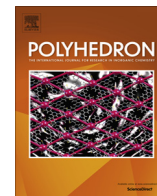




Contents lists available at ScienceDirect

Polyhedron

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

Investigation of ligand steric effect on the hydrogen gas produced via a nickel-catalyzed dehydrogenation of ammonia-borane utilizing unsymmetrical triazolylidene ligands

Meghan O. Talbot^a, Theresa N. Pham^a, Marites A. Guino-o^{a,*}, Ilia A. Guzei^b, Anastasiya I. Vinokur^b, Victor G. Young Jr.^c

^a Mail OSS 402, Chemistry Department, University of St. Thomas, 2115 Summit Avenue, St. Paul, MN 55105-1079, USA

^b 2124 Chemistry Department, University of Wisconsin-Madison, 1101 University Ave, Madison, WI 53706, USA

^c Department of Chemistry, University of Minnesota-Twin Cities, 92C Kolthoff Hall, 207 Pleasant Street S.E., Minneapolis, MN 55455, USA

ARTICLE INFO

Article history:

Received 9 October 2015

Accepted 23 February 2016

Available online xxxxx

Keywords:

Triazolylidene ligands
Dehydrogenation
Ammonia-borane
Nickel-catalyzed
Triazolium salts

ABSTRACT

Seven new unsymmetrical triazolylidene ligands 4-(4-R-phenyl)-1-R'-1,2,4-triazolyl-1-ylidene (where R = H, CH₃, CF₃, F; and R' = CH₃, iPr, Bzl, methylcyclohexane) were employed in a nickel-catalyzed dehydrogenation of ammonia borane to investigate the steric effects associated with the different N(1) substitutions in the triazole ring. The bulkier substituents benzyl and methylcyclohexane afforded the highest weight percent H₂ gas produced. To quantify the steric effect, both percent buried volume (%V_{bur}) and solid angle G parameter (%) were employed. The G-parameter is a more useful tool when only the crystal structures of the precursor ligands are available.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Ammonia borane (H₃N–BH₃, **AB**) is a promising hydrogen gas storage material, because it has a potential hydrogen gas release of 19.6 chemical wt.% (3 equiv) per molecule and contains both protic N–H and hydridic B–H hydrogen atoms that can be exploited to easily release hydrogen gas molecules [1]. Several groups have investigated the dehydrogenation of **AB** using different heterogeneous and homogeneous catalysts [1]. Among the catalyst systems, we are most interested in the homogeneous Ni(NHC)₂ (NHC = N-heterocyclic carbene), because it produced 18 wt.% of hydrogen gas (>2.5 equiv) from **AB** [2]. Three different NHCs were studied; two were imidazolylidenes, and one was a triazolylidene. Of the three, the most active nickel catalyst contained the triazolylidene ligand (or Enders carbene) [2]. A follow-up *in situ* ¹¹B NMR study showed that **AB** initially released 1 equiv H₂ and NH₂BH₂ [3]. After three hours, the reaction eventually produced borazine, polyborazine (PB) and >1.5 equiv of H₂ gas. ¹¹B{¹H} NMR spectra also showed NHC–BH₃ peaks, indicative of NHC dissociation from nickel [3].

Four mechanistic computational studies were proposed for this system [4–7]. Yang and Hall suggested that one NHC is simultaneously acting as a ligand and a proton acceptor from **AB** [4]. Zimmerman's group proposed that **AB** displaces one NHC, making nickel-monocarbene as the active catalyst, while the free NHC also dehydrogenates **AB** [5]. Zimmerman's route explained the experimental kinetic isotope effect (KIE) result better. KIE measurements suggest that the rate-limiting transition state possibly involved both the N–H and B–H bond dissociation [2]. The group also explained the formation of oligomeric aminoborane intermediate species and studied the link between the first and second equiv H₂ gas release [5]. Ai's group compared two mechanisms, intramolecular vs intermolecular paths [6]. Intramolecular is when the hydrogen gas molecule came from the same **AB** molecule, while intermolecular is when a H₂ gas is from two different **AB** molecules. Nickel-dicarbene is the active catalyst when it is intramolecular dehydrogenation, while nickel-monocarbene is active when it is an intermolecular dehydrogenation [6]. In Bhunya's recent study, the group broadly classified homogeneous catalysts as type I and type II [7]. Both types produce NH₂BH₂ after the first dehydrogenation of **AB**. NH₂BH₂ coordinates with type I catalysts and forms linear polyaminoborane, but fails to produce more than 1 equiv of hydrogen gas. Type II catalysts differs from type I by not coordinating the NH₂BH₂ product. The free NH₂BH₂ facilitates the release of multiple equivalents of H₂ gas and forms

* Corresponding author. Tel.: +1 651 962 5526.

E-mail addresses: maguino@stthomas.edu (M.A. Guino-o), iguzei@chem.wisc.edu (I.A. Guzei), vyoung@umn.edu (V.G. Young Jr.).

borazine and polyborazylene [7]. Ni(NHC)₂ catalyst is classified as type II. They were able to account for <2.5 equiv H₂ gas released observed experimentally.

The last study implies that the ideal metal catalyst should coordinate and dehydrogenate **AB** but not coordinate the free NH₂BH₂ in order to produce more than one equiv of H₂ gas. If this is the case, NHC's steric bulk may have an effect on the Ni(NHC)₂ system. Our primary goal is to observe the influence of triazolylidene's bulk, if there is any, on the hydrogen gas volume produced during the first hour of the reaction. This article describes results obtained from dehydrogenation reactions utilizing seven new nickel-triazolylidene catalysts and examines the steric effect of the ligand. The unsymmetrical triazolylidene ligands utilized in this study are shown in Fig. 1.

