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# Synthesis of a Room-Temperature-Stable Dimeric Copper(I) Hydride

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## Keywords

carbenes; copper; hydrides; ligand effects; low nuclearity

Discovered as early as 1844.<sup>[1]</sup> copper(I) hydride complexes have attracted considerable interest. In combination with a hydrosilane, as a hydride source, they promote the hydrosilylation of ketones and aldehydes, and they are efficient catalysts in the regioselective conjugate reduction of a number of carbonyl derivatives, including unsaturated ke-tones, aldehydes, and esters.<sup>[2]</sup> The most extensively studied copper hydride is certainly the hexameric [(Ph<sub>3</sub>P)CuH]<sub>6</sub>, first described by Osborn et al.<sup>[3]</sup> and then developed as a useful synthetic tool by Stryker et al.<sup>[4]</sup> Despite the numerous applications of the Stryker reagent, several studies have focused on the synthesis of copper hydride complexes of lower nuclearity. Huang et al.<sup>[5]</sup> reported the synthesis and X-ray crystal structure of the trinuclear ( $\mu_3$ -H) dicationic complex A (<Figure 1). Caulton et al.<sup>[6]</sup> attempted to generate a mononuclear four-coordinate Cu<sup>I</sup> complex containing a terminal hydride, but obtained and crystallographically characterized the dinuclear complex **B** of type  $[L_2CuH]_2$ . More recently, Lipshutz et al.<sup>[7]</sup> have prepared complex C featuring the bidentate (R)-DTBM-segphos ligand.<sup>[8]</sup> This tricoordinate mononuclear complex is exceptionally stable since it can be stored in solution for weeks at room temperature, if kept under argon; however, it has only been spectroscopically identified by a <sup>1</sup>H NMR signal corresponding to the hydride at  $\delta = 2.55$  ppm.

In the last few years, it has been shown that N-heterocyclic carbenes (NHCs) were able to stabilize highly reactive main-group species,<sup>[9]</sup> and also low-coordinate metal centers.<sup>[10,11]</sup> Using this property, Sadighi et al.<sup>[12]</sup> reported the preparation of the dimeric (NHC)copper hydride complex **D**. The authors stated that this complex "is somewhat unstable, persisting long enough in solution at ambient temperature to permit the easy recording of its <sup>1</sup>H NMR spectrum but decomposing considerably after 1 h in solution or after several days in the solid form". However, despite its instability, they managed on a very small scale to obtain single crystals suitable for X-ray diffraction. Note that the <sup>1</sup>H NMR of a very similar (NHC)CuH complex was reported by Nolan et al.<sup>[13]</sup> but described as too unstable to be isolated.

We have recently shown that cyclic (alkyl)-(amino)carbenes (CAACs) compete advantageously with NHCs for stabilizing highly reactive main-group species.<sup>[14]</sup> Moreover,

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Dedicated to Professor Eiichi Nakamura on the occasion of his 60th birthday

they give rise to extremely thermally stable transition-metal complexes,<sup>[15]</sup> and can even stabilize low-coordinate rhodium and palladium centers<sup>[16]</sup> that are not accessible with other ligands, including NHCs.<sup>[10,11]</sup> Herein we report the preparation, single-crystal X-ray diffraction study, and surprising reactivity of a room-temperature-stable [(CAAC)CuH]<sub>2</sub> complex.

In the hope of preparing a copper(I) hydride of low nuclearity, the bulky menthyl-substituted CAAC  $\mathbf{1}^{[17]}$  was chosen as ligand. A simple addition at room temperature of a THF solution of the free carbene 1 to copper(I) chloride cleanly afforded the monomeric complex 2 in 87% yield (Scheme 1).<sup>[18]</sup> The corresponding copper *tert*-butoxide complex **3** was obtained in 92% yield by addition of sodium *tert*-butoxide to 2. Then, the reduction of 3 was carried out under various experimental conditions, but the best results were obtained using HLiBEt<sub>3</sub> in diethylether/THF solution at -60°C. The (CAAC)copper(I) hydride complex 4 was isolated as a bright orange powder in 84% yield. In contrast to the corresponding (NHC)CuH dimer D, complex 4 is perfectly stable in solution and in the solid state at room temperature for weeks. The infrared spectrum of 4 shows an absorption assigned as v(CuH)at 981 cm<sup>-1</sup>. This frequency is close to that observed for complex **B** (950 cm<sup>-1</sup>),<sup>[6]</sup> but somewhat higher than that reported for complex **D** (881 cm<sup>-1</sup>).<sup>[12]</sup> The unusual stability of dimer 4 is mainly due to the presence of the bulky and rigid menthyl substituent, which precludes any oligomerization processes. Indeed, the replacement of this group by a flexible unsubstituted cyclohexyl group did not allow for the isolation of the corresponding dimer. These observations are reminiscent to the isolation of the fourteen-electron [(1)RhCl(CO)] complex, whereas the cyclohexyl-CAAC unit leads to the classical  $[(L)RhCl(CO)_2]$ complex.<sup>[16]</sup>

