Polyhedron xxx (xxxx) 116811

Contents lists available at ScienceDirect

Polyhedron

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

Insertion reactions and structural studies of $[(NHC)CuH]_2$ with nitrogen-based substrates

Ba L. Tran *, Jeremy D. Erickson

Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA, 99352, United States

ARTICLE INFO

Keywords:
Copper hydride
N-heterocyclic carbene
Insertion
Azide
Pyrazine
Nitrous oxide

ABSTRACT

The stoichiometric and catalytic reactions of Cu-H dimers supported by *N*-heterocyclic carbenes (NHCs) have mainly focused on the insertions of aldehydes, ketones, CO_2, and unsaturated hydrocarbons. In this report, we investigated the stoichiometric reactions of dimeric $[(NHC)CuH]_2$ (NHC = IPr*, 6Dipp) with unsaturated nitrogen-based substrates of PhN = NPh, N_3Ad, pyrazine, and N_2O. The spectroscopic and structural chacterizations of the resulting monomeric, two-coordinate Cu(I) complexes containing diphenyl hydrazido, triazenido, **pyrazinyl**, and hydroxide ligands are discussed. The hydrazido complex of (IPr*)Cu(NPh-NHPh) and triazenido complex of [(IPr*)Cu(HNNNAd)] are resistant to N—N bond cleavage and loss of N_2, respectively, to form the corresponding amido complexes even when heated at 80 °C over several hours.

1. Introduction

The reactivity and structural characterization of copper-hydride (Cu-H) complexes have been of interest to synthetic inorganic research for over five decades [1–7]. Many of the early studies on the coordination chemistry and reactivity of Cu-H complexes employed a variety of phosphine ligands to promote transformations of carbonyl compounds [5,6,8,9]. In 2004, Sadighi and co-workers introduced the application of bulky *N*-heterocyclic carbene (NHC) to stabilize and structurally characterized the $[(NHC)CuH]_2$ dimer [10]. This seminal study initiated a vibrant area of research for the coordination and reaction chemistry for this new class of (NHC)Cu-H complexes in stoichiometric and catalytic reactions [7,11,12]. The past two decades has witnessed significant development in the stoichiometric and catalytic transformations of unsaturated hydrocarbons mediated by variety of Cu-H complexes supported by bulky phosphine and *N*-heterocyclic carbene ligands [7,12–20].

The selective insertion of π substrates into the Cu-H bond under mild conditions constitute a foundational elementary step in CuH-catalyzed reactions. Specifically, the insertion of alkynes, alkenes, and dienes into Cu-H bonds to produce the corresponding vinyl, alkyl, and allyl Cu(I) intermediates that can further react with electrophiles to forge new carbon–carbon, carbon–nitrogen, and carbon-boron bonds [13,19,20]. This sequence of substrate insertion and electrophilic functionalization has proven to be an efficient approach to build advanced intermediates from readily available building blocks. Carbonyl compounds [7–9,21], CO_2 [22–27], and unsaturated hydrocarbons [13,14] have been the primary substrates for the insertion reactions of Cu-H complexes. In this work, we report the insertion reactions of $[(NHC)CuH]_2$ dimers (NHC = IPr*, 6Dipp) with a series of unsaturated nitrogen-based substrates of azobenzene, organoazide, pyrazine, and N_2O (Scheme 1) to produce the corresponding the two-coordinate hydrazine, triazenido, pyrazinido, and hydroxide Cu(I) complexes.

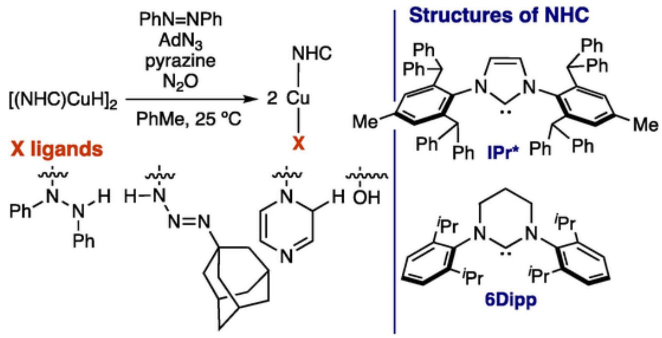
2. Experimental

2.1. Materials and general considerations

All reactions were conducted under a nitrogen atmosphere unless otherwise noted. Anhydrous solvents were purified by passage through neutral alumina using an Innovative Technology, Inc., PureSolv solvent purification system. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA, USA). All reagents were purchased from commercial sources and used as received unless otherwise noted. All commercial solid reagents were placed under dynamic vacuum for 48 h before use in the glovebox. All commercial liquid reagents and C_6D_6 underwent three cycles of freeze, pump, and thaw before storing over activated 4 Å molecular sieves in the glovebox under an atmosphere of N_2 before use. N_2O (99.999 %) was obtained from Advanced Specialty Gases, and was used as received. Complexes of $[(IPr^*)CuH]_2$ [28] and $[(6Dipp)CuH]_2$ [29] were prepared according to published protocols.

* Corresponding author.
E-mail address: ba.tran@pnnl.gov (B.L. Tran).

https://doi.org/10.1016/j.poly.2023.116811
Received 2 October 2023; Accepted 18 December 2023
0277-5387/© 20XX



Scheme 1. The reactions of [(NHC)CuH]$_2$ with PhN = NPh, N$_3$Ad, pyrazine, and N$_2$O.

2.2. Single crystal X-ray diffraction

Data was collected on a Bruker D8 QUEST diffractometer equipped with a Incoatec IμS 3.0 Microfocus Mo X-ray source, PHOTON II detector, and KAPPA goniometer. The crystals were mounted on a cryoloop with Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. Data collection, cell parameter determination, integration of the data frames and final cell parameter refinement were conducted using APEX 4 software. Absorption correction of the data was carried out using SADABS. Structure determination and refinement was done with SHELXT and SHELXL through OLEX II GUI [30]. Hydrogen atom positions were idealized and rode on the atom of attachment, except for the hydrogen belonging to the NHNNAd ligand of complex **3**, which was located in the Fourier difference map and refined with minimal restraint. All graphics for all crystal structures were generated using Mercury software.

