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Neutral Dinuclear Copper(I)-NHC Complexes: Synthesis and Application in the Hydrosilylation of Ketones

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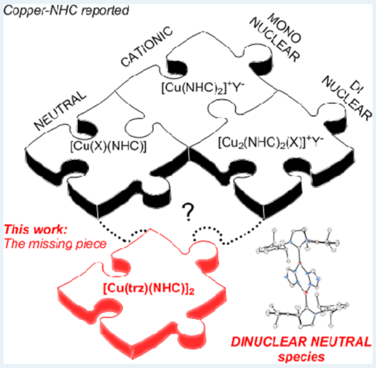
Supporting Information

ABSTRACT: The synthesis of a class of highly stable neutral dinuclear Cu(I)-NHC complexes using 1,2,4-triazole as a bridging ligand is described. Various NHCs were used to generate a library of $[Cu(\mu\text{-trz})(NHC)]_2$ complexes. Interestingly, $[Cu(\mu\text{-trz})(IPr)]_2$ was found to be highly active in the hydrosilylation of ketones, without the need for an external base or any other additive. A wide range of aryl and alkyl ketones, as well as sterically hindered ketones, was successfully reduced to alcohols using the lowest catalyst loading reported to date.



KEYWORDS: *N-heterocyclic carbenes, copper(I), hydrosilylation, ketones, dinuclear*

In the past decade, copper-NHC complexes have been heavily studied and employed in catalysis.[1] In this synthetic exploration effort, mostly mononuclear complexes, both neutral and cationic, have been reported. Dinuclear complexes with bridging or chelating ligands are also found in the literature, although in significantly smaller numbers. Among those that have been reported, cationic complexes are usually formed by two copper(I) NHC fragments bridged by an anionic ligand such as hydride,[2] fluoride,[3] alkenyl,[4a] and boryl[4b] with the general formula $[Cu_2(\mu\text{-X})(NHC)_2]Y$ (Figure 1). Neutral species are more scarce with only two known examples,[5] one of which is the highly unstable copper hydride, reported by Sadighi and co-workers.[5a] The latter proved highly unstable when conventional five-membered NHCs were used; however, recently, increased stability of related complexes was achieved by using expanded-ring NHCs[6] or highly donating cyclic alkylaminocarbene (CAAC) ligands.[7] Examples of polynuclear complexes (presenting three or more copper centers) are rare and have been obtained using multidentate NHC ligands.[8] Despite recent advances in the use of nonconventional NHC ligands,[9] five-membered NHCs based on the imidazolium core are still the most widely studied and are the most readily available. Noting the significant difference in catalytic efficiency between the mononuclear cationic copper complexes, $[Cu(NHC)_2]Y$, and its neutral relatives, $[Cu(X)(NHC)]$,[10] we sought to synthesize stable neutral dinuclear copper-NHC complexes bearing conventional five-membered NHC ligands and to evaluate their reactivity in known copper-catalyzed transformations (Figure 1). In order to achieve the isolation of neutral dinuclear complexes, 1,2,4-triazole **1** (Htrz) was selected for its ability to coordinate two adjacent copper centers. Htrz and its corresponding triazolate anion (trz) have been widely used for this bridging task.[11] However, only one example of a well-defined neutral dinuclear copper(I) complex, bearing triphenylphosphine as a ligand, has been reported to date.[12] It should be noted that these authors did not report their use in catalysis but simply their synthesis.

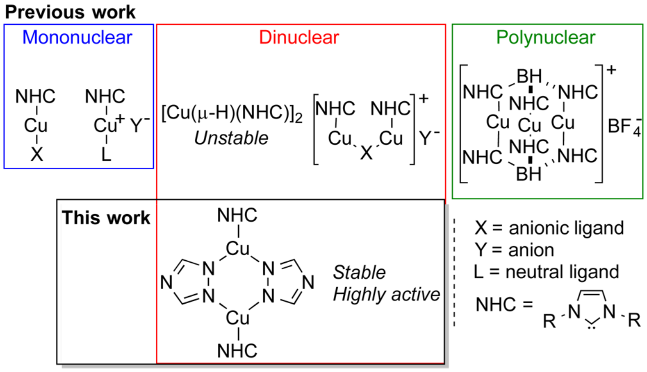


Figure 1. Previous work describing mono-, di-, and trinuclear copper-NHC complexes and details of the present report on dinuclear complexes.

