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Copper-NHC Mediated Semi-Hydrogenation and Hydroboration of Alkynes: Enhanced Catalytic Activity Using Ring-Expanded Carbenes

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Supporting Information Placeholder

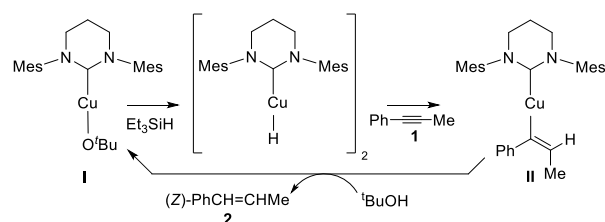
ABSTRACT: A series of two-coordinate copper *tert*-butoxide complexes bearing 5-, 6- and 7-membered ring N-heterocyclic carbenes, prepared by protonolysis of (NHC)CuMes with ^tBuOH, have been used as catalytic precursors in the semi-hydrogenation of alkynes with silanes/^tBuOH and the hydroboration of alkynes with HBPIn. Both processes proceed with high regioselectivity and show enhancements with 6- and 7-membered ring carbenes.

INTRODUCTION

Manipulation of the stereoelectronic properties of a ligand to enhance activity within a metal coordination sphere is the name of the game in homogeneous catalysis. In the case of heterocyclic carbene ligands, this has driven the development of alternatives to the original¹ Arduengo-type unsaturated/saturated 5-membered ring N-heterocyclic carbenes (NHCs),^{2,3} in particular; cyclic alkyl amino carbenes (CAACs),⁴ abnormal/mesoionic carbenes⁵ and bisoxazoline derived NHCs.⁶ An additional class of carbene ligands that has received some attention in recent years is one based on ring-sizes of > 5.⁷ Often referred to as ring-expanded carbenes or RE-NHCs, these offer enhanced donor capabilities and an increased steric profile in comparison to their 5-membered ring counterparts;⁸ features that should help to facilitate key processes in catalytic cycles including oxidative addition (electronic enhancement) and reductive elimination (steric enhancement). Moreover, the wide N-C-N angle that is a particular feature of RE-NHCs results in the N-substituted wingtips being pushed down towards the metal, stabilizing low coordination numbers and/or unusual oxidation states.⁹ As a result, there may be further enhancement of a desired catalytic pathway, or alternatively, the advent of new processes.

The use of metal RE-NHC complexes in catalysis is still relatively limited and has for the most part focussed on Pd,¹⁰ together with a smaller number of reports employing Ru,¹¹ Rh,¹² Ir,¹³ Ni,¹⁴ Pt,¹⁵ Cu¹⁶ and Au.¹⁷ The paucity of work is somewhat surprising given that, in the vast majority of direct comparisons between RE-NHCs (most commonly, 6- and 7-membered ring systems) and imidazolidin-2-ylidene, a beneficial effect is observed

We have been interested in the reactivity of RE-NHCs in conjunction with the first-row metals Ni^{14a,b,d,9a,18} and Cu.¹⁹ During efforts to prepare a hitherto unknown mononuclear copper hydride complex, (6-Mes)CuH^{19a,20} through reaction of the *tert*-butoxide complex (6-Mes)CuO^tBu (**I**) with silanes, we found that the combination of **I** and Et₃SiH in the presence of PhC≡CMe (**1**) and ^tBuOH at room temperature led to semi-hydrogenation of the alkyne to give just the *Z*-isomer of PhCH=CHMe (**2**, Scheme 1). A likely pathway for the reaction involves *syn*-hydrocupration of the alkyne to afford a Cu-alkenyl species, followed by protonolysis by the alcohol. Circumstantial support for this mechanism was provided by the isolation and structural characterization of alkenyl complex **II** from a stoichiometric reaction of **I**, Et₃SiH and **1**.