2.3. Synthesis of (IPr*)Cu(NPh-NHPh) (1)

Inside a nitrogen-filled glovebox, a 20 mL oven-dried scintillation vial was added PhN = NPh (20.0 mg, 0.110 mmol), [(IPr*)CuH]$_2$ (100 mg, 0.0510 mmol), a small stir bar, and toluene (3 mL). The soluble orange solution became a yellow suspension after 12 h at 25 °C. The resulting yellow solids were collected on a medium porosity frit, washed with 3 mL pentane, and dried under dynamic vacuum. Yield: 75 % (88.0 mg, 0.0765 mmol). Yellow single crystals suitable for XRD were grown by layering pentane over a concentrated toluene solution of **1** at 25 °C. **^{1}H NMR (500 MHz, C$_6$D$_6$)**: δ7.31 (d, J = 7.4 Hz, 8H, Ar-H), 7.07 (t, J = 7.5 Hz, 10*H*, Ar-H), 7.04 – 6.85 (m, 32H, Ar-H), 6.70 (d, J = 7.9 Hz, 2H, Ar-H), 6.64 (t, J = 7.0 Hz, 1H, Ar-H), 6.59 (t, J = 7.2 Hz, 1H, Ar-H), 5.57 (s, 4H, CHPh$_2$), 5.51 (s, 1H, N—H), 5.44 (s, 2H, H-C=C-H), 1.81 (s, 6H, Me). **^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$)**: δ 183.0 (Cu-carbene), 161.1, 151.9, 143.9, 143.1, 141.6, 140.4, 135.0, 130.4, 130.2, 129.8, 129.1, 128.9, 128.6, 127.2, 126.8, 123.3, 116.6, 112.9, 112.3, 51.9, 21.4. **IR** (KBr): ν 3370 (w), 3157 (w), 3128 (w), 1584 (s), 1492 (s), 1472 (vs), 1377 (s), 1305 (m), 1282 (m), 1258 (w), 1169 (w), 1159 (w), 1075 (w), 1028 (m) cm^{-1}. Anal. Calcd for C$_{81}$H$_{67}$CuN$_4$: C, 83.87; H, 5.82; N, 4.83. Found: C, 84.03; H, 5.95; N, 4.80.

2.4. Synthesis of (6Dipp)Cu(NPh-NHPh) (2)

Inside a nitrogen-filled glovebox, a 20 mL oven-dried scintillation vial was added PhN = NPh (40.0 mg, 0.220 mmol), [(6Dipp)CuH]$_2$ (100 mg, 0.106 mmol), a small stir bar, and toluene (3 mL). After 12 h at 25 °C, the resulting yellow solution was filtered into a new 20 mL scintillation vial and layered with pentane (10 mL) to give microcrystalline product. Yield: 70 % (96.0 mg, 0.147 mmol). Yellow single crystals suitable for XRD were grown by slow diffusion of pentane into a concentrated THF solution at 25 °C.**^{1}H NMR (500 MHz, C$_6$D$_6$): δ**7.20 (t, J = 7.8 Hz, 2H, Ar-H), 7.06 (dd, J = 8.5, 7.2 Hz, 4H), 7.01 (d, J = 7.8 Hz, 2H, Ar-H), 6.69 (t, J = 7.1 Hz, 1H, Ar-H), 6.65 (t, J = 7.1 Hz, 1H, Ar-H), 6.43 (d, J = 8.1 Hz, 2H, Ar-H), 4.78 (s, 1H, N—H), 2.89 (sep, J = 6.85 Hz, 4H, CHMe$_2$), 2.66 (t, J = 6.0 Hz, 4H, CH$_2$ backbone), 1.25 (d, J = 7.0 Hz, 12H, CH*Me*$_2$), 1.41 (m, 2H, CH$_2$ backbone), 1.12 (d, J = 7.0 Hz, 12H, CH*Me*$_2$). **^{13}C{^{1}H} NMR** (151 MHz, C$_6$D$_6$) δ 202.3 (Cu-carbene), 160.6, 151.5, 145.5, 141.7, 129.2, 128.0, 127.9, 124.5, 116.2, 112.6, 111.8, 45.3, 28.5, 24.4, 24.3, 19.8. Anal. Calcd for C$_{40}$H$_{51}$CuN$_4$: C, 73.75; H, 7.89; N, 8.60. Found: C, 74.05; H, 8.10; N, 8.89.

2.5. Synthesis of (IPr*)Cu(NHNNAd) (3)

In a nitrogen-filled glovebox, to a 4 mL vial was charged N$_3$Ad (20.0 mg, 0.113 mmol), [(IPr*)CuH]$_2$ (100 mg, 0.0511 mmol), a stir bar, and toluene (1.5 mL). The orange suspension became a white suspension after 6 h at 25 °C. The colorless solids were collected a medium porous glass frit, washed with 3 mL of pentane, and dried under dynamic vacuum. Yield = 65 % (76 mg, 0.066 mmol). **^{1}H NMR** (500 MHz, 25 °C, C$_6$D$_6$): δ 7.92 (s, 1H, NH), 7.40 (d, J = 7.0 Hz, 8H, Ar-H), 7.16–7.12 (m, 10*H*, Ar-H), 7.02–6.95 (m, 26H, Ar-H), 5.54 (s, 2H, H-C=C-H), 5.45 (s, 4H, CHPh$_2$), 2.03 (br s, 3H, Ad), 1.92 (br s, 6H, Ad), 1.78 (s, 6H, Me), 1.68–1.65 (m, 6H, Ad). **^{13}C{^{1}H} NMR** (151 MHz, C$_6$D$_6$): δ 183.7 (Cu-carbene), 143.7, 143.0, 141.4, 140.0, 135.0, 130.1, 130.0, 129.6, 128.9, 128.6, 126.6, 126.4, 122.8, 56.4, 51.5, 44.0, 37.3, 30.4, 21.0. **IR** (KBr): ν 3351 (vw), 3060 (w), 3026 (w), 2900 (vs), 2847 (m), 1599 (m), 1494 (s), 1472 (vs), 1446 (vs), 1405 (m), 1336 (s), 1304 (w), 1263 (m), 1197 (w), 1172 (w), 1116 (m), 1078 (m), 1031 (s) cm^{-1}.

