Synthesis and Characterization of a Tripodal Tris(nitroxide) Aluminum Complex and Its Catalytic Activity toward Carbonyl Hydroboration

Audra J. Woodside,† Mackinsey A. Smith,† Thomas M. Herb,‡ Brian C. Manor,§ Patrick J. Carroll,§ Paul R. Rablen,† and Christopher R. Graves*†‡

†Department of Chemistry & Biochemistry, Albright College, 13th and Bern Streets, Reading, Pennsylvania 19612, United States
‡Department of Chemistry, Swarthmore College, 500 College Avenue, Swarthmore, Pennsylvania 19081, United States
§Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, United States

Supporting Information

ABSTRACT: An aluminum complex of a tripodal tris(nitroxide)-based ligand has been prepared and characterized. The complex has the ability to participate in metal–ligand cooperative catalysis, which has been exploited for the hydroboration of both aldehydes and ketones. This represents new, transition-metal-like reactivity for an earth-abundant metal.

The development of catalyst systems implementing readily available resources is an important effort toward more sustainable synthetic practices.1 Aluminum is highly abundant in the earth’s crust,2 making it an inexpensive and attractive choice for catalyst development. However, the lack of readily available redox chemistry has limited the applicability of conventional aluminum complexes in catalytic oxidative and reductive chemistries of organic molecules. In recent years, aluminum complexes of redox-active and/or noninnocent ligands have offered a platform through which to expand the utility of aluminum complexes in catalysis by moving away from traditional solely Lewis acid activation.3

Our efforts in this area have focused on the preparation of aluminum coordination complexes implementing ligands containing nitroxide functional groups.4,5 We have previously prepared complexes of the pyridyl hydroxyl amines ((pyNO)−AlCl ((pyNO)− = N-tert-butyl-N-(2-(5-R-pyridyl))-nitroxyl, R = H, CH3, CF3) and explored their electrochemical behavior. However, in those systems the aluminum is coordinatively saturated and relatively unreactive. Herein we report the preparation of the aluminum complex of the tripodal tris(nitroxide) ligand [(−BuNO)C6H4CH2,N]− (TriNOx3−)6 and deduce its electronic structure. We also demonstrate the catalytic activity of the (TriNOx3−)Al complex toward the hydroboration of aldehydes and ketones and propose a mechanism that operates through metal–ligand cooperative bifunctional catalysis.

The reaction between TriNOxH3 and AlMe3 at room temperature results in deprotonation of two of the hydroxyl amines commensurate with transfer of the third OH proton to the bridgehead nitrogen of the ligand to give the zwitterion (HTriNOx)AlMe (1) (Scheme 1). Both the Al−CH3 (≈ 0.06 ppm) and N−H (δ 11.14 ppm) functional groups are assignable in the 1H NMR spectrum of 1. The formation of 1 is similar to that of the [O3PH]AlCl ([O3PH]2− = [(2-O-3,5-fBu2C6H2)3PH]2−) complex prepared by Su and Liang in the reaction between AlCl3 with [(2-HO-3,5-fBu2C6H2)3P]7 and represents a rare example of a dianionic scorpionate ligand. On heating a sample of 1 at 100 °C, the third deprotonation occurs to give the desired (TriNOx3−)Al complex (2), as evidenced by 1H NMR spectroscopy. The (TriNOx)Al complex 2 was also prepared through deprotonation of the ligand precursor with 3 equiv of NaN(SiMe3)2 followed by salt metathesis with AlCl3. The complex is most conveniently isolated as the pyridine adduct (TriNOx3−)Al-py (2-py), which was prepared in 79% yield via the salt metathesis route.

The complex 2-py was readily characterized by 1H and 13C NMR spectroscopy. The complex exhibits one singlet resonance in the 1H NMR spectra assignable to the fBu groups, indicating 3-fold symmetry of the tripodal ligand when it is bound to the metal ion. The protons of the bridgehead CH2 groups are diastereotopic, resulting in two doublets (J ≈ 11 Hz) in the 1H NMR, both of which integrate to three protons. The 13C NMR spectra has six unique aromatic...
The geometry of the complex (TriNOx\textsuperscript{3−})Al-py was optimized using density functional theory. Overall the computed structure is in good agreement with the solid-state structure, with the bond distances centered around the aluminum ion being within ~0.05 Å (Table S4). Similarly, all of the bond angles are also in good agreement, with none of the angles deviating by more than 5°. The HOMO (~4.522 eV), HOMO-1 (~4.626 eV), and HOMO-2 (~4.766 eV) are totally ligand based, with electron density primarily localized on the N−O arms.

The complex (TriNOx\textsuperscript{3−})Al-py has the potential to exist over multiple redox states owing to the three nitroxide groups of the ligand. The cyclic voltammogram of 2-py was collected (Figure S11) and shown to exhibit two reversible features, which we assign to the sequential one-electron oxidation processes of the ligand to form the [(TriNOx\textsuperscript{3−})Al\textsuperscript{+}] and [(TriNOx\textsuperscript{3−})Al\textsuperscript{2+}] species. Optimization of the singly [(TriNOx)Al\textsuperscript{+}] and doubly reduced [(TriNOx)Al\textsuperscript{2+}] compounds and visualization of their frontier orbitals support these assignments (see the Supporting Information). The SOMO of the [(TriNOx)Al\textsuperscript{+}] complex is ligand-based and primarily localized on one N−O group and the attached aromatic ring. The LUMO of the [(TriNOx)Al\textsuperscript{2+}] complex is also ligand-based, with the hole being delocalized over all three of the ArN−O moieties.