Scheme 1 Semi-hydrogenation of PhC≡CMe (**1**) by (6-Mes)CuO^tBu (**I**)

Recent years have witnessed a number of reports on homogeneous alkyne semi-hydrogenation catalysts, the aim being to develop systems that alleviate some of the issues of selectivity and over-reduction associated with the well-known commercially used heterogeneous Lindlar catalyst.²¹ Much of the focus has been on cheap and sustainable metals, including Mn,²² Fe,²³ Co²⁴ and Ni.²⁵ Copper complexes²⁶ have proved very versatile

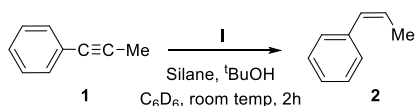
in preventing the over reduction of typically challenging substrates such as aryl- and diaryl substituted alkynes, especially ones containing functional groups. Encouraged by our initial findings above, as well as the reports by Tsuji and Lalic with the 5-membered ring NHC precursor (IPr)CuO^tBu,^{26a,b} we now describe a catalytic investigation with a series of (NHC)CuO^tBu complexes that differ both in ring-size (5, 6 and 7-membered ring carbenes) and N-substituents. In the course of investigating the influence of other variables (reductant, substrate and alcohol) on catalytic activity, we have established that this same range of (NHC)CuO^tBu complexes catalyze the α -hydroboration of internal alkynes. In both catalytic processes, the presence of RE-NHC ligands leads to higher activity than found with the 5-membered ring analogues.

RESULTS AND DISCUSSION

The preliminary catalytic study shown in Scheme 1 employed 5 mol% **I**, 1.1 equiv Et₃SiH and 1.1 equiv ^tBuOH.^{19a} Under these conditions, the conversion of PhC≡CMe (**1**) to Z-PhCH=CHMe (**2**) was very slow, requiring almost 2 weeks to go to completion at room temperature. The reaction time could be cut to 17 h by raising the temperature to 60 °C, although there was now a slight loss of selectivity (96:4 Z:E). No evidence for over-reduction to alkane was found.

In a number of instances, Et₃SiH has been shown to be a relatively unreactive silane for semi-reduction reactions.^{23b,26a,b} Indeed, upon trialling a range of other trialkyl and mixed aryl/alkyl silanes for the semi-reduction of **1** (Table 1, Entries 1-5), we observed improved activity in all cases, as evidenced by product formation within 2 h, even at a lowered catalyst loading of 1 mol%. Polymethylhydrosiloxane (PHMS) proved to be particularly active (Entry 6), generating an 85% yield of product within only 1 h.

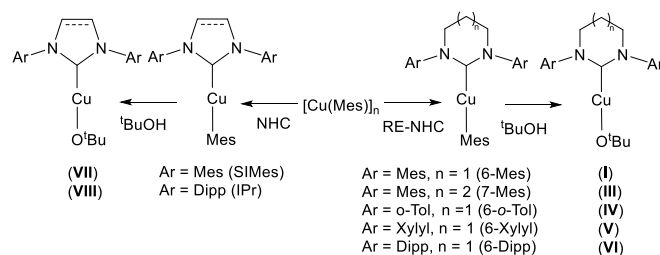
Table 1. Catalytic semi-hydrogenation of PhC≡CMe by **1 as a function of silane^a**



Entry	Silane	I (mol%)	Yield of 2 (%) ^b
1	EtMe ₂ SiH	1	Trace
2	Me ₂ PhSiH	1	5
3	MePh ₂ SiH	1	34
4	Ph ₃ SiH	1	2
5	Ph ₃ SiH	5	57
6 ^c	PHMS	1	85

^aConditions: **1** (0.22 mmol), **I** (1 or 5 mol%), 1.1 equiv silane, 1.1 equiv ^tBuOH, C₆D₆ (0.5 mL), 25 °C, 2 h. ^bYield of **2** determined by ¹H NMR spectroscopy using 1,3,5-(MeO)₃C₆H₃ as an internal standard. ^cReaction time of 1 h.

Investigation of the reaction as a function of NHC ligand led us to prepare a number of new (RE-NHC)CuO^tBu complexes using the method employed previously for **I**, namely incorporation of free RE-NHC into polynuclear [Cu(Mes)]_n to give (NHC)CuMes (ESI), followed by protonolysis with ^tBuOH. This afforded the new 7-Mes, 6-*o*-Tol and 6-Xylyl derivatives **III-V** as highly air-sensitive, cream colored solids in yields of 17-93%. To broaden the scope of the (NHC)CuO^tBu complexes for investigation, the same synthetic approach was used to make the known 6-Dipp analogue **VI**,^{20d} as well as the known five-membered ring SiMes and IPr derivatives **VII**²⁷ and **VIII**.^{20a}



