Synthesis, Structure, and Alkyne Reactivity of a Dimeric (Carbene)copper(I) Hydride

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*Summary: The monomeric, two-coordinate carbene complex (IPr)CuO-t-Bu (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) reacts readily with silanes such as triethoxysilane, forming a dimeric copper(I) hydride complex (**2**) with a very short copper−copper distance. Hydrocupration of 3-hexyne by **2** affords a monomeric copper(I) vinyl complex.*

Copper(I) hydride complexes have been the subject of considerable interest, both as mild and selective reducing agents in stoichiometric reactions[1] and as likely intermediates in copper(I)-catalyzed reductions.[2] The best studied of these, with respect to structure[3] as well as reactivity, is the hexameric [(Ph₃P)CuH]₆, but pentameric analogues have been characterized,[3a] as have octanuclear clusters[4] and hexamers[4,5] supported by other phosphines. Solution-phase studies have suggested the existence of lower-nuclearity complexes, including monomeric complexes of the form (R₃P)CuH.[6] A bis(phosphine)copper(I) μ-hydride dimer, supported by a tris(phosphine) ligand in the κ² binding mode, has been crystallographically characterized.[7]

More recently, N-heterocyclic carbene (NHC) ligands, developed by Arduengo and co-workers[8] and used to great advantage in catalysis,[9] have shown promise as supporting ligands in the copper-catalyzed hydrosilylation of carbonyl compounds.[10] In view of the ability of

Scheme 1ᵃ

L (IPr) = [structure]; Ar = 2,6-(*i*-Pr)₂C₆H₃
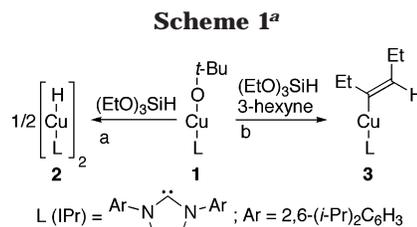
ᵃ Solvents and conditions: (a) C₆D₆, room temperature, ca. 10 min; (b) C₆H₆, room temperature, 45 min; 92%.

these ligands to stabilize low-coordinate, reactive complexes of copper(I),[11] we believed that (NHC)copper(I) hydrides might prefer an unusually low nuclearity and coordination number and, as a result, might display different reactivity patterns toward organic substrates. Herein we report the synthesis of a carbene-ligated copper(I) *tert*-butoxide (**1**) and its facile, clean conversion to a rather unstable (NHC)copper(I) hydride (**2**). Single-crystal X-ray diffraction of **2** reveals a dimeric structure with a very short Cu−Cu distance. Generation of **2** in the presence of 3-hexyne gives rise to the monomeric vinylcopper(I) complex **3**; this appears to be the first hydrocupration reaction to produce a well-defined σ-organocopper product.

The synthetic routes to (NHC)copper(I) complexes **2** and **3** are shown in Scheme 1.[12] The *tert*-butoxide complex **1** is readily prepared from the corresponding chloride[10] on reaction with sodium *tert*-butoxide.[13,14] To our surprise, an attempted reaction of imidazolium chloride, copper(I) chloride, and sodium *tert*-butoxide (2 equiv) did not afford this complex but, rather, a species shown crystallographically to contain a homoleptic [(NHC)₂Cuᴵ] cation.[15] The crystal structure of **1** (Figure 1) displays a monomeric, two-coordinate geometry, with a Cu−O bond distance of 1.8640(18) Å.[16] The full structure displays a close approach (2.11 Å) of O(1) to the calculated position of an IPr backbone hydrogen in

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(8) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(9) For a recent review, see: Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

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(12) For complete synthetic, spectroscopic, and crystallographic details, see the Supporting Information.

(13) Complex **1** was prepared by reaction of LCuCl (1.58 g, 3.26 mmol) with NaO*t*Bu (0.313 g, 3.26 mmol) in THF (15 mL) for 1.5 h, followed by filtration and concentration in vacuo: tan powder, yield 1.44 g (87%).

(14) Synthesis of a linked (NHC)Cuᴵ alkoxide: Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340−2341.