2.6. Synthesis of (IPr*)Cu(pyrazin-1(2H)-yl) (4)

Inside a nitrogen-filled glovebox, a 20 mL oven-dried scintillation vial was added 10 equiv of pyrazine (41.0 mg, 0.510 mmol), [(IPr*)CuH]$_2$ (100 mg, 0.0511 mmol), a small stirring bar, and toluene (6 mL). After 24 h at 25 °C, the resulting reaction mixture was filtered through a glass pipette containing Celite into a new 20 mL scintillation vial. The resulting yellow solution was concentrated to dryness, triturated with pentane (10 mL), and vigorously stirred for 1 h. The solids were collected on a 30 mL medium porosity frit, washed with 10 mL pentane, and dried under dynamic vacuum. Yield: 60 % (65.0 mg, 0.0610 mmol). Yellow single crystals suitable for XRD were grown by layering pentane over a concentrated toluene solution of **4** at 25 °C. **^{1}H NMR (500 MHz, C$_6$D$_6$)**: δ7.29–7.27 (m, 8H, Ar-H), 7.19–7.16 (m, 8H, Ar-H), 7.09 (d, J = 3.6 Hz, 1H, pyrazine C—H), 7.03–6.99 (m, 22H, Ar-H), 6.95 –6.93 (m, 6H, Ar-H), 6.56 (d, J = 3.6 Hz, 1H, pyrazine C—H), 6.44 (t, J = 3.1 Hz, 1H, pyrazine C—H), 5.49 (s, 2H, H-C=C-H), 5.46 (s, 4H, CHPh$_2$), 3.55 (d, J = 3.1 Hz, 2H, pyrazine CH$_2$), 1.69 (s, 6H, Me). **^{13}C{^{1}H} NMR** (151 MHz, C$_6$D$_6$): δ 182.4 (Cu-carbene), 143.4, 143.1, 141.7, 140.6, 138.4, 134.8, 130.5, 129.8, 129.8, 129.2, 128.6, 127.3, 126.9, 123.5, 120.7, 117.0, 51.6, 50.9, 21.2.

2.7. Reaction of [(IPr*)CuH]$_2$ and N$_2$O to produce (IPr*)CuOH (5)

Note: The gas-additional manifold was placed under vacuum for 24 h prior to use. Inside a nitrogen-filled glovebox, to an oven-dried 3 mL scintillation vial was added [(IPr*)CuH]$_2$ (20.0 mg, 0.0102 mmol) and 700 μL of C$_6$D$_6$ by microsyringe. This orange solution was transferred to an oven-dried J. Young NMR tube. The J. Young NMR tube was removed from the glovebox and attached to a gas-addition manifold. The J. Young NMR tube was subjected to one freeze–pump–thaw cycle before back-filling with 1 atm of N$_2$O (99.999 %). The orange solution transformed into a colorless solution in 6 h. **^{1}H NMR (500 MHz, C$_6$D$_6$)**: δ7.48 (d, J = 7.6 Hz, 8H, Ar-H), 7.21–7.07 (m, 8H, Ar-H), 7.06 – 6.88 (m, 28H, Ar-H), 5.67 (s, 4H, CHPh$_2$), 5.53 (s, 2H, H-C=C-H), 1.73 (s, 6H, Me), −0.46 (s, 1H, OH).

We have also independently synthesized (IPr*)CuOH from the reaction of (IPr*)CuCl and CsOH to confirm the signal of Cu-OH at −0.46 ppm in C_6D_6. The ^{1}H NMR data is consistent with that reported in the literature for this compound [31]. The use of a lecture bottle of 99 % N_2O appears inadequate as rapid hydrolysis of orange solution of $[(IPr^*)CuH]_2$ to a colorless solution of (IPr*)CuOH was observed upon introduction of N_2O.

3. Results and discussion

3.1. Isolation of thermally stable two-coordinate hydrazido and triazenido complexes

Reactions of azobenzene (PhN = NPh) with dimeric hydride complexes of $[(dippe)NiH]_2$ or $[(nacnac)FeH]_2$ can lead to complex reaction pathways of H_2 extrusion to form (dippe)Ni(η^2-PhN = NPh) or cleavage of the N—N bond of hydrazido ligand of (nacnac)Fe-(NPh-NHPh) to give (nacnac)Fe-NHPh [dippe = 1,2-bis(diisopropylphosphino) ethane, nacnac = CH[*MeC* = *N*(2,6-*iPr*$_2$*C*$_6$*H*$_3$)]$_2$ [32,33]. Treating $[(IPr^*)CuH]_2$ dimer with 2.1 equiv. of PhN = NPh in toluene at room temperature for 12 h produced a yellow suspension, which was collected on a medium porosity frit to give the hydrazido complex of (IPr*) Cu(NPh-NHPh) (**1**) in 75 % yield (Scheme 2). ^{1}H NMR spectroscopic analysis of **1** in C_6D_6 shows the presence of a new singlet at 5.51 ppm with an integration of 1H. Single crystals of **1**, grown from slow diffusion of pentane into a concentrated toluene solution of **1** at 25 °C, were analyzed by single-crystal X-ray diffraction (SCXRD) measurement. The solid-state structure of **1** verified the linear geometry of **1** (Fig. 1), consisting of a Cu-carbene distance of 1.8714(39) Å and Cu1-N3 = 1.8392 (35) Å for the 1,2-diphenylhydrazido ligand. There is no evidence of additional binding to the Cu(I) center from the 1,2-diphenylhydrazido ligand based on the Cu1-N4 distance of ~ 2.79 Å.