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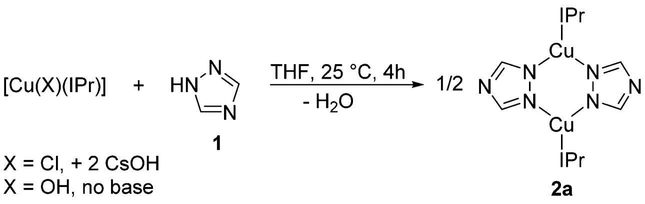
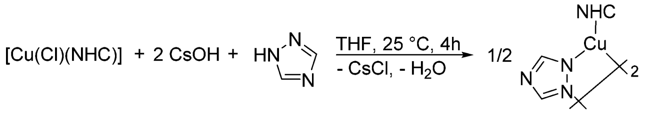
In order to synthesize the desired complexes, [Cu(Cl)(IPr)][13] (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was used as a benchmark reagent in initial synthetic efforts (Scheme 1). When this complex was reacted with **1** at room temperature in THF, no reaction was observed, whereas the addition of CsOH leads to complete formation of the desired [Cu(μ-trz)(IPr)]$_2$ (**2a**). [Cu(OH)(IPr)][14] was also reacted with **1**, in the absence of CsOH, to yield **2a** as expected, revealing that the copper-NHC hydroxide species might be an intermediate in the initial reaction.

Scheme 1. Synthesis of 2a from Various Copper-NHC Precursors



Considering [Cu(Cl)(NHC)] complexes are easily accessed and isolated, with regard to the corresponding [Cu(OH)(NHC)] analogues, we opted, for the sake of simplicity, to target the in situ generation of the hydroxides. Gratifyingly, various [Cu(μ-trz)(NHC)]$_2$ complexes were obtained in excellent yields using this strategy (Table 1). Additionally, the purification of the product proved straightforward, since excess Htrz and CsOH can be removed by simple filtration through Celite. Both aromatic (Table 1, entries 1−3) and aliphatic substituents (Table 1, entries 4 and 5) on the nitrogens of the NHC are well tolerated, giving the desired complexes in high yields. Whereas **2a**,**b** are soluble in THF, **2c**,**d** proved insoluble in this solvent and CH$_2$Cl$_2$ had to be used instead. In addition, the scaling up of **2a**−**c** to 1 g was achieved without any issue. These complexes are air stable in the solid state.[15]

Table 1. Synthesis of [Cu(μ-trz)(NHC)]$_2$ Complexes[a]



Entry	NHC	solvent	[Cu(μ-trz)(NHC)]$_2$	yield (%)[b]
1	IPr	THF	NHC = IPr (**2a**)	90 (92)[c]
2	IMes	THF	NHC = IMes (**2b**)	93 (97)[c]
3	SIMes	CH$_2$Cl$_2$	NHC = SIMes (**2c**)	92 (95)[c]
4	I^{t}Bu	CH$_2$Cl$_2$	NHC = I^{t}Bu (**2d**)	91
5	ICy	CH$_2$Cl$_2$	NHC = ICy (**2e**)	89

[a] Reaction conditions: [Cu(Cl)(NHC)] (100 mg), **1** (1.1 equiv), CsOH (2.0 equiv), solvent (2 mL), 25 °C, 4 h, under argon. [b] Isolated yield. [c] Large-scale (1 g) isolated yield given in parentheses. IMes = *N*,*N*′-bis-[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene, SIMes = *N*,*N*′-bis[2,4,6-(trimethyl)phenyl]imidazolin-2-ylidene, I^{t}Bu = *N*,*N*′-(di-*tert*-butyl)imidazol-2-ylidene, ICy = *N*,*N*′-(dicyclohexyl)imidazol-2-ylidene.

X-ray analysis of **2a** confirmed the expected structure, as shown in Figure 2. All other complexes were fully characterized, and their structures were confirmed by X-ray diffraction on single crystals (see the Supporting Information).[16]

2a displays a distorted-trigonal geometry around each copper atom, displaying two different bond distances with the two nitrogens N31 and N32^1. The same geometry and comparable bond distances are found in copper-NHC pyridyl-azolate complexes, despite the latter showing a more distorted trigonal geometry in comparison to **2a**.[17] A distinctive feature in **2a** is the six-membered ring formed by the four nitrogens of the two triazolate bridging ligands and the two copper atoms, the latter being separated by a distance of 3.7687(11) Å. Analyzing the torsion angles of this ring, an almost flat conformation was found; moreover, the ring is practically perpendicular to the NHC−Cu−Cu−NHC plane, most likely to minimize steric repulsions. These characteristics were found in all other complexes (**2b**−**e**) with a different degree of distortion caused by the steric demand of the NHC ligand (%V_{Bur}),[18] mainly evidenced by the deviation in linearity of the Cu1^1−Cu1−C1 torsional angle such as in **2d** (C1−Cu1−Cu1^1 = 161.76(4)°; see Figure S6 in the Supporting Information).