The (TriNOx\textsuperscript{3−})Al-py complex is able to act as both a Lewis acid through the aluminum ion and as a Lewis base through the nitrogen atoms of the nitroxide arms. For example, reaction of 2-py with excess methyl triflate results in N-methylation of two of the N−O arms of the ligand along with coordination of one triflate anion to the aluminum ion. Increasing the amount of MeOTf does not result in methylation of the third nitroxide nitrogen. The [(Me\textsubscript{2}TriNOx)AlOTf\textsuperscript{−}]OTf product 3 was isolated in 89% yield (Scheme 1). The \textsuperscript{1}H NMR spectra of 3 shows three unique \textsubscript{fBu} resonances and six unique resonances assignable to the TriNOx\textsuperscript{3−} ligand along with signatures for both the \textsubscript{fBu} substituents and methylene carbons. Single crystals of the (TriNOx\textsuperscript{3−})Al-py complex were grown from a concentrated pyridine solution at −5 °C, allowing for X-ray crystallography to corroborate the formulation of 2-py. The molecule crystallizes in the centric space group C2/c. The asymmetric unit is disordered by having both enantiomers superimposed in unequal proportions. Figure 1 shows a representation of the major disorder component, and details of the refinement are given in the Supporting Information. The aluminum ion is pentacoordinate with a distorted-trigonal-bipyramidal geometry (τ\textsubscript{5} = 0.88).\textsuperscript{6} The average N−O distance in 2-py is 1.44 Å, which compares well with analogous parameters for the series of rare-earth (TriNOx\textsuperscript{3−})RE complexes prepared by the Schelter group (N−O \textsubscript{av} = 1.44 Å)\textsuperscript{6,9,10} and suggests a fully reduced TriNOx\textsuperscript{3−} ligand.

The reduction of ketones was previously accomplished in 54% yield at room temperature after 20 h, in comparison to no product without the catalyst. Increasing the reaction temperature to 75 °C resulted in a reduced yield of 70% product under otherwise identical reaction conditions. The activity of the catalyst was significantly improved by removal of the pyridine: use of 10 mol% of the free-base complex 2 and 1.2 equiv of HBPin, the reduction of acetophenone was accomplished in 54% yield at room temperature after 20 h, in comparison to no product without the catalyst. Increasing the reaction temperature to 75 °C resulted in 70% product under otherwise identical reaction conditions. The activity of the catalyst was significantly improved by removal of the pyridine: use of 10 mol% of the free-base complex 2 and 1.2 equiv of HBPin gave the borate ester i in quantitative yield after 20 h at room temperature (Scheme 2). These optimized conditions were applicable to a broader scope of ketones. Interestingly, incorporation of either electron-withdrawing or electron-donating groups significantly reduced the yield of borate ester product (ii and iii). The reduction of benzophenone was more difficult, with the reduced product iv being generated in only 18% yield. Increasing the reaction temperature to 75 °C did give product iv in 53% yield. The reduction of 4-phenyl-3-buten-2-one proceeded cleanly to give v in 60% yield. In this case, heating the sample to 75 °C resulted in a reduced yield of...
In comparison to those systems, our catalyst is less insert into the carbonyl in a key mechanistic step. Our complexes that have an Al mechanism for our catalyst. The previous systems implement similar yields. We attribute this at least partially to a diactive and higher catalyst loadings are required to obtain spectroscopy using hexamethylcyclotrisiloxane (0.083 mmol) as an internal standard.

"Reaction conditions: ketone (0.5 mmol), HBPin (0.6 mmol), 2 (0.05 mmol), CDCl3 (1.0 mL). Yields were determined by 1H NMR spectroscopy using hexamethylcyclotrisiloxane (0.083 mmol) as an internal standard.

"Reaction conditions: aldehyde (0.5 mmol), HBPin (0.6 mmol), 2 (0.025 mmol), CDCl3 (1.0 mL). Yields were determined by 1H NMR spectroscopy using hexamethylcyclotrisiloxane (0.083 mmol) as an internal standard.

in conclusion, we have prepared an aluminum complex implementing a multidentate ligand incorporating multiple nitroxide functional groups. In addition to allowing for multiple redox states for the complex, the N–O groups also add Lewis basic sites that can be coupled with the Lewis acidic aluminum ion to enable new activation parameters that result in transition-metal-like catalysis. This chemistry around an earth-abundant metal makes for an economically attractive lead for future research. We are currently investigating other reduction chemistries for which the (TriNOx3−)Al complex is catalytically viable and also deducing how changes in the ligand framework are manifested in changes in reactivity of the complex.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00933.

Experimental, crystallographic, and computational details, NMR spectra, visualization of molecular orbitals, and proposed catalytic cycle for the hydroboration reaction (PDF)

Cartesian coordinates for DFT-optimized structures (MOL)

Accession Codes

CCDC 1862705–1862707 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail for C.R.G.: cgraves1@swarthmore.edu.

ORCID

Paul R. Rablen: 0000-0002-1300-1999

Christopher R. Graves: 0000-0001-5853-2446

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Notes
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■ REFERENCES

(16) The acceptor number (AN) was calculated by the Gutmann—Beckett method using the formula $AN = 2.21 \times (31LA \cdot Et_3PO - 41)$.