We further examined the thermal stability of **1** because low-coordinate hydrazido species, such as the three-coordinate (nacnac)Fe (NPh-NHPh), is thermally unstable, in which heating leads to N—N bond cleavage to produce a three-coordinate (nacnac)Fe-NHPh [32, 33]. In contrast, (IPr*)Cu(NPh-NHPh) is remarkably stable at 80 °C for 3 h and 24 h without evidence of decomposition by ^{1}H NMR spectroscopy (Figure S3). We have also demonstrated that the less bulky $[(6Dipp)CuH]_2$ dimer can insert PhN = NPh to produce (6Dipp)Cu (NPhN-HPh) (**2**) in isolated yield of 70 % (Scheme 2). The solid-state structure of (6Dipp)Cu(NPh-NHPh) is presented in Fig. 1 and contains nearly identical metrical parameters to that of complex **1**. Complex **2** is also thermally stable as heating a C_6D_6 solution of **2** at 80 °C for 3 h did not lead to decomposition.

Triazenido complexes are susceptible to the loss of N_2 to generate the corresponding amido species [34]. Based on the solution and thermal stability of hydrazido complex, (IPr*)Cu(NPh-NHPh), we investigated the synthesis and isolation of a two-coordinate (NHC)Cu-triazenido for spectroscopic, structural characterization, and thermal stability. The reaction of $[(IPr^*)CuH]_2$ with 2.1 equiv. of 1-azidoadamantane (N_3Ad) in toluene at 25 °C for 6 h produced (IPr*)Cu (NHNNAd) (**3**) as a white precipitate in isolated yield of 65 % (Scheme 3). The presence of a Cu-(NHNNAd) moiety was supported by ^{1}H NMR, IR, and SCXRD data. The NH group of the HN_3Ad ligand has a ^{1}H NMR resonance at 7.92 ppm (Figure S6A), which is in the range for the reported N—H signal of the triazenido ligand [34]. IR analysis of **3** in Nujol shows a weak signal at 3351 cm^{-1}, consistent with the reported infrared data for $(C_5Me_5)_2$Hf(H)(NHNNPh) [34] and (nacnac)Fe(NHNNAd) [35] at 3340 cm^{-1} and 3371 cm^{-1}, respectively. Single crystals of **3** for structural characterization by SCXRD analysis were obtained by slow diffusion of pentane into a toluene solution of **3** at room temperature over 24 h. Salient features of the solid-state structure of **3** shows a Cu-carbene bond distance of 1.876(5) Å and a Cu-N3 bond distance of 1.857(5) Å for triazenido ligand (Fig. 2). The angle of C1-Cu1-N3 for the carbene, Cu(I), and triazenido ligand of 176.1(2) ° deviates slightly

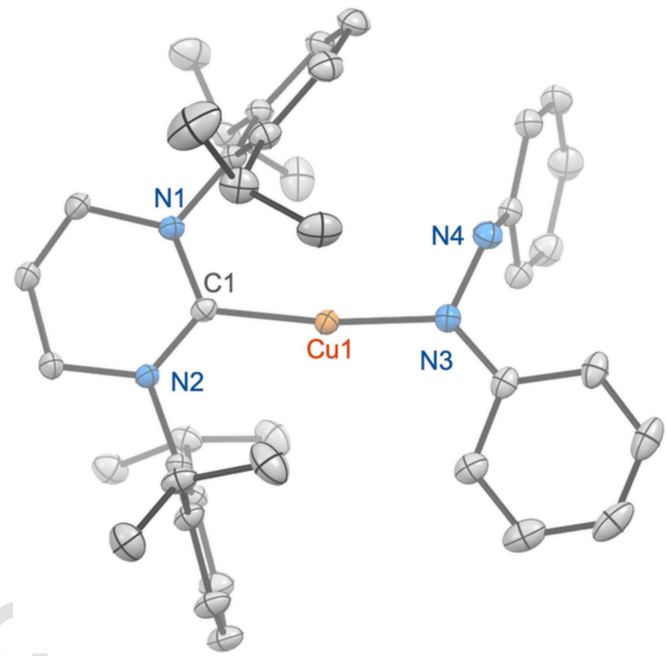
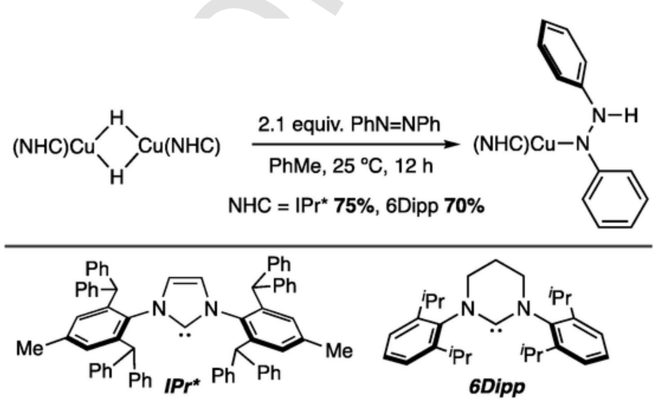
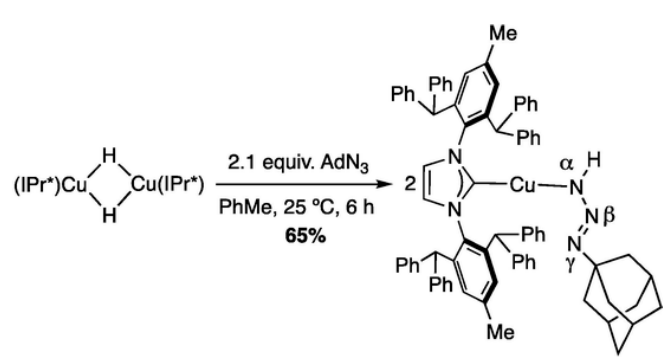


Fig. 1. The molecular structures of (IPr*)Cu(NPh-NHPh) (1) and (6Dipp)Cu (NPh-NHPh) (2) are shown with thermal ellipsoids at 50 % probability. Selected key bond distances (Å) and angles (°) of 1: C1-Cu1 = 1.8714(39); Cu1-N3 = 1.8392 (35); N3-N4 = 1.4219(49); C1-Cu1-N3 = 172.43(17); Cu1-N3-N4 = 116.92(27). Selected key bond distances (Å) and angles (°) of 2: C1-Cu1 = 1.8821(11); Cu1-N3 = 1.8494(10); N3-N4 = 1.4244(14); C1-Cu1-N3 = 171.86(5); Cu1-N3-N4 = 116.92(7).