Scheme 2. Synthesis of (NHC)CuO^tBu complexes

The X-ray structures of **III** and **IV** are shown in Figure 1. As **VI** and **VII** were only previously characterized by NMR spectroscopy,^{18,27} they too were isolated for structural analysis (Figure 1). Table 2 shows a comparison of the Cu-N_{NHC}/Cu-O distances and the N-C-N bond angle across the series of *tert*-butoxide complexes shown in Scheme 2. A further comparison of the different NHCs was provided by calculations of the percentage buried volume (%V_{bur}) using the SambVca programme.²⁸ There is a fairly steady increase in steric profile of the 6-membered NHC ligands on moving from *o*-tolyl (**IV**, entry 3) to mesityl (**I**, entry 1) to dipp (**VI**, entry 4) substituents, whereas the increase in ring size upon moving from 6-Mes to 7-Mes (entries 1 and 2) brings about only a small increase.

The activity of **I** versus **III-VIII** for the semi-reduction of **2** with PHMS is summarized in Table 3. Entries 1, 2 and 6 reveal a clear trend in decreasing product yield as a function of ring-size in the order 6 > 5 > 7 for N-mesityl substituted carbenes. These differences are highlighted more clearly at a lower Cu loading (Entries 7-9). The results also reveal a dependency on the N-substituent, with product yield decreasing in the order N-mesityl > N-xylyl >> N-*o*-tolyl >> N-dipp (Entries 1, 3-5). This suggests there is a 'Goldilocks' effect in which substituents are either too small (tolyl) or too large (dipp) to be effective, whereas the 2,6-dimethylphenyl substitution pattern present in