The dimeric structure of **4** was ascertained by an X-ray diffraction study<sup>[18]</sup> of single crystals grown from a concentrated hexane solution at  $-20^{\circ}$ C overnight (Figure 2). This complex features a quasi-linear C1-Cu1-Cu2-C28 framework, with the two CAAC ligands which are almost coplanar with a *trans* arrangement. The Cu1–Cu2 [2.3058(5) Å] and CAAC–Cu [1.861(3)–1.862(3) Å] distances are very short, but comparable to those observed with the NHC ligand [2.3059(11) and 1.878(6)–1.882(6) Å].<sup>[12]</sup> The high quality of the crystals allowed H1 and H2 to be isotropically refined. Surprisingly, the Cu1–H1 and Cu1–H2 distances are long [1.71(6)–1.73(5) Å], while the Cu2–H1 and Cu2–H2 bond lengths are rather short [1.55(5)–1.52(6) Å], the H1–H2 separation being 2.29 Å. This unusual feature might result from the unsymmetrical nature of the CAAC ligand.

In the hope of obtaining a stable mononuclear tricoordinate copper(I) hydride, complex **4** was treated with various L ligands. The desired complex **5** was not obtained, but instead complexes **6a–c** were isolated in 60 to 72% yields (Scheme 2). This unprecedented rearrangement, which is irreversible, suggests that the presence of a second L ligand, in addition to the extremely strong  $\sigma$ -donating properties of CAAC, makes the copper very electron-rich. Consequently, the hydride is readily released and migrates to the electrophilic carbene carbon.

These results as a whole demonstrate the superiority of CAACs over NHCs for stabilizing very reactive organometallic species. The catalytic activity of copper(I) hydride dimers such as **4** is under active investigation.

# **Experimental Section**

#### General

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR

spectra were recorded on Varian Inova 300, 500 and Bruker Avance 300 spectrometers. Mass spectroscopy analyses were operated in multimode, and recorded on an Agilent LC TOF spectrometer.

#### Copper(I) chloride complex 2

A THF solution (5 mL) of free carbene **1** (500 mg, 1.3 mmol) was added at room temperature to a THF solution (5 mL) of CuCl (143 mg, 1.4 mmol). The reaction mixture was stirred for 12 h at room temperature. The solvent was removed under vacuum, and the residue was washed with hexane (10 mL). After extraction with methylene chloride (10 mL), the solvent was removed under vacuum, and complex **2** was isolated as a white solid (543 mg, 87% yield). m.p. 256–258°C.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38 (m, 1H), 7.26 (m, 2H), 2.86 (sept, *J* = 6.7 Hz, 2H), 2.69 (td, *J* = 13.5 Hz, *J* = 3.2 Hz, 2H), 2.31 (d, *J* = 13.5 Hz, 1H), 1.81–1.98 (m, 5H), 1.77 (d, *J* = 13.5 Hz, 1H), 1.38 (d, *J* = 6.1 Hz, 6H), 1.33 (m, 11H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 8.0 Hz, 3H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.90 ppm (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 251.4 (C<sub>carbene</sub>), 146.3 (C<sub>ar</sub>), 145.9 (C<sub>ar</sub>), 136.1 (C<sub>ar</sub>), 130.6 (CH<sub>ar</sub>), 125.8 (CH<sub>ar</sub>), 125.6 (CH<sub>ar</sub>), 78.3 (C<sub>q</sub>), 66.0 (C<sub>q</sub>), 53.5 (CH<sub>2</sub>), 52.0 (CH), 49.0 (CH<sub>2</sub>), 36.6 (CH<sub>2</sub>), 31.9, 30.3, 30.1, 29.8, 28.6, 27.8, 25.9, 25.2 (CH<sub>2</sub>), 23.8 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>), 20.9 ppm (CH<sub>3</sub>); HRMS (ESI) calcd for C<sub>27</sub>H<sub>43</sub>CuNCl·[*M* – H + Li]<sup>+</sup>: 485.2462; found: 485.2946.