Scheme 2. The reactions of $[(NHC)CuH]_2$ with PhN = NPh to produce the corresponding (NHC)Cu(NPh-NHPh) complexes.



Scheme 3. The insertion reaction of $[(IPr^*)CuH]_2$ and N_3Ad to produce linear (IPr*)Cu(NHNNAd) (3).

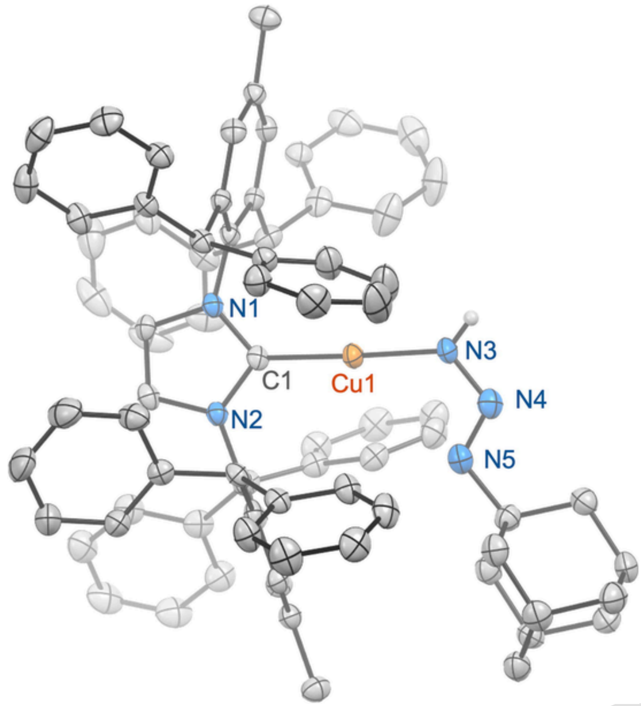


Fig. 2. The molecular structure of (IPr*)Cu(NHNNAd) (3) is shown with thermal ellipsoids at 50 % probability. Selected key bond distances (Å) and angles (°) of 3: C1-Cu1 = 1.876(5); Cu1-N3 = 1.857(5); N3-N4 = 1.360(7); N4-N5 = 1.245(7); C1-Cu1-N3 = 176.1(2); N3-N4-N5 = 112.8(4). The hydrogen atom of the N—H group in the NHNNAd ligand was located and refined without constraint.

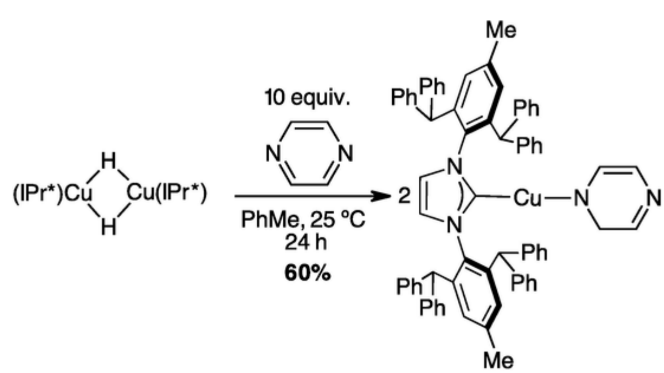
from an idealized angle for a linear geometry of 180 °. The monoanionic NHNNAd ligand is bent with an angle of N2-N3-N4 at 112.8(4) °. Lastly, the NHNNAd ligand contains a N3-N4 bond distance of 1.360(7) Å and a N4-N5 bond distance of 1.245(7) Å.

We also investigated the solution and thermal stability of **3** by ¹H NMR spectroscopy. Qualitiatively, a C_6D_6 solution of **3** remained stable for at least one week at 25 °C, in which spectroscopic monitoring of the sample was halted. Complex **3** exhibited considerable stability in solution upon heating at 80 °C. Thermolysis of **3** produced a mixture of unidentified products instead of the direct formation of the corresponding amido species from N_2 loss of **3**. Nevertheless, the concentration of **3** at 80 °C after 5 h and 24 h was observed in 72 % and 22 %, respectively, by integrating the H-C═C-H backbone of the IPr* ligand of **3** against an internal standard of 1,3,5-trimethoxybenzene (Figure S6C). The resistance of the two-coordinate, 14-electron triazenido complex **3** towards N_2 extrusion even at 80 °C for 5 h is unusual because triazenido complexes generally extrudes N_2 to produce amido complexes [34]. Mechanistic and computational studies on the conversion of $(C_5Me_5)_2$Hf-triazenido to $C_5Me_5)_2$Hf-amido suggest that the bidentate coordination of the triazenido ligand with the Hf center facilitates 1,3-hydride migration from the α-nitrogen to the γ-nitrogen to release N_2 [34,36]. It is possible that the combination of a stable linear geometry of (IPr*)Cu(NHNNAd) and the steric protection of the Cu(I) conferred by the bulky IPr* ligand disfavors the interaction of the γ-nitrogen of the NHNNAd ligand with the Cu(I) center to promote the extrusion of N_2 from (IPr*)Cu(NHNNAd) to readily generate the corresponding amido complex, (IPr*)Cu(NHAd).

3.2. Reaction with electron-deficient pyrazine

The hydrogenation of arenes and heteroarenes is a challenging transformation that enables access to unique chemical space from abundant aromatic starting materials [37]. Many of the known metal-hydride complexes that can catalyzed this transformation are composed of Ir, Ru, Rh [37]. A major barrier for this type of transformation is the disruption of aromaticity by insertion of the heteroarene into a metal-hydride bond. We explored whether Cu-H species can mediate this transformation by analyzing the insertion reactions of $[(IPr^*)CuH]_2$ with 5.0 equiv. of pyridine, benzothiophene, benzofuran, 1-methylindole, and pyrazine in C_6D_6 at room temperature by ¹H NMR spectroscopy. No reactions were observed for pyridine, benzothiophene, benzofuran, and 1-methylindole. Additionally, the integrity of $[(IPr^*)CuH]_2$ remained intact as evidenced by ¹H NMR spectroscopic analysis of the reaction mixture at 24 h, with the exception of pyridine. The reaction mixture of $[(IPr^*)CuH]_2$ and pyridine in C_6D_6 at room temperature for 72 h produced an intractable mixture and a small amount of black precipitate, presumably from the formation of copper metal.