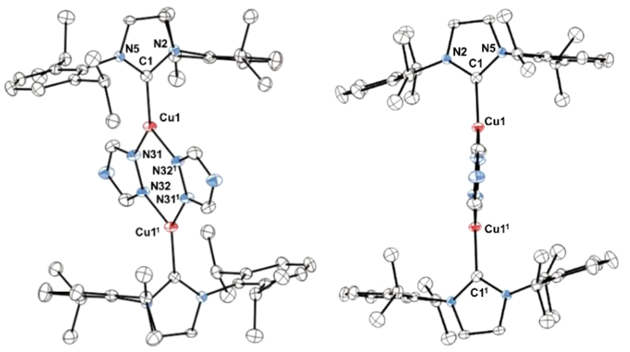
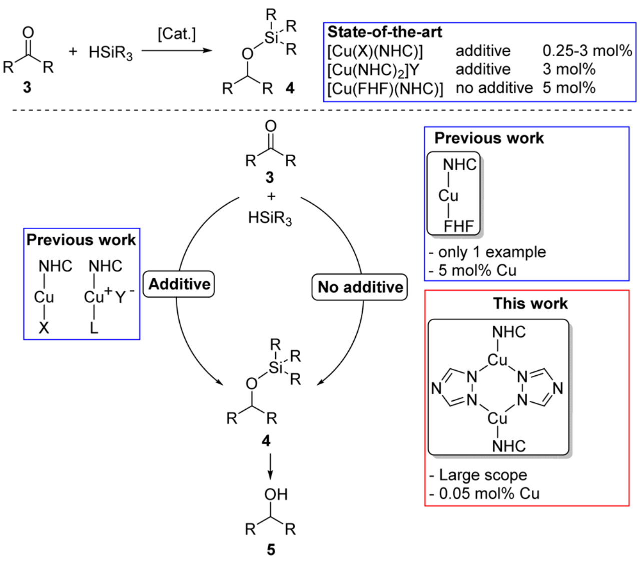


Figure 2. Two views of the molecular structure of **2a**. Solvent molecules and H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.[16] Selected bond lengths (Å), angles (deg), and torsion angles (deg): Cu1−C1 = 1.896(2); Cu1−N32^1 = 1.964(2); Cu1−N31 = 2.001(2); N32^1−Cu1−C1 = 134.57(10); N31−Cu1−C1 = 119.15(10); N31−Cu1−N32^1 = 106.17(9); C1−Cu1−Cu1^1 = 170.22(7); N31−Cu1−C1−N2 = −76.7(2); N32^1−Cu1−C1−N2 = 98.9(2); N31−Cu1−C1−N5 = 99.3(2); N32^1−Cu1−C1−N5 = −85.0(2); Cu1−N31−N32−Cu1^1 = 5.4(2); N31−Cu1−N32^1−N31^1 = 4.37(15); N32^1−Cu1−N31−N32 = −4.59(16).[16]

Interested in the applications of these dimers in catalysis, we sought to compare their performance with that of the corresponding mononuclear copper-NHC complexes in a well-studied reaction. We hoped that the bridging triazolate could act as an internal base, thus avoiding the use of any external additives. Among the various transformations catalyzed by copper-NHC species, in which a base is typically needed,[19] the hydrosilylation of ketones was selected as a model reaction (Scheme 2).

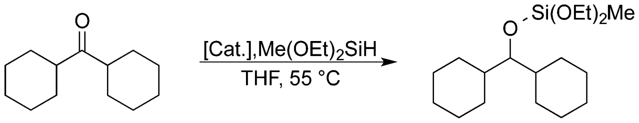
Nolan and co-workers reported that the neutral complexes [Cu(Cl)(ICy)] and [Cu(Cl)(SIMes)] and the cationic complexes [Cu(ICy)$_2$]BF$_4$ and [Cu(IPr)$_2$]BF$_4$ were able to promote this transformation using 3 mol % of catalyst with a substoichiometric amount of base (3−12 mol % of NaO^{t}Bu).[20] The authors proposed an initial activation of the copper precatalyst by the base, forming in situ the corresponding [Cu(O^{t}Bu)(NHC)] species, which, upon reacting with the silane, generated the [Cu(H)(NHC)] intermediate involved in the hydrosilylation.[20a,c] Because both the chloride and the cationic NHC complexes were not able to react directly with the silane to give the intermediate copper hydride species, the use of a *tert*-butoxide base proved necessary. Later on, using both kinetic and computational studies, it was shown that the base activates both precatalyst and silane, forming a hypervalent silicon species. The latter permitted a better hydride transfer to copper, generating the copper hydride needed for the