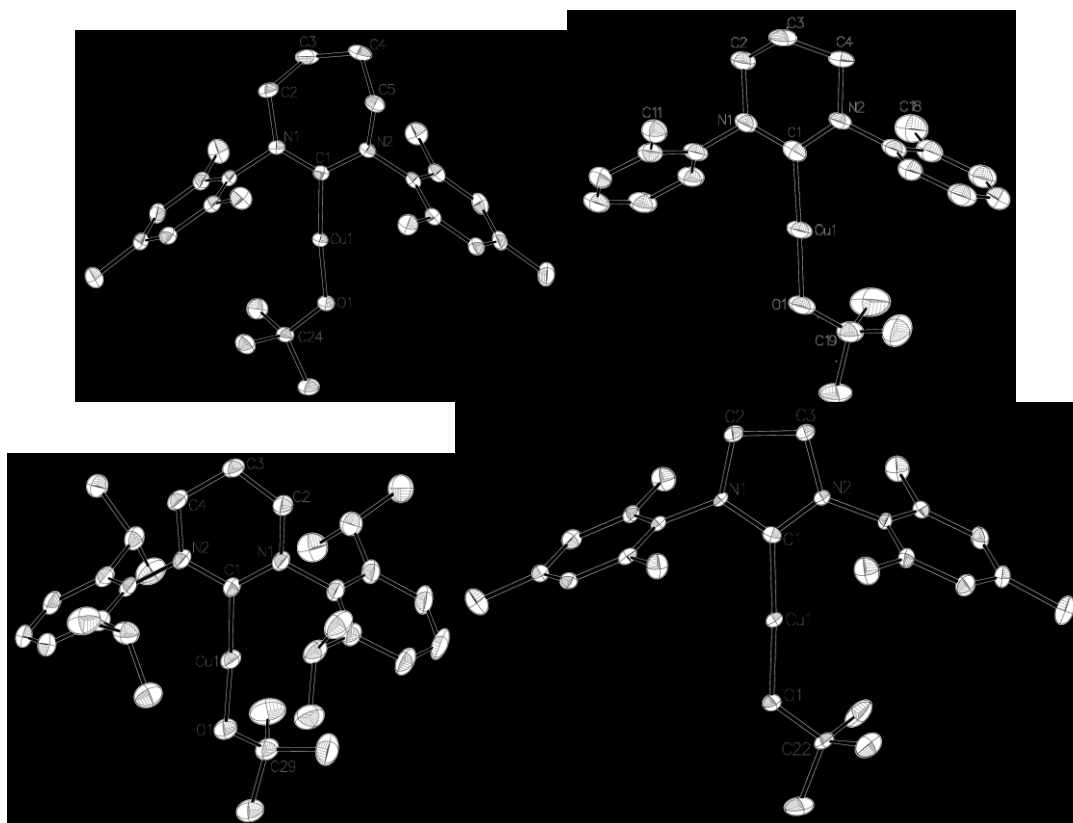


Figure 1. Molecular structures of **III**, **IV**, **VI** and **VII** with ellipsoids shown at 30% probability level. In all cases, hydrogen atoms have been omitted for clarity. Also omitted for **IV** is the minor disordered component of **C11**. For **VI**, only one of the two molecules present in the asymmetric unit is shown.

Table 2. Structural comparison of (NHC)CuO^tBu complexes

Entry	(NHC)CuO ^t Bu	r(Cu-C _{NHC})/Å	r(Cu-O)/Å	N-C-N/°	%V _{bur} ^a
1	I	1.874(2)	1.8016(15)	117.65(18)	44.0 (38.6)
2	III	1.8818(14)	1.8032(10)	119.51(13)	45.4 (40.2)
3	IV	1.881(5)	1.809(3)	117.3(4)	38.1 (33.5)
4	VI	1.885(3)	1.808(2)	116.8(3)	52.0 (46.4)
5	VII	1.844(3)	1.788(2)	107.8(3)	38.2 (32.9)
6	VIII ^{20a}	1.8641(18)	1.8104(13)	103.42(15)	44.6 (39.1)

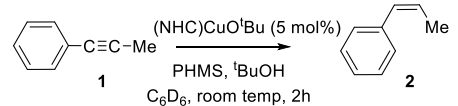
^aValue calculated at M-C_{NHC} distance of 2.0 Å and, in parentheses, 2.28 Å. Parameters used: Bondi radii scaled by 1.17, a 3.5 Å sphere radius, 0.1 exhaustiveness and excluding hydrogens.

both **I** and **V** is ‘just right’ to be effective. Interestingly, studies with the 6-Dipp complex **VI** revealed that this effectively inactive complex could be ‘activated’ to some extent by changing from ^tBuOH, to EtOH or ⁱPrOH, which afforded product yields of 52 and 31% respectively after 2 h (2 mol% loading).²⁹ Activity increased further with ⁱPrOH over a longer reaction time (73% after 48 h), but was unchanged with EtOH. Such variations could reflect the relative stabilities of the alkoxide complexes (6-Dipp)CuOⁱPr and (6-Dipp)CuOEt in their own right,³⁰ their susceptibility to react with silane to yield [(6-Dipp)CuH]₂, as well as the ease of protonolysis of the alkenyl intermediate. The *tert*-butoxide precursors were subsequently tested in the

semi-hydrogenation of PhC≡CPh (**3**), as well as the terminal alkynes, 1-hexyne (**4**) and PhC≡CH (**5**). For **3**, there was a change in order of activity (Scheme 3), with the SiMes complex **VII** now the most active. **I** and **III** were the least effective of the copper precursors, at least in part as a result of the limited solubility of the alkenyl complexes (6/7-Mes)CuC(Ph)=CH(Ph), which deposited as a fine yellow powders during the course of catalytic runs.³¹ The 6-Mes derivative (6-Mes)CuC(Ph)=CH(Ph) (**IX**) was isolated and structurally characterized (ESI). With the terminal alkynes **4** and **5**, no precipitation took place and, as a result, the performance of **I** and **III** improved (Scheme 3). Similar activity was found for all of the copper complexes, with the exception of **IV**, suggesting again that the *N-ortho*-tolyl group is simply too small to be effective.