Qualitative ¹H NMR analysis on the reaction of $[(IPr^*)CuH]_2$ with 10 equiv. of pyrazine cleanly produced complex (IPr*)Cu(pyrazin-1(2H)-yl) (**4**). The ¹H NMR (C_6D_6, 25 °C) spectrum shows the loss of the Cu-H signal at 3.74 ppm with concomitant growth of a new signal as a doublet at 3.55 (d, J = 3.1 Hz) and an integration of 2H to supporting the methylene group of the pyrazin-1(2H)-yl ligand. We also observed new signals in the aromatic regions of a doublet at 7.09 ppm (J = 3.6 Hz, 1H), a doublet at 6.56 ppm 6.52 (d, J = 3.6 Hz, 1H), and a triplet at 6.44 ppm (t, J = 3.1 Hz, 1H) that are consistent with a Cu-pyrazin-1(2H)-yl moiety (Figure S7, S8A). Lastly, new resonances corresponding to the imidazolyl H-C═C-H and $-CHPh_2$ were observed at 5.49 ppm (2H) and 5.46 ppm (4H), respectively. Complex **4** has been verified by SCXRD analysis. Unfortunately, the quality of the SCXRD data only allows for the determination of the connectivity of complex **4** (Figure S8C in the Supporting Information). On a preparative scale, treating $[(IPr^*)CuH]_2$ with 10 equiv. of pyrazine at room temperature for 24 h generated complex **4** in isolated 60 % yield (Scheme 4). Similarly, ¹H NMR analysis on the reaction of $[(6Dipp)CuH]_2$ with 10.0 equiv. of pyrazine in C_6D_6 by ¹H NMR spectroscopy also revealed clean conversion to the corresponding (6Dipp)Cu(pyrazin-1(2H)-yl). The diagnostic signals for the Cu-pyrazin-1(2H)-yl moiety include a doublet at 6.71 ppm (J = 3.7 Hz, 1H), a triplet 6.04 (t, J = 3.3 Hz, 1H), a doublet at 5.83 (J = 3.7 Hz, 1H), and doublet at 2.94 ppm (J = 3.3 Hz, 2H). The solid-state structure of two-coordinate complex of (6Dipp)Cu (pyrazin-1(2H)-yl) is presented in Figure S9 of the Supporting Information.



Scheme 4. The insertion reaction of $[(IPr^*)CuH]_2$ and pyrazine to produce (IPr*)Cu(pyrazin-1(2H)-yl) (4).

3.3. Oxygen atom tranfer reaction of N_2O and [(IPr*)CuH]$_2$

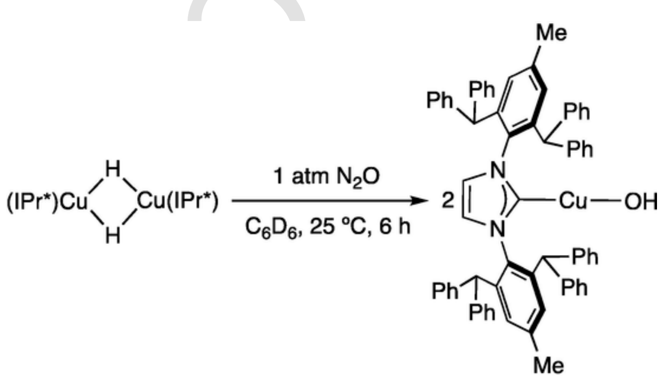
The fundamental oxygen-atom transfer reaction from the insertion of N_2O into metal-hydride complexes to produce hydroxide complexes with concomitant loss of N_2 [38–40] has important implications in the catalytic hydrogenation of N_2O [41–43] and catalytic dehydrogenative coupling of alchols [44]. The decomposition of N_2O to its elements is thermodynamically favorable, but kinetically challenging [40]. We posit that the coordinative unsaturation and high reactivity of Cu-H species can undergo reactivity with N_2O at ambient condition. The addition of 1 atm of N_2O (99.999 %) to an orange solution of [(IPr*)CuH]$_2$ (14 mM, C_6D_6) became a light yellow solution after 2 h and colorless after 6 h. Subsequent ^{1}H NMR spectroscopic analysis of reaction mixture shows clean formation of (IPr*)CuOH (**5**) with the diagnostic signal of Cu-OH at −0.46 ppm (Scheme 5, Figure S10) [28]. The persistence of the characteristic orange solution of [(IPr*)CuH]$_2$ after the addition of 1 atm of N_2O is in stark contrast to the rapid consumption of [(NHC)CuH]$_2$ upon the addition of 1 atm of CO_2 [45,46]. The formation of (IPr*)CuOH, from the reaction of [(IPr*)CuH]$_2$ and N_2O, provides an opportunity to regenerate [(IPr*)CuH]$_2$ in the presence of excess hydride source for a plausible synthetic or catalytic cycle for the reduction of N_2O.

4. Conclusions

We have examined the insertion reactions of [(NHC)CuH]$_2$ dimers (NHC = IPr*, 6Dipp) with a variety of unsaturated nitrogen-based substrates ranging from azide to electron-deficient heterocycle to gaseous N_2O. The resulting two-coordinate hydrazido and triazenido Cu(I) complexes are particularly stable in solution, even at 80 °C over hours. This observation is in stark contrast to the thermal instability of known Fe-hydrazido and -triazenido complexes, which undergo thermal decomposition to the corresponding Fe-amido complexes. The isolation of these unusually stable species highlight the unique stability of the linear (NHC)Cu(I) complexes. [(NHC)CuH]$_2$ dimers supported by NHC ligands of varying steric properties can insert electron-deficient heteroarene, such as pyrazine, but failed to react with pyridine, benzothiophene, benzofuran, and 1-methylindole. The insertion of symmetric pyrazine into the Cu-H bonds of [(IPr*)CuH]$_2$ and [(6Dipp)CuH]$_2$ under our thermal reaction condition produced (NHC)Cu(pyrazin-1(2H)-yl) species. This reactivity provides an opportunity to explore whether the steric properties of NHC ligands of [(NHC)CuH]$_2$ dimers can promote different hydride-transfer pathways for unsymmetric heteroarene to generate different regioisomers.