#### Copper(I) tert-butoxide complex 3

A THF solution (5 mL) of complex 2 (500 mg, 1.0 mmol) was added at room temperature to a THF solution (5 mL) of tBuONa (100 mg, 1.0 mmol). The reaction mixture was stirred for 12 h at room temperature. After filtration under argon, the filtrate was concentrated under reduced pressure, affording complex 3 as a yellow solid (492 mg, 92% yield). m.p. 211-213°C (decomp.); <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta = 7.21-7.13$  (m, 1H), 7.11 (m, 2H), 3.24– 3.15 (m, 2H), 2.92 (sept, J = 6.7 Hz, 2H), 2.15 (d, J = 12.7 Hz, 1H), 1.98 (d, J = 13.5 Hz, 2H), 1.98 (d, J = 13.5 Hz, 2H), 2.92 (sept, J = 6.7 Hz, 2H), 2.93 (1H), 1.88–1.81 (m, 3H), 1.69 (d, J = 6.7 Hz, 3H), 1.59 (d, J = 6.7 Hz, 3H), 1.55 (s, 9H), 1.32 (d, J = 7.0 Hz, 3H), 1.25 (d, J = 6.8 Hz, 3H), 1.22 (d, J = 6.8 Hz, 3H), 1.03 (s, 6H), 1.00 (d, J = 6.9 Hz, 3H), 0.95 ppm (d, J = 6.5 Hz, 3H); two protons cannot be assigned, but according to the integration, they are located under the CH<sub>3</sub> of the *i*Pr signals between 1.21 and 1.24 ppm; <sup>13</sup>C NMR (125 MHz,  $C_6D_6$ ):  $\delta = 253.1$  ( $C_{carbene}$ ), 146.1 ( $C_{ar}$ ), 145.6 ( $C_{ar}$ ), 136.9 (Car), 129.9 (CHar), 125.3 (CHar), 76.6 (Ca), 69.5 (Ca), 65.4 (Ca), 53.2 (CH2), 51.8 (CH), 49.3 (CH<sub>2</sub>), 37.3 (CH<sub>3</sub>), 36.3 (CH<sub>2</sub>), 30.9 (CH), 29.9 (CH<sub>3</sub>), 29.8 (CH), 29.6 (CH), 29.5 (CH<sub>3</sub>), 28.5 (CH), 28.2 (CH<sub>3</sub>), 27.4 (CH<sub>3</sub>), 25.3 (CH<sub>2</sub>), 25.0 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>), 20.7 ppm (CH<sub>3</sub>); HRMS (ESI) calcd for C<sub>31</sub>H<sub>51</sub>CuNO·[*M* – H]<sup>+</sup>: 516.3261; found: 516.3249.

#### Copper(I) hydride dimer complex 4

One equivalent of "super hydride" (HLiBEt<sub>3</sub>, 1m in THF) was added to an Et<sub>2</sub>O solution (5 mL) of complex **3** (500 mg, 0.9 mmol) at -60°C. The reaction mixture, which immediately became bright orange, was stirred at -60°C for one hour, then 30 min at room temperature. After concentration under reduced pressure, the resulting orange solid was extracted with hexane, and after removing the solvent, complex **4** was obtained as a bright orange powder (360 mg, 84% yield). X-ray quality crystals were grown in a concentrated hexane solution at -20°C overnight. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.33–7.19 (m, 6H), 3.17 (m, 6H), 2.46 (qd, *J* = 13.2 Hz, *J* = 2.8 Hz, 2H), 2.20 (d, *J* = 13.3 Hz, 2H), 2.01 (sept, *J* = 6.8 Hz, 2H), 1.93–1.83 (m, 6H), 1.70 (d, *J* = 6.8 Hz, 6H), 1.67 (d, *J* = 6.8 Hz, 6H), 1.56 (d, *J* = 13.3 Hz, 2H), 1.43 (d, *J* = 6.9 Hz, 6H), 1.37 (d, *J* = 6.6 Hz, 6H), 1.35 (d, *J* = 6.6 Hz, 6H), 1.26 (m, 2H), 1.24 (s, 6H), 1.20 (s, 6H), 1.17 (m, 2H), 1.15 (d, *J* = 6.9 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H), 1.0 ppm (m, 4H); the hydride cannot be identified, owing to overlapping with menthyl protons. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 259.9 (C<sub>carbene</sub>), 147.7 (C<sub>ar</sub>), 147.3 (C<sub>ar</sub>), 137.9