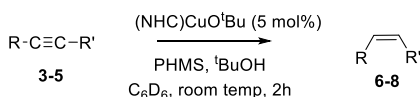
Further studies (Scheme 4) with a low loading of **I** (0.5 mol%) were probed to discriminate the reactivity of different internal alkynes. Replacement of the Me group in **1** by a trimethylsilyl group (**10**) shut down reactivity, whereas a butyl group afforded good product yields with both electron-donating and -withdrawing substituents on the aryl ring (**11-14**). Dialkyl substituted alkynes (**16, 17**) proved reactive in the short (3 h) term, but underwent no further conversions over 24 h. The same behavior was observed upon incorporation of functionalized substituents onto an aryl ring (**15**).³²

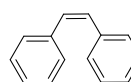
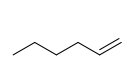
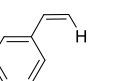
Table 3. Catalytic semi-hydrogenation of PhC≡CMe by (NHC)CuO^tBu^a



Entry	(NHC)CuO ^t Bu	Yield of 2 (%) ^b
1	I	94
2	III	82
3	IV	22
4	V	87
5	VI	Trace
6	VII	85
7	VIII	33
8 ^c	I	86
9 ^c	III	66
10 ^c	VII	76

^aConditions: **1** (0.22 mmol), (NHC)CuO^tBu (5 mol%), 1.1 equiv PHMS, 1.1 equiv ^tBuOH, C₆D₆ (0.5 mL), 25 °C, 2 h. ^bYield of **2** determined by ¹H NMR spectroscopy using 1,3,5-(MeO)₃C₆H₃ as an internal standard. ^c2 mol% (NHC)CuO^tBu.

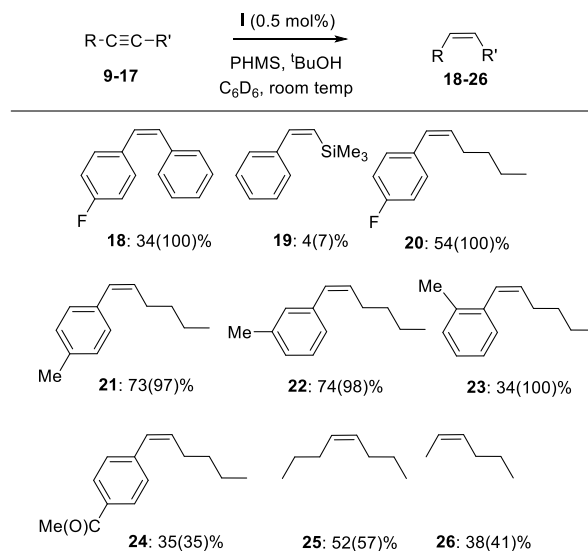


		
I 29%	I 82%	I 60%
III 27%	III 88%	III 54%
IV 45%	IV 5%	IV 38%
V 77%	V 90%	V 59%
VII 99%	VII 90%	VII 59%
VIII 30%		

Scheme 3. Semi-hydrogenation activity of (NHC)CuO^tBu as a function of alkyne. Conditions as given in Table 3.

Catalytic Hydroboration of Alkynes. Given the central role of [(NHC)CuH]₂ in the catalytic semi-hydrogenation, the activity of **I** was tested with other E-H substrates besides silanes (Scheme 1). Although NH₃·BH₃ gave very little conversion of **1**,²² HBPIn proved to be reactive, although to

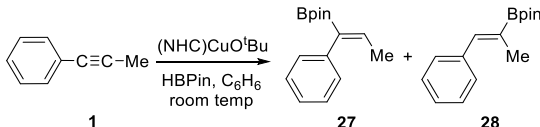
bring about quantitative hydroboration rather than semi-hydrogenation (Table 4).³³ The reaction was highly regioselective, giving a 96:4 ratio of α- and β-vinyboronate products **27** and **28**.^{34,35} The preferential formation of the α-product **27** is consistent with a hydrocupration pathway.³³ Indeed, a low temperature ¹H NMR spectrum following addition of HBPIn to **1** confirmed generation of [(6-Mes)CuH]₂.^{20d,36} As with semihydrogenation, the use of Cu catalysts for hydroboration has received considerable interest. While many of the studies (including some with NHC ligands) have focussed on terminal alkynes,³⁷ there are far fewer examples of Cu-catalyzed hydroboration of more challenging internal alkynes.³⁸



Scheme 4. Substrate scope for semi-hydrogenation with **I** showing conversions after 3 h and (in parentheses) 24 h. Conditions: RC≡CR' (0.22 mmol), **I** (0.5 mol%), 2 equiv PHMS, 2 equiv ^tBuOH, C₆D₆ (0.5 mL), 25 °C. Product yields determined by ¹H NMR spectroscopy using 1,3,5-(MeO)₃C₆H₃ as an internal standard.