(15) Homoleptic [(NHC)₂Cu]⁺ complexes have been studied previously: Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405−3409. Because such a cation was unwanted in this context, we did not pursue this route beyond the initial crystallographic identification of a product with puzzling ¹H NMR signals (inequivalent to those of **1**).
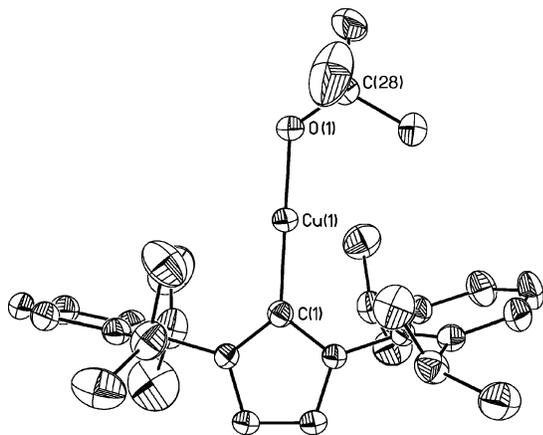
Figure 1. Representation of **1**, shown as 50% ellipsoids. Hydrogen atoms (calculated) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−C(1) = 1.8641(18), Cu(1)−O(1) = 1.8104(13); C(1)−Cu(1)−O(1) = 179.05(7), Cu(1)−O(1)−C(28) = 122.85(12).
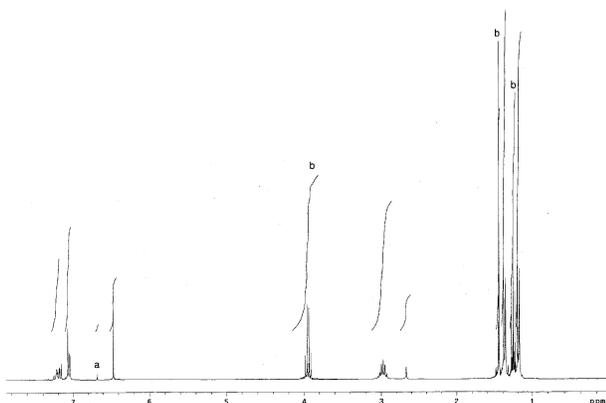

Figure 2. ^{1}H NMR spectrum of **2**, generated in situ in C_6D_6. Other species present: (a) free IPr; (b) (t-BuO)Si-(OCH$_2$CH$_3$)$_3$.

an adjacent molecule (see Figure S5 in the Supporting Information), reminiscent of the O- - -H−C interactions in the corresponding acetate complex.[11]

Reaction of **1** with triethoxysilane in benzene, pentane, or ethereal solvents results in a rapid reaction, with the prompt appearance of an intense yellow color. The formation of the new species **2**, plus the byproduct (t-BuO)Si(OEt)$_3$ and a small amount of free IPr arising from decomposition of **2** in solution, is observed by ^{1}H NMR (Figure 2) when the reaction is carried out in C_6D_6 solution.[17] A new singlet at 2.67 ppm is integrated to one hydrogen per IPr ligand; the same peak is observed on reaction of **1** with tetramethyldisiloxane,[18] and its relative intensity does not change if an excess of silane

is added. This chemical shift falls within the range found for hydrides and deuterides in several phosphine-supported copper complexes.[3b,4,7] A rather broad absorbance in the infrared spectrum, assigned to the bridging copper hydrides, shifts from 881 cm^{-1} for **2** to 638 cm^{-1} for the corresponding deuteride (ν_H/ν_D = 1.38).[19,20] These frequencies are similar to, but somewhat lower than, those reported by Caulton and co-workers for a phosphine-supported copper(I) μ-hydride dimer.[7]

The hydride complex **2** is somewhat unstable, persisting long enough in solution at ambient temperature to permit the easy recording of its ^{1}H NMR spectrum but decomposing considerably after 1 h in solution or after several days in solid form. This incipient decomposition (which results in the slow formation of a Cu^0 precipitate), combined with the high solubility of the complex even in pentane, has complicated our attempts to obtain **2** completely free of the alkoxysilane byproduct. When synthesized in and washed with pentane at −45 °C and then dried under vacuum, **2** is obtained in 60% nominal yield but contains some residual *tert*-butoxysilyl byproduct (12 mol % per Cu, about 6 wt %) and free IPr (4 mol % per Cu), as judged by ^{1}H NMR (see Figure S1 in the Supporting Information).[21] Recrystallization from various solvent combinations gave either lower yields (ca. 33%) of **2**, still containing minor amounts of these byproducts and solvents as contaminants, or significant decomposition over the time frame of the recrystallizations, even at −40 °C.