Scheme 2. Cu-NHC Catalysts for the Hydrosilylation of Ketones[20−23]



hydrosilylation to proceed.[21] Recently, other methodologies have been reported using different [Cu(Cl)(NHC)] complexes, exclusively based on the fine tuning of the NHC ligand, but without overcoming the need for a significant amount of base.[22] To date, the only copper(I)-NHC precatalysts able to perform this reaction without the use of any external base are the copper bifluoride complexes [Cu(HF_2)(NHC)], used exclusively for the hydrosilylation of benzyl acetone.[23] In this case, F^- acts as an internal base. It should be mentioned that Htrz possesses acidity (pK_a = 14.8, in DMSO) comparable to that of HF (pK_a = 15, in DMSO), which suggests that the triazolate anion can also act as an internal base. For these reasons, the dinuclear copper complexes $[Cu(\mu\text{-trz})(NHC)]_2$ were tested in this reaction, using the hindered dicyclohexyl ketone (**3a**) as a model substrate (Table 2). All complexes bearing aromatic substituents on the nitrogens of the NHC, **2a**−**c**, showed high activity (Table 2, entries 1−3), whereas those bearing aliphatic substituents **2d**,**e** were not active under these conditions (Table 2, entries 4 and 5). Among these catalysts, **2a** proved the most active and was chosen for further optimization. Surprisingly, reducing the catalyst loading to 0.05 mol % did not affect the catalytic activity of **2a**, converting **3a** in 2 h into the corresponding silyl ether (Table 2, entry 7). Under these conditions, **2a** is the most efficient catalyst of all the copper-NHC catalysts reported to date for this transformation (TON = 2000). Next, the amount of silane was reduced to 1.1 equiv without any loss in efficiency (Table 2, entry 9). Using these optimized conditions followed by deprotection with TBAF, **5a** was isolated in excellent yield (Scheme 3, method A).

Table 2. Synthesis of $[Cu(\mu\text{-trz})(NHC)]_2$ Complexes[a]



entry	catalyst	loading (mol %)	silane (equiv)	time (h)	conversn[b] (%)
1	**2a**	1	2	0.75	>99
2	**2b**	1	2	0.75	95
3	**2c**	1	2	0.75	84
4	**2d**	1	2	0.75	0
5	**2e**	1	2	0.75	5
6	**2a**	0.05	1.5	0.75	85
7	**2a**	0.05	1.5	2	>99
8	**2a**	0.01	1.5	2	0
9	**2a**	**0.05**	**1.1**	**2**	**>99**
10[c]	**2a**	0.05	1.1	4	72

[a]Reaction conditions unless specified otherwise: **3a** (0.5 mmol), $Me(OEt)_2SiH$ (0.55−1 mmol), $[Cu(\mu\text{-trz})(NHC)]_2$ (0.01−0.5 mol %), THF (0.75 mL), 55 °C, under argon. [b]Yield determined by GC, on the basis of **3a**; average of two reactions. [c]35 °C.

Scheme 3. Optimized Procedures for the Hydrosilylation of 3a and Its Subsequent Deprotection To Yield 5a

Method A. i) $[Cu(\mu\text{-trz})(IPr)]_2$ (0.05 mol%), $Me(OEt)_2SiH$ (1.1 equiv.), THF, 55 °C, 2h; ii) TBAF, MeOH, 25 °C, 45 min. **95%**.

Method B. i) $[Cu(\mu\text{-trz})(IPr)]_2$ (0.25 mol%), PMHS (2 equiv.), THF, 55 °C, 14h; ii) MeOH, NaOH 2M , 25 °C, 90 min. **97%**.