Using **1** once again as a test substrate, **I** was shown to retain both high activity and high regioselectivity even at catalyst loadings as low as 0.2 mol% (Table 4, entries 1-3). As expected given the proposed hydrocupration pathway, the 6-Mes alkenyl complex **II** exhibited similarly high activity to **I** (entry 4). In comparison to **I**, both **IV** and **VI** again gave poor yields. In addition, both of the 5-membered ring NHC complexes **VII** and **VIII** now also showed poor activity, while the 7-Mes complex **III** proved to be the most active (entry 5).

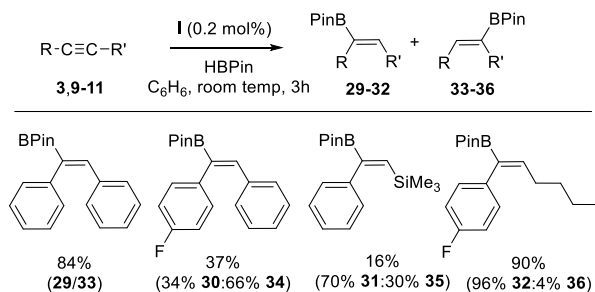
Table 4. (NHC)CuO^tBu catalyzed hydroboration of PhC≡CMe (1) with HBPIn^a



Entry	(NHC)CuO ^t Bu (mol%)	t (h)	Yield of 27+28 (%) ^b	27:28 ratio ^b
1	I (1)	1	97	96:4
2	I (0.5)	2	64	96:4
3	I (0.2)	3	59	96:4
4 ^c	II (0.2)	3	77	96:4
5	III (0.2)	3	89	96:4
6	IV (0.2)	3	2	-
7	VI (0.2)	3	44	63:37
8	VII (0.2)	3	13	96:4
9	VIII (0.2)	3	21	78:22

^aConditions: (NHC)CuO^tBu, 1.1 equiv HBPIn, C₆D₆ (0.5 mL), room temperature. Values are the average of two runs. ^bDetermined by GC using 1,3,5-(MeO)₃C₆H₃ as an internal standard. ^cII = (6-Mes)CuC(Ph)=CH(Me).

A preliminary probe of the activity of **I** towards series of internal alkynes with different substituents (Scheme 5) revealed similarities to the results of semi-hydrogenation e.g. reduced activity of ArC≡CSiMe₃ relative to ArC≡CMe and ArC≡C(butyl).



Scheme 5. Yield and α- (**29-32**) and β- (**33-36**) ratio (in parentheses) of hydroboration products catalyzed by **I**.

A recent DFT study of (NHC)Cu catalyzed alkyne hydroboration³⁹ showed that the rate-determining step in the formation of α-hydroboration products was the initial interaction of the alkyne with (NHC)CuH. When HBPIn was added to (6-Mes)CuC(Ph)=CH(Me) (**II**) at 196 K and the reaction monitored at 222 K by ¹H NMR spectroscopy, [(6-Mes)CuH]₂ had already formed, consistent with the high reactivity of the intermediate formed upon interaction of the borane with the alkenyl complex that makes it too short-lived to detect even at low temperature.

SUMMARY AND CONCLUSIONS

A series of (NHC)CuO^tBu complexes bearing 5-, 6- and 7-membered ring N-heterocyclic carbene ligands have been prepared and investigated as precursors for the semi-hydrogenation and hydroboration of alkynes with silanes and pinacolborane respectively. Both reactions take place with high selectivity to afford (Z)-alkenes and α-hydroboration products respectively through a common hydrocupration pathway.

The enhancement of catalysis by 6- and 7-membered ring NHCs compared to their 5-membered ring counterparts is the major finding of these studies. Moreover, we have also observed that 2,6-dimethylphenyl derived N-substituents on the NHC are optimal for catalysis. Additional studies of (NHC)Cu catalyzed reactions are underway in our group to probe the generality of ring-expanded NHC enhancements in catalysis.