Despite the high solubility and ready decomposition of **2**, the slow diffusion of hexamethyldisiloxane into a pentane solution of **2**, on a very small scale (ca. 10 mg) at −40 °C, afforded single crystals suitable for X-ray diffraction. Four molecules crystallized in the asymmetric unit, with π-stacking interactions between the ligand *N*-aryl groups.[22] Figure 3 shows one of the molecules in the crystal structure; corresponding bond lengths and angles differ only slightly between this molecule and the others. Complex **2** crystallizes in dimeric form, distorted slightly from a linear L−Cu−Cu−L arrangement, with an average distance of 2.30 Å between the two copper(I) centers. For comparison, the copper−copper distance in the metal is 2.56 Å,[23] and

(16) Crystal data for $C_{31}H_{45}CuN_2O$ (**1**): monoclinic, space group $P2_1/c$, a = 10.4662(5) Å, b = 23.4546(12) Å, c = 13.7109(7) Å, β = 112.44°, V = 3110.9(3) Å^3, Z = 4, ρ_{calcd} = 1.121 g/cm^3, $F(000)$ = 1128, T = 194(2) K. Least-squares refinement converged normally with residuals of R1 (based on F) = 0.0361, wR2 (based on F) = 0.1050, and GOF = 1.079 based on $I > 2\sigma(I)$.

(17) Triethoxysilane (0.0124 mL, 0.067 mmol) was added to a solution of **1** (0.0335 g, 0.064 mmol) in C_6D_6 (ca. 0.75 mL) at ambient temperature, resulting in a clear, bright yellow solution. The ^{1}H NMR spectrum was recorded as soon as possible thereafter.

(18) A reaction was also observed with phenylsilane, but a complex mixture of related products was formed, as judged by ^{1}H NMR, and this reaction was not examined further. To our surprise, in light of catalytic reactions such as those described in ref 10a, no reaction with triethylsilane was observed, even in the presence of excess NaOtBu; see, however, ref 19.

(19) Triethylsilane does react with (IPr)CuF, which will be the subject of a forthcoming communication, to give a product with IR and ^{1}H NMR spectra identical with those of **2** prepared as described in the text. Because triethylsilane-d is commercially available, this synthetic variation was used to prepare the hydride and deuteride for comparison by IR spectroscopy.

(20) We are at present uncertain of the nuclearity of **2** in solution; however, attainment of a higher nuclearity on dissolution would seem counterintuitive, and all (IPr)Cu^I complexes that crystallize as monomers are faintly, if at all, colored.

(21) Triethoxysilane (0.30 mL, 1.6 mmol) was allowed to react with **1** (0.601 g, 1.15 mmol) in Et$_2$O (10 mL) for 4.5 h, followed by concentration in vacuo and washing with pentane, all at −45 °C. Drying in vacuo briefly at −45 °C and then for ca. 4 h at ambient temperature afforded **1** as a light-sensitive yellow powder: yield 0.309 g (nominally 60%; estimated 90% pure based on ^{1}H NMR (see Figure S1 in the Supporting Information)).

(22) Four molecules of **2** were present in the crystallographic asymmetric unit. See Figure S7 in the Supporting Information for the other molecules and Figure S8 for the π-interaction between adjacent molecules. Crystal data for $C_{54}H_{72}Cu_2N_4$ (**2**): triclinic, space group $P\bar{1}$, a = 10.6912(13) Å, b = 25.051(3) Å, c = 39.516(5) Å, α = 94.099(2)°, β = 91.754(3)°, γ = 90.797(3)°, V = 10550(2) Å^3, Z = 8, ρ_{calcd} = 1.139 g/cm^3, $F(000)$ = 3856, T = 194(2) K. Least-squares refinement converged normally with residuals of R1 (based on F) = 0.0765, wR2 (based on F) = 0.1999, and GOF = 0.932 based on $I > 2\sigma(I)$.

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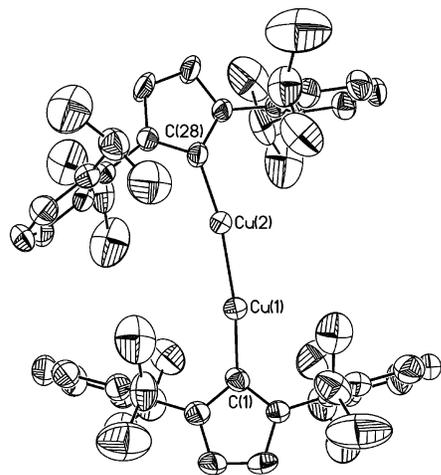
Figure 3. X-ray structure of **2**, shown as 50% ellipsoids. For clarity, hydrogen atoms (calculated) are omitted, and only one molecule (of four) in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): $Cu(1)-C(1) = 1.878(6)$, $Cu(1)-Cu(2) = 2.3059(11)$, $Cu(2)-C(28) = 1.882-(6)$; $C(1)-Cu(1)-Cu(2) = 169.4(2)$, $Cu(1)-Cu(2)-C(28) = 170.33(19)$.