CRediT authorship contribution statement

Ba L. Tran: Conceptualization, Investigation. **Jeremy D. Erickson:** .



Scheme 5. The oxygen-atom transfer of N_2O to [(IPr*)CuH]$_2$ to produce (IPr*)CuOH.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division, Catalysis Science Program, FWP 47319. We thank Dr. Evan A. Patrick for assistance with the reaction of N_2O.

Appendix A. Supplementary data

Additional spectroscopic and structural data are included in the Supporting Information. CCDC contains the supplementary crystallographic data for **2297414** (IPr*)Cu(NPh-NHPh), **2297413** (6Dipp)Cu(NPh-NHPh), and **2297415** (IPr*)Cu(NHNNAd). These data can be obtained free of charge via http://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. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2023.116811.

References

[1] G.V. Goeden, K.G. Caulton, Soluble copper hydrides: Solution behavior and reactions related to carbon monoxide hydrogenation, J. Am. Chem. Soc. 103 (1981) 7354–7355.
[2] M.R. Churchill, S.A. Bezman, J.A. Osborn, J. Wormald, Synthesis and molecular geometry of hexameric triphenylphosphinocopper(I) hydride and the crystal structure of $H_6Cu_6(PPh_3)_6$. $HCONMe_2$, Inorg. Chem. 11 (1972) 1818–1825.
[3] G.M. Whitesides, J. San, Filippo, E.R. Stredronsky, C.P. Casey, Reaction of copper (I) hydride with organocopper(I) compounds, J. Am. Chem. Soc. 91 (1969) 6542–6544.
[4] J.A. Dilts, D.F. Shriver, Nature of soluble copper(I) hydride, J. Am. Chem. Soc. 90 (1968) 5769–5772.
[5] W.S. Mahoney, D.M. Brestensky, J.M. Stryker, Selective hydride-mediated conjugate reduction of α, β-unsaturated carbonyl compounds using $[(Ph_3P)CuH]_6$, J. Am. Chem. Soc. 110 (1988) 291–293.
[6] W.S. Mahoney, J.M. Stryker, Hydride-mediated homogeneous catalysis. Catalytic reduction of α, β-unsaturated ketones using $[(Ph_3P)CuH]_6$ and H_2, J. Am. Chem. Soc. 111 (1989) 8818–8823.
[7] A.J. Jordan, G. Lalic, J.P. Sadighi, Coinage metal hydrides: synthesis, characterization, and reactivity, Chem. Rev. 116 (2016) 8318–8372.
[8] S. Rendler, M. Oestreich, Polishing a diamond in the rough: "Cu-H" catalysis with silanes, Angew. Chem., Int. Ed. 46 (2007) 498–504.
[9] C. Deutsch, N. Krause, B.H. Lipshutz, CuH-catalyzed reactions, Chem. Rev. 108 (2008) 2916–2927.
[10] N.P. Mankad, D.S. Laitar, J.P. Sadighi, Synthesis, structure, and alkyne reactivity of a dimeric (carbene)copper(I) hydride, Organometallics 23 (2004) 3369–3371.
[11] S. Díez-González, S.P. Nolan, Copper, silver, and gold complexes in hydrosilylation reactions, Acc. Chem. Res. 41 (2008) 349–358.
[12] T. Fujihara, K. Semba, J. Terao, Y. Tsuji, Regioselective transformation of alkynes catalyzed by a copper hydride or boryl copper species, Catal Sci. Technol. 4 (2014) 1699–1709.
[13] M.T. Pirnot, Y.M. Wang, S.L. Buchwald, Copper hydride catalyzed hydroamination of alkenes and alkynes, Angew. Chem. Int. Ed. 55 (2016) 48–57.
[14] R.Y. Liu, S.L. Buchwald, CuH-catalyzed olefin functionalization: From hydroamination to carbonyl addition, Acc. Chem. Res. 53 (2020) 1229–1243.
[15] A.M. Suess, M.R. Uehling, W. Kaminsky, G. Lalic, Mechanism of copper-catalyzed hydroalkylation of alkynes: an unexpected role of dinuclear copper complexes, J. Am. Chem. Soc. 137 (2015) 7747–7753.
[16] M. Mailig, A. Hazra, M.K. Armstrong, G. Lalic, Catalytic anti-markovnikov hydroallylation of terminal and functionalized internal alkynes: synthesis of skipped dienes and trisubstituted alkenes, J. Am. Chem. Soc. 139 (2017) 6969–6977.
[17] M.R. Uehling, R.P. Rucker, G. Lalic, Catalytic anti-markovnikov hydrobromination of alkynes, J. Am. Chem. Soc. 136 (2014) 8799–8803.
[18] Y. Xi, J.F. Hartwig, Diverse asymmetric hydrofunctionalization of aliphatic internal alkenes through catalytic regioselective hydroboration, J. Am. Chem. Soc. 138 (2016) 6703–6706.
[19] Y. Xi, J.F. Hartwig, Mechanistic studies of copper-catalyzed asymmetric hydroboration of alkenes, J. Am. Chem. Soc. 139 (2017) 12758–12772.
[20] X. Feng, H. Jeon, J. Yun, Regio- and enantioselective copper(I)-catalyzed hydroboration of borylalkenes: asymmetric synthesis of 1,1-diborylalkanes, Angew. Chem. Int. Ed. 52 (2013) 3989–3992.
[21] D.A. Ekanayake, A. Chakraborty, J.A. Krause, H. Guan, Hydrogenation reactions catalyzed by HN(CH2CH2iPr2)2-ligated copper complexes, Inorg. Chem. Front. 8 (2021) 4634–4649.
[22] R. Watari, Y. Kayaki, S.-I. Hirano, N. Matsumoto, T. Ikariya, Hydrogenation of carbon dioxide to formate catalyzed by a copper/1,8-diazabicyclo[5.4.0]undec-7-ene system, Adv. Synth. Catal. 357 (2015) 1369–1373.
