH}_3)_2\}_2$ (**1**) and $\{(\mu\text{-CH}_3\text{pyNO}^-)\text{Al}(\text{CH}_3)_2\}_2$ (**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 $\{(\mu\text{-pyNO}^-)\text{Al}(\text{CH}_3)_2\}_2$ and $\{(\mu\text{-CH}_3\text{pyNO}^-)\text{Al}(\text{CH}_3)_2\}_2$ complexes were interrogated using UV–Vis electronic absorption spectroscopy and electrochemistry. The cyclic voltammograms of the complexes show two separate oxidation processes, the potentials of which are both dependent on the substitution pattern of the ^RpyNO⁻ ligands.

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1. Introduction

The synthesis of metal complexes of redox-active and non-innocent ligands has become an important area of research in recent years [1–3] and has expanded the tool-set for the metal-based manipulation of small molecules [4]. Aluminum is among the most abundant elements, comprising >8% of the earth's crust [5], making it a readily available and inexpensive metal. The development of aluminum complexes that have novel reaction patterns aims to expand the utility of the metal by offering more sustainable systems for small molecule transformations. The Berben group has been investigating the coordination chemistry of redox-active ligands to aluminum, which has resulted in a series of complexes that have enabled ligand-facilitated reactivity and catalysis [6]. We have similarly been interested in the synthesis of aluminum complexes of redox-active ligands, and have prepared Al- α -diimine complexes across all three ligand oxidation states [7,8]. Recently, we reported the preparation of a series of Al-nitroxide complexes of the type (^RpyNO⁻)₂AlCl (^RpyNO⁻ = *N*-*tert*-butyl-*N*-(2-pyridyl)nitroxyl, R = H, CH₃, CF₃) and discussed the structural, spectroscopic, and computational aspects of the compounds [9]. We have continued this work and in the current contribution we report the reaction of the ^RpyNOH (R = H, CH₃) ligand-precursors

with AlMe₃. The spectroscopic and structural characterization of the resultant coordination complexes is also provided.

2. Materials and methods

2.1. Physical measurements

¹H and ¹³C NMR spectra were recorded at ambient temperature in C₆D₆ using a Varian 400 MHz spectrometer (399.78 MHz for ¹H, 100.52 MHz for ¹³C). 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*-Pr₄N][BAR^F] (BAR^{F-} = B(3,5-CF₃)₂-C₆H₃S₄) 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.

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2.2. X-ray structure determination

X-ray diffraction data were collected on a Bruker 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 were rendered using Mercury as made available from the Cambridge Crystallographic Data Centre.

2.3. Preparation of compounds

All reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X/Q5 Cu-0226S catalyst purifier system. Glassware was dried overnight at 150 °C before use. C_6D_6 was purchased from Sigma Aldrich and stored over potassium metal prior to use. Tetrahydrofuran, methylene chloride, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes, toluene, and pentane), or two columns of neutral alumina (for THF and methylene chloride). The ligand precursors *N-tert-butyl-N-(2-pyridyl)hydroxylamine* and *N-tert-butyl-N-2-(5-methylpyridyl)-hydroxylamine* were prepared as previously reported [14]. $[n-Pr_4N][BAR^F]$ was prepared according to literature procedures [15]. All other reagents were purchased from commercial sources and used as received.

2.3.1. Synthesis of $\{(\mu-pyNO^-)Al(CH_3)_2\}_2$ (**1**)

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 (0.30 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 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 **1** as a yellow solid. Yield: 0.11 g, 0.25 mmol (83%). 1H NMR (C_6D_6): 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, 2H), 1.27 (s, 18H, $C(CH_3)_3$), -0.24 (s, 12H, $Al-CH_3$). ^{13}C NMR (C_6D_6): δ 159.5, 143.0, 137.5, 115.5, 114.0, 62.6 ($C(CH_3)_3$), 28.6 ($C(CH_3)_3$), -6.3 ($AlCH_3$). *Anal. Calc.* for $C_{22}H_{38}Al_2N_4O_2$: C, 59.44; H, 8.62; N, 12.60. Found: C, 59.34; H, 8.46; N, 12.55%. UV–Vis spectrum (CH_2Cl_2), λ_{max} (ϵ_M): 284 (24,400), 355 (5430).

2.3.2. Synthesis of $\{(\mu-CH_3pyNO^-)Al(CH_3)_2\}_2$ (**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 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 (C_6D_6): δ 7.77 (bs,

2H), 6.57 (s, 4H), 1.52 (s, 6H, $pyCH_3$), 1.34 (s, 18H $C(CH_3)_3$), -0.18 (s, 12H, $AlCH_3$). ^{13}C NMR (C_6D_6): δ 158.8, 143.3, 139.7, 114.6, 110.2, 63.3 ($C(CH_3)_3$), 28.7 ($C(CH_3)_3$), 17.0 ($pyCH_3$), -5.5 ($AlCH_3$). *Anal. Calc.* for $C_{24}H_{42}Al_2N_4O_2$: C, 61.00; H, 8.96; N, 11.86. Found: C, 60.86; H, 9.04; N, 11.93%. UV–Vis spectrum (CH_2Cl_2), λ_{max} (ϵ_M): 285 (14,090), 355 (3344).

2.3.3. Synthesis of $(pyNO^-)Al(CH_3)_2-Al(CH_3)_3$ (**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 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: 0.12 g, 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 $C(CH_3)_3$), -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 ($C(CH_3)_3$), 28.5 ($C(CH_3)_3$), -5.8 ($AlCH_3$), -7.0 ($AlCH_3$). *Anal. Calc.* for $C_{14}H_{28}Al_2N_2O$: 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).

3. Results and discussion

3.1. Synthesis, characterization, and solid state structures of aluminum complexes **1–3**

Reaction of one equivalent of a 2-(*t*-butyl-hydroxylamine)pyridine (RpyNOH) with $AlMe_3$ in toluene cleanly affords the $\{[\mu-O-\kappa^2-N_{py}, O-2-(t-Bu)NO]py^R]AlMe_2\}_2$ complexes $\{(\mu-pyNO^-)AlMe_2\}_2$ (**1**) and $\{(\mu-CH_3pyNO^-)AlMe_2\}_2$ (**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.

Complexes **1** and **2** were readily characterized by 1H and ^{13}C NMR spectroscopies. The 1H NMR spectrum of **1** in C_6D_6 lacks the O–H signal of the ligand precursor, indicating that the deprotonation reaction between the hydroxylamine hydrogen and one of the basic $Al-CH_3$ 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 $Al-CH_3$ groups appear as a single resonance at -0.24 ppm.¹ The 3:2 integration ratio between the *t*-Bu group in the ligand backbone and the unreacted $Al-CH_3$ groups indicates addition of one ligand per aluminum ion and helps support the formulation of **1**. The 1H NMR spectrum of **2** in C_6D_6 is similar to that of **1**, lacking the O–H signal of the ligand precursor and having a 3:2 ratio for the *t*-Bu protons (δ 1.34 ppm) and $Al-Me$ groups (δ -0.18 ppm).¹ In addition, there is a singlet at

¹ The solid-state structures of complexes **1** and **2** would suggest that two resonances for the $Al-CH_3$ groups should be observed in the 1H and ^{13}C NMR spectra of the complexes. However, only one resonance is observed in the respective NMR spectra. This suggests that in solution the *N*-*t*-Bu nitrogens are rapidly inverting, thereby equilibrating the $Al-CH_3$ groups on the NMR timescale and resulting in a single $Al-CH_3$ resonance in both the 1H and ^{13}C NMR spectra.

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