We altered the size of the triazolylidene by changing the wing-tip substituent in N(1) position of the triazole ring as demonstrated by ligands **1–4**. Ligands **5–7** explore possible electronic effects without changing the steric bulk. This is accomplished through para substitution of the N(4) phenyl group; this approach has merit based on Cavallo's computational studies [8].

2. Experimental

2.1. Materials and NMR experiments

Ammonia-borane, **AB** (97%, Aldrich), sodium hydride (95% dry, Aldrich), bis(1,5-cyclooctadiene)nickel(0) or Ni(COD)₂ (Aldrich), 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene, **8** (Acros Organics) and diglyme (anhydrous, 99.5%, Aldrich) were kept in the drybox under controlled atmosphere conditions (O₂ < 2 ppm, H₂O < 10 ppm) and used without further purification. Triazolylidene precursor salts (**1–7**) were synthesized based on literature methods [9], recrystallized, isolated and kept in the drybox prior to use. All solution preparations and dehydrogenation reactions were performed using standard techniques for inert atmosphere conditions (drybox and Schlenk line).

All NMR spectra were recorded on JEOL 400 MHz spectrometer. Deuterated benzene used in ¹¹B{¹H} NMR experiments were dried over molecular sieves (3 Å) and kept in the dry box.

2.2. Single crystal X-ray diffraction experiments

Crystal structures of precursor salts **1–3**, **5** and **7** were already published [9].

Crystal data for the precursor salt of ligand **4**, C₁₅H₂₀BrN₃ (*M* = 322.25 g/mol): monoclinic, space group *P2*₁ (No. 4), *a* = 9.550

(3) Å, *b* = 26.884(7) Å, *c* = 11.883(3) Å, β = 90.078(18)°, *V* = 3051.0 (15) Å³, *Z* = 8, *T* = 100.14 K, μ (Mo Kα) = 2.686 mm⁻¹, *D*_{calc} = 1.403 g/cm³, 71984 reflections measured (3.03° ≤ 2θ ≤ 56.606°), 15062 unique (*R*_{int} = 0.0446, *R*_{sigma} = 0.0350) which were used in all calculations. The final *R*₁ was 0.0300 (*I* > 2σ(*I*)) and *wR*₂ was 0.0750 (all data).

Single crystal experiment for the precursor salt of ligand **4** was carried using the Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation [10]. The systematic absences in the diffraction data were consistent for the space groups *P2*₁ and *P2*₁/*m*. The *E*-statistics strongly suggested the noncentrosymmetric space group *P2*₁ that yielded chemically reasonable and computationally stable results of refinement [11–13]. A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There are four symmetry independent ion pairs in the asymmetric unit. The phenyl rings on the four main cations were constrained to an idealized geometry. The cyclohexyl rings in cations N1A, N1B, and N1C were refined with distance restraints.

The crystal selected for the single-crystal X-ray diffraction experiment proved to be pseudomerohedrally twinned between two components and each of the components exhibited inversion twinning. Thus there are four components comprising this crystal. The main component is present 51.3(8)% of the time, its inversion twin is 11.9(8)%, the minor component (reflection twin) is 32.1(7)%, its inversion twin is 4.7(7)%. The pseudomerohedrally twin components are related by a reflection through the plane (001).

Crystal data for the precursor salt of ligand **6**, C₁₂H₁₃F₃IN₃ (*M* = 383.15 g/mol): orthorhombic, space group *Pccn* (No. 56), *a* = 16.1647(14) Å, *b* = 21.8962(18) Å, *c* = 7.9065(7) Å and α, β, δ = 90°, *V* = 2798.5(4) Å³, *Z* = 8, *T* = 123(2), μ (Cu Kα) = 18.238 mm⁻¹, *D*_{calc} = 1.819 g/cm³. The final *R*₁ was 0.0311 (*I* > 2σ(*I*)) and *wR*₂ was 0.0748 (all data). A second polymorph was found: monoclinic, space group *P2*₁/*n* (No. 14), *a* = 5.4269(3) Å, *b* = 23.3617(15) Å, *c* = 11.8271(7) Å and α, δ = 90°, β = 99.373(4)°, *V* = 1479.44(15) Å³, *Z* = 4, *T* = 100(2).

Single crystal experiments for the precursor salt of ligand **6** was carried out using the Bruker VENTURE PHOTON-100 system with Cu Kα (λ = 1.54178 Å) [10]. Cell parameters were refined and integrated using SAINT. The final structure was solved and refined using SHELXT-2014 and SHELXL-2014/6 [14,15].

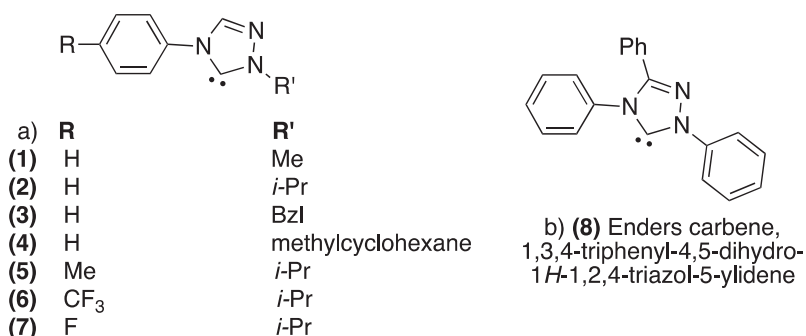


Fig. 1. (a) Triazolylidene (NHC) ligands employed in this study and (b) Enders carbene.

Download English Version:

<https://daneshyari.com/en/article/7764578>

Download Persian Version:

<https://daneshyari.com/article/7764578>

[Daneshyari.com](https://daneshyari.com)