(C<sub>ar</sub>), 128.5 (CH<sub>ar</sub>), 125.2 (CH<sub>ar</sub>), 125.0 (CH<sub>ar</sub>), 75.1 (C<sub>q</sub>), 66.0 (C<sub>q</sub>), 53.3 (CH<sub>2</sub>), 52.4 (CH), 50.2 (CH<sub>2</sub>), 36.5 (CH<sub>2</sub>), 30.7 (CH), 30.5 (CH<sub>3</sub>), 30.2 (CH<sub>3</sub>), 29.8 (CH<sub>3</sub>), 29.4 (CH<sub>3</sub>), 29.1 (CH<sub>3</sub>), 28.8 (CH), 28.7 (CH<sub>3</sub>), 26.7 (CH<sub>2</sub>), 26.4 (CH<sub>3</sub>), 24.5 (CH<sub>3</sub>), 24.3 (CH<sub>3</sub>), 23.6 (CH<sub>3</sub>), 21.2 ppm (CH<sub>3</sub>).

Representative procedure for the synthesis of complexes **6a–c**: Two equivalents of PCy<sub>3</sub> (2.2 mmol, 628 mg) and one equivalent of copper(I) hydride dimer **4** (1 g, 1.1 mmol) were mixed as solids in a Schlenk tube and 40 mL of Et<sub>2</sub>O was added at room temperature. The solution discolored slowly, and the reaction mixture was stirred overnight. After evaporation of the solvent under reduced pressure, the oily residue was extracted twice with hexane (2 × 10 mL) to afford **6a** as a colorless oil (1.2 g, 63% yield).

#### 6a

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.26–7.12 (m, 3H), 4.68 (sept, *J* = 6.8 Hz, 1H), 4.13 (sept, *J* = 6.7 Hz, 1H), 3.75 (s, 1H), 2.91 (m, 2H), 2.56 (sept, *J* = 6.8 Hz, 1H), 2.38 (d, *J* = 12.3 Hz, 2H), 1.98–1.91 (m, 6H), 1.88–1.82 (m, 6H), 1.80–1.65 (m, 9H), 1.62–1.53 (m, 6H), 1.49–1.47 (m, 6H), 1.43–1.32 (m, 21H), 1.23–1.18 ppm (m, 12H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 153.4 (C<sub>ar</sub>), 152.2 (C<sub>ar</sub>), 146.0 (C<sub>ar</sub>), 125.8 (CH<sub>ar</sub>), 124.4 (CH<sub>ar</sub>), 123.6 (CH<sub>ar</sub>), 65.0 (CH, d, *J* = 67.1 Hz), 62.1 (C<sub>q</sub>, *J* = 4.9 Hz), 58.2 (*J* = 3.8 Hz, CH<sub>2</sub>), 54.5 (C<sub>q</sub>), 51.6 (CH<sub>2</sub>), 49.8 (CH), 37.6 (CH<sub>2</sub>), 33.1, 32.5, 32.3, 31.3, 31.2 (*J* = 25.5 Hz, CH<sub>2</sub>), 29.5, 28.6, 28.1 (CH<sub>2</sub>, *J* = 10 Hz), 27.4, 27.3, 26.8 (CH<sub>2</sub>), 26.2, 24.4, 23.9, 23.0, 20.9 ppm; <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = +14.2 ppm; HRMS (ESI) calcd for C<sub>45</sub>H<sub>76</sub>NPCu [*M* – H]<sup>+</sup>: *m*/*z* 724.5006; found: 724.5006.