[23] C.M. Zall, J.C. Linehan, A.M. Appel, Triphosphine-ligated copper hydrides for CO_2 hydrogenation: structure, reactivity, and thermodynamic studies, J. Am. Chem. Soc. 138 (2016) 9968–9977.
[24] E.A. Romero, T. Zhao, R. Nakano, X. Hu, Y. Wu, R. Jazzar, G. Bertrand, Tandem copper hydride–lewis pair catalysed reduction of carbon dioxide into formate with dihydrogen, Nat. Catal. 1 (2018) 743–747.
[25] R. Shintani, K. Nozaki, Copper-catalyzed hydroboration of carbon dioxide, Organometallics 32 (2013) 2459–2462.
[26] L. Zhang, Z. Hou, N-heterocyclic carbene (NHC)–copper-catalysed transformations of carbon dioxide, Chem. Sci. 4 (2013) 3395–3403.
[27] A.W. Beamer, J.A. Buss, Synthesis, structural characterization, and CO_2 reactivity of a constitutionally analogous series of tricopper mono-, di-, and trihydrides, J. Am. Chem. Soc. 145 (2023) 12911–12919.
[28] A.L. Speelman, B.L. Tran, J.D. Erickson, M. Vasiliu, D.A. Dixon, R.M. Bullock, Accelerating insertion reactions of (NHC)Cu-H via remote ligand functionalization, Chem. Sci. 12 (2021) 11495–11505.
[29] A.J. Jordan, C.M. Wyss, J. Bacsa, J.P. Sadighi, Synthesis and reactivity of new copper(I) hydride dimers, Organometallics 35 (2016) 613–616.
[30] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, Olex2: a complete structure solution, refinement and analysis program, J. Appl. Cryst. 42 (2009) 339–341.
[31] O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallo, C.S.J. Cazin, N-heterocyclic carbene copper(I) catalysed n-methylation of amines using CO2, Dalton Trans. 44 (2015) 18138–18144.
[32] A.R. Sadique, E.A. Gregory, W.W. Brennessel, P.L. Holland, Mechanistic insight into NN cleavage by a low-coordinate iron(II) hydride complex, J. Am. Chem. Soc. 129 (2007) 8112–8121.
[33] J.M. Smith, R.J. Lachicotte, P.L. Holland, NN bond cleavage by a low-coordinate iron(II) hydride complex, J. Am. Chem. Soc. 125 (2003) 15752–15753.
[34] G.L. Hillhouse, J.E. Bercaw, Monosubstituted triazenido complexes as intermediates in the formation of amido complexes from hafnium hydrides and aryl azides, Organometallics 1 (1982) 1025–1029.
[35] Y. Yu, A.R. Sadique, J.M. Smith, T.R. Dugan, R.E. Cowley, W.W. Brennessel, C.J. Flaschenriem, E. Bill, T.R. Cundari, P.L. Holland, The reactivity patterns of low-coordinate iron-hydride complexes, J. Am. Chem. Soc. 130 (2008) 6624–6638.
[36] H. Xie, L. Wang, Y. Li, J. Kuang, Z. Wu, T. Fan, Q. Lei, W. Fang, N-insertion reaction mechanisms of phenyl azides with a hafnium hydride complex: a quantum chemistry calculation, New J. Chem. 41 (2017) 5007–5011.
[37] D.S. Wang, Q.A. Chen, S.M. Lu, Y.G. Zhou, Asymmetric hydrogenation of heteroarenes and arenes, Chem. Rev. 112 (2012) 2557–2590.
[38] A.W. Kaplan, R.G. Bergman, Nitrous oxide mediated synthesis of monomeric hydroxoruthenium complexes. reactivity of (dmpe)2Ru(H)(OH) and the synthesis of a silica-bound ruthenium complex, Organometallics 17 (1998) 5072–5085.
[39] K. Severin, Synthetic chemistry with nitrous oxide, Chem. Soc. Rev. 44 (2015) 6375–6386.
[40] G.A. Vaughan, P.B. Rupert, G.L. Hillhouse, Selective o-atom transfer from nitrous oxide to hydride and aryl ligands of bis(pentamethylcyclopentadienyl)hafnium derivatives, J. Am. Chem. Soc. 109 (1987) 5538–5539.
[41] R. Zeng, M. Feller, Y. Ben-David, D. Milstein, Hydrogenation and hydrosilylation of nitrous oxide homogeneously catalyzed by a metal complex, J. Am. Chem. Soc. 139 (2017) 5720–5723.
[42] J.-H. Lee, M. Pink, J. Tomaszewski, H. Fan, K.G. Caulton, Facile hydrogenation of N_2O by an operationally unsaturated osmium polyhydride, J. Am. Chem. Soc. 129 (2007) 8706–8707.
[43] I. Ortega-Lepe, P. Sánchez, L.L. Santos, P. Lara, N. Rendón, J. López-Serrano, V. Salazar-Pereda, E. Álvarez, M. Paneque, A. Suárez, Catalytic nitrous oxide reduction with H_2 mediated by pincer Ir complexes, Inorg. Chem. 61 (2022) 18590–18600.
[44] T.L. Gianetti, S.P. Annen, G. Santiso-Quinones, M. Reiher, M. Driess, H. Grützmacher, Nitrous oxide as a hydrogen acceptor for the dehydrogenative coupling of alcohols, Angew. Chemie. Int. Ed. 55 (2016) 1854–1858.
[45] C.M. Wyss, B.K. Tate, J. Bacsa, T.G. Gray, J.P. Sadighi, Bonding and reactivity of a μ-hydrido dicopper cation, Angew. Chem. Int. Ed. 52 (2013) 12920–12923.
[46] E.A. Patrick, M.E. Bowden, J.D. Erickson, R.M. Bullock, B.L. Tran, Single-crystal to single-crystal transformations: stepwise CO2 insertions into bridging hydrides of [(NHC)CuH]2 complexes, Angew. Chem. Int. Ed. 62 (2023).