the shortest copper–copper distance we have found in the literature is 2.348(2) Å.[24] The short copper–copper distance in **2** may be interpreted as resulting at least in part from a net bonding interaction between the two d^{10} metal centers,[25] or as primarily a consequence of short bonds from each metal to small bridging ligands.[26] It is worth noting, however, that the copper–copper distance in another hydride-bridged dimer is slightly longer, at 2.371(2) Å.[7,27]

Treatment of **1** with triethoxysilane in the presence of 3-hexyne (5 equiv) results in an intense orange color, which fades over a period of minutes. Concentration in vacuo after 45 min affords a single copper complex, as judged by ^{1}H NMR spectroscopy.[28] The same product is generated when **2** is isolated prior to redissolution in C_6D_6 and addition of 3-hexyne. The spectrum is consistent with the formation of (IPr)Cu[(*E*)-3-hexenyl] (**3**); the resonance for the vinylic hydrogen, at 5.51 ppm, appears as a distinctive triplet of triplets, with coupling to both geminal and vicinal methylene groups. Diffusion of hexamethyldisiloxane vapor into a solution of **3** in diethyl ether afforded crystals suitable for X-ray diffraction, and the resulting structure (Figure 4) confirms

Figure 4. X-ray structure of **3**, shown as 50% ellipsoids. For clarity, hydrogen atoms (calculated) and ligand-based *i*-Pr groups are omitted. Selected bond lengths (Å) and angles (deg): $Cu(1)-C(1) = 1.897(3)$, $Cu(1)-C(30) = 1.902(4)$, $C(30)-C(31) = 1.317(7)$; $C(1)-Cu(1)-C(30) = 177.29(18)$, $Cu(1)-C(30)-C(31) = 122.0(4)$.

the formation of a monomeric (NHC)copper(I) vinyl complex.[29] While analogous reactions are most probably involved in the hydrogenation[1b] or reductive coupling[30] of alkynes by copper hydrides, this appears to be the first hydrocupration of a carbon–carbon multiple bond to give a well-defined σ-organocopper product.

In conclusion, we have demonstrated the clean stoichiometric reaction between a monomeric, two-coordinate (NHC)copper(I) alkoxide and certain silanes. Solution ^{1}H NMR spectroscopy is consistent with the expected copper(I) hydride product, and structural characterization of this product shows a dimeric arrangement and an unusually low nuclearity for copper-(I) hydrides, with a very short copper–copper distance. This complex effects the well-defined hydrocupration of 3-hexyne, allowing the isolation of a monomeric vinylcopper complex in high yield.

Supporting Information Available: Text, figures and tables giving synthetic and computational details, spectroscopic data, additional crystal structures, and structural parameters for **1**–**3**; X-ray data for **1**–**3** are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) A (pyridine)copper hydride dimer, sandwiched between two Cr-(CO)$_5$ fragments and bearing μ_3-hydrides, also exhibits a short Cu–Cu distance, 2.3603(13) Å: Klüfers, P.; Wilhelm, U. *J. Organomet. Chem.* **1991**, *421*, 39–54.

(28) Triethoxysilane (0.350 mL, 1.90 mmol) was added to a solution of **1** (0.571 g, 1.09 mmol) and 3-hexyne (0.650 mL, 5.72 mmol) in benzene (7 mL). The reaction mixture was stirred for 45 min and concentrated in vacuo, affording **3** as a tan powder: yield 0.537 g (92%).
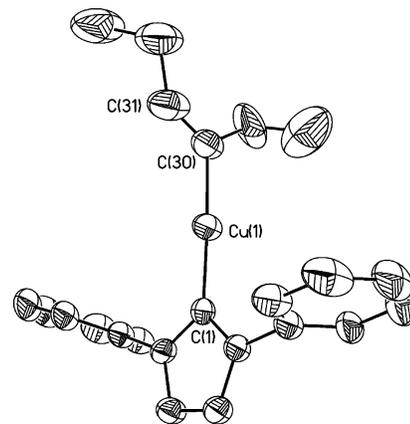
(29) Crystal data for C$_{33}$H$_{47}$CuN$_2$ (**3**): triclinic, space group $P\bar{1}$, $a = 10.6579(11)$ Å, $b = 12.5522(12)$ Å, $c = 12.9530(13)$ Å, $\alpha = 92.124(2)°$, $\beta = 103.080(2)° \gamma = 106.695(2)°$, $V = 1607.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.106$ g/cm^3, $F(000) = 576$, $T = 194(2)$ K. Least-squares refinement converged normally with residuals of R1 (based on F) = 0.0607, wR2 (based on F) = 0.1540, and GOF = 0.963 based on $I > 2\sigma(I)$.

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