#### 6b

Colorless oil (826 mg, 72% yield); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.28–7.14 (m, 3H), 4.73 (sept, *J* = 6.9 Hz, 1H), 4.20 (sept, *J* = 6.8 Hz, 1H), 3.80 (s, 1H), 2.90–2.81 (m, 1H), 2.63 (sept, *J* = 6.8 Hz, 1H), 2.43 (d, *J* = 12.5 Hz, 1H), 2.08–1.95 (m. 1H), 1.85 (d, *J* = 12.5 Hz, 1H), 1.69 (d, *J* = 6.7 Hz, 3H), 1.55–1.50 (m, 12H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 0.97–1.06 (m, 5H), 0.65 (d, *J* = 8.8 Hz, 1H), 0.49 ppm (d, *J* = 6.6 Hz, 9H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 153.3 (C<sub>ar</sub>), 151.9 (C<sub>ar</sub>), 146.7 (C<sub>ar</sub>), 125.6 (CH<sub>ar</sub>), 124.6 (CH<sub>ar</sub>), 123.9 (CH<sub>ar</sub>), 63.5 (*J* = 72.5 Hz, CH), 62.2 (C<sub>q</sub>), 58.4 (*J* = 7.6 Hz, CH<sub>2</sub>), 54.3 (CH<sub>2</sub>), 51.9 (C<sub>q</sub>), 49.9 (CH), 37.8 (CH<sub>2</sub>), 33.6, 32.6, 30.9, 29.4, 28.5, 27.9, 27.5, 27.2, 26.7 (CH<sub>2</sub>), 26.1, 24.8, 23.8, 23.0, 20.7, 13.3 ppm (d, *J* = 23.3 Hz, P(CH<sub>3</sub>)<sub>3</sub>); <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -47.1 ppm.

#### 6c

Light yellow oil (690 mg, 60% yield); <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta = 7.29-7.16$  (m, 3H), 4.75 (sept, J = 6.8 Hz, 1H), 4.18 (sept, J = 6.7 Hz, 1H), 3.83 (s, 1H), 2.96 (d, J = 12.5 Hz, 1H), 2.82 (m, 1H), 2.63 (sept, J = 6.7 Hz, 1H), 2.40 (d, J = 12.4 Hz, 1H), 2.10 (br. d, J = 11.7 Hz, 1H), 1.82 (d, J = 12.4 Hz, 1H), 1.77 (d, J = 6.6 Hz, 3H), 1.55 (d, J = 6.8 Hz, 3H), 1.52–1.48 (m, 9H), 1.45–1.38 (m, 3H), 1.32 (d, J = 6.5 Hz, 3H), 1.27 (d, J = 6.4 Hz, 3H), 1.22 (d, J = 6.8 Hz, 3H), 1.11–1.01 (m, 5H), 0.92 ppm (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 153.3$  (C<sub>ar</sub>), 152.1 (C<sub>ar</sub>), 148.1 (C<sub>q</sub>, NC), 146.5 (C<sub>ar</sub>), 125.6 (CH<sub>ar</sub>), 124.6 (CH<sub>ar</sub>), 123.9 (CH<sub>ar</sub>), 62.4 (CH), 62.1 (C<sub>q</sub>), 58.8 (CH<sub>2</sub>), 55.1 (C<sub>q</sub>), 54.4 (C<sub>q</sub>), 52.4 (CH<sub>2</sub>), 50.1 (CH), 37.7 (CH<sub>2</sub>), 36.0 (CH<sub>3</sub>), 31.1 (CH<sub>3</sub>), 30.2 (CH<sub>3</sub>), 29.4 (CH), 28.4 (CH), 27.8 (CH<sub>3</sub>), 27.6 (CH), 27.5 (CH<sub>3</sub>), 27.3 (CH<sub>3</sub>), 26.5 (CH<sub>2</sub>), 26.2 (CH<sub>3</sub>), 24.0 (CH<sub>3</sub>), 23.5 (CH<sub>3</sub>), 20.9 ppm (CH<sub>3</sub>).

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Stable at RT Spectroscopically characterized

С

Unstable at RT Crystallographically characterized

D



The most stable types of known copper hydride complexes.



**Scheme 1.** Synthesis of copper(I) hydride dimer 4.



## Figure 2.

Molecular view of complex **4** in the solid state. For clarity, H atoms are omitted, except for the hydrides. Selected bond lengths (Å) and angles (°): N1-C1: 1.326(4), C1-Cu1: 1.861(3), Cu1-H1: 1.71(6), Cu1-H2: 1.73(5), Cu2-H1: 1.55(5), Cu2-H2: 1.52(6), Cu2-C28: 1.862(3), C28-N2: 1.336(4); C1-Cu1-H1: 133.9(17), C1-Cu1-H2: 142.7(18), H1-Cu1-H2: 83(2), H1-Cu2-H2: 96(3), C28-Cu2-H1: 130(2), C28-Cu2-H2: 133(2).



Scheme 2. Reactivity of copper(I) hydride dimer 4 with L ligands.