Despite these satisfactory results, we still wanted to use a less expensive and a more environmentally friendly silane in lieu of $Me(OEt)_2SiH$; for these reasons, the use of polymethylhydrosiloxane (PMHS) was investigated next. When PMHS was tested under the optimal conditions, no conversion was observed. However, when the catalyst loading was increased to 0.25 mol %, complete consumption of **3a** was achieved, showing the feasibility of using this environmentally friendly and safe hydride source. At this point, the deprotection and purification steps were altered; TBAF and flash chromatography were replaced by NaOH in methanol, followed by a simple extraction to remove siloxanes formed during the deprotection step (Scheme 3, method B). Interestingly, when the scope of the reaction was investigated using 0.05 mol % of **2a** and PMHS, a wide range of ketones were successfully converted into the corresponding alcohols after simple deprotection (Scheme 4). Acetophenone derivatives bearing, in the para position, both electron-withdrawing (EWG; **5c**−**e**) and electron-donating (EDG; **5f**) groups were well tolerated. The same tolerance was noted for the ortho-substituted **5g**. Following this trend in reactivity, a test using 4,4′-dimethoxybenzophenone, as a challenging substrate (electronically), showed that a longer reaction time was needed. Nevertheless, full conversion into **5k** was achieved. Moreover, branched aliphatic substitutions on the α-carbon of acetophenone (R′ in Scheme 4), such as a *tert*-butyl moiety, did not affect the yield (**5i**). When highly hindered aliphatic ketones were considered, acyclic 5-nonanone (**5o**), adamantone (**5q**), and 1-adamantyl methyl ketone (**5r**) were all successfully converted to the desired alcohols. Encouraged by these results, we tested the methodology on a more complex molecule: i.e., *trans*-androsterone. Gratifyingly, this steroid was fully converted to the corresponding alcohol **5s** in excellent yield, further demonstrating the robustness of this methodology. It should be mentioned that only one diastereoisomer of the product was observed in the last entry, suggesting that this method might be used in a diastereoselective manner.

In conclusion, a novel and highly stable family of neutral dinuclear Cu(I)-NHC complexes was synthesized and fully

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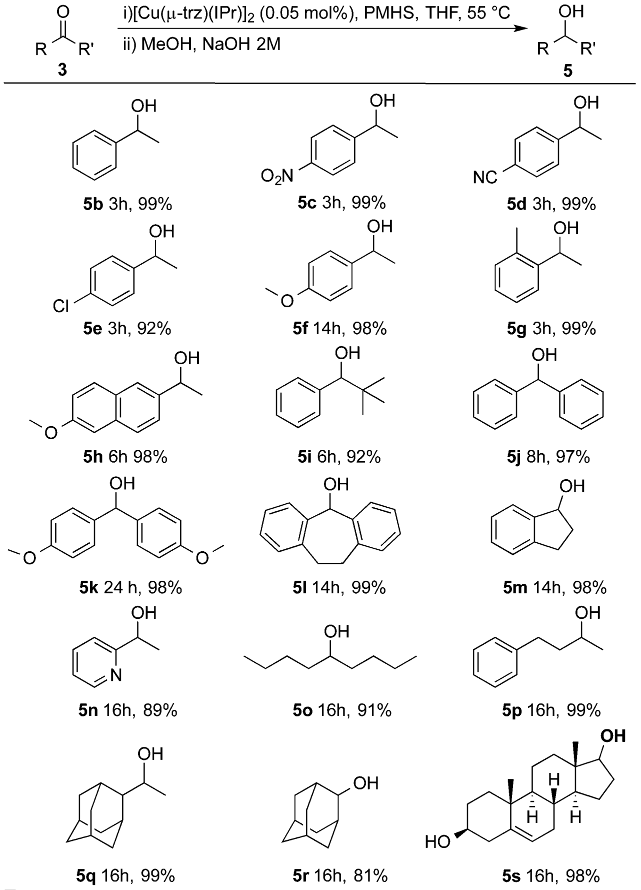
Scheme 4. Hydrosilylation of Ketones using 2a and PMHS[a]



[a]Reaction conditions: (i) **3** (1 mmol), PMHS (2 mmol), $[Cu(\mu\text{-}trz)(IPr)]_2$ (0.05 mol %) THF (1.5 mL), 55 °C; (ii) MeOH (1 mL), $NaOH_{aq}$ 2 M (2 mL), 25 °C, 90 min.

characterized. Among these complexes, **2a** was found to be the most efficient catalyst to date in the hydrosilylation of ketones, reducing a wide range of aryl and alkyl ketones to the corresponding alcohols without the use of any additive. The method was also successfully applied to hindered ketones, which are usually very difficult to reduce. Ongoing work in our laboratory is focusing on the use of this novel family of complexes in related copper-catalyzed transformations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02723.

Experimental details, characterization data, and X-ray crystallographic data for **2a**−**e** (PDF)
Crystallographic data for **2a** (CIF)
Crystallographic data for **2b** (CIF)
Crystallographic data for **2c** (CIF)
Crystallographic data for **2d** (CIF)
Crystallographic data for **2e** (CIF)

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Notes

The authors declare no competing financial interest.

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(16) CCDC 1442422 (**2a**), CCDC 1442423 (**2b**), CCDC 1442424 (**2c**), CCDC 1442425 (**2d**), and CCDC 1442426 (**2e**) contain supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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