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. Solvents were purified using an MBraun SPS solvent system (hexane, pentane, Et₂O) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene, THF). C₆D₆ and THF-*d*₈ were vacuum transferred from potassium. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 400/500 NMR and Agilent 500 MHz spectrometers and referenced to solvent signals as follows: benzene (¹H, δ 7.16; ¹³C {¹H}, δ 128.0), THF (¹H, δ 3.58; ¹³C {¹H}, δ 67.2; ¹⁹F, externally to CFCl₃ (δ 0.0)). High resolution mass spectrometry was conducted using a MaXis HD quadrupole APCI time-of-flight (APCI-QTOF) mass spectrometer (Bruker) with analyses performed in APCI positive mode. GC-MS analysis was performed on an Agilent 7890A Gas Chromatograph. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK. Literature methods were used for the preparation of Cu(Mes)_n,⁴⁰ (6-Mes)CuO^tBu (**I**),^{19a} 6-*o*-Tol,⁷ 6-Xylyl,⁷ 6-Dipp⁷ and 7-Mes.⁷

(7-Mes)CuO^tBu (III). 7-Mes (141 mg, 0.42 mmol) and Cu(Mes)_n (77 mg, 0.42 mmol) were combined in benzene (5 mL) in a J. Youngs resealable ampule and stirred for 1 h. The resulting solution was concentrated and pentane added to yield a colorless precipitate of (7-Mes)CuMes. The solid was isolated by cannula filtration and dried under vacuum. It was then dissolved in benzene (5 mL) and ^tBuOH (1 mL) added. After stirring for 2 h at room temperature, the solution was reduced to dryness and the residue re-dissolved in a minimum amount of C₆H₆ and then re-precipitated with hexane. This process was repeated twice more, after which the resulting precipitate was isolated as a colorless solid. Crystalline material was obtained from benzene/hexane. Yield 163 mg (93 %). ¹H NMR (500 MHz, C₆D₆): 6.75 (s, 4H, Ar), 3.05 (m, 4H, NCH₂CH₂), 2.24 (s, 12H, CH₃), 2.10 (s, 6H, CH₃), 1.49 (quint, ³J_{HH} = 3.0 Hz, 4H, NCH₂CH₂), 1.18 (s, 9H, C(CH₃)₃). ¹³C {¹H} NMR (126 MHz, C₆D₆): δ 213.3 (s, NCN), 145.3 (s), 137.4 (s), 134.3 (s), 130.3 (s), 68.3 (s), 52.0 (s), 37.0 (s), 25.5 (s), 21.0 (s), 18.7 (s). Anal. calcd for C₂₇H₃₉N₂O₂Cu: C, 68.83; H, 8.34; N, 5.95; found C, 68.96; H, 8.34; N, 5.84.

(6-*o*-Tol)CuO^tBu (IV). Prepared as for **III** by reaction of 6-*o*-Tol (prepared in-situ from [6-*o*-Tol-H]BF₄ (500 mg, 1.42 mmol) and KHMDS (312 mg, 1.56 mmol)) with Cu(Mes)_n (259 mg 1.42 mmol) followed by reaction with ^tBuOH to yield **IV** as an off-white solid. Yield 95 mg (17%). Crystalline material was obtained from benzene/hexane. ¹H NMR (500 MHz, C₆D₆): 7.16-6.94 (m, 8H, Ar), 2.62-2.46 (m, 4H, NCH₂), ³J_{HH} = 2.13 (s, 6H, CH₃), 1.28 (m, 2H, NCH₂CH₂), 1.26 (s, 9H, C(CH₃)₃). ¹³C {¹H} NMR (126 MHz, C₆D₆): 201.9 (s, NCN), 146.9 (s), 134.7 (s)^{*}, 134.6 (s)[‡], 131.8 (s)[‡], 131.7 (s)^{*}, 128.6 (s), 128.4 (s), 128.3 (s), 128.2 (s), 127.7 (s), 68.6 (s), 45.4 (s)^{*}, 45.3 (s)[‡], 37.1 (s), 21.1 (s)^{*}, 21.0 (s)[‡], 18.0 (s)[‡], 17.9 (s)^{*}. More than one set of signal was

apparent (ESI), which we assign to major ([‡]) and minor ([†]) conformers.^{18a} Anal. calcd for C₂₂H₂₉N₂O₂Cu: C, 65.89; H, 7.29; N, 6.99; found C, 65.85; H, 7.27; N, 6.68.

(6-Xylyl)CuO^tBu (V). Prepared as for **III** by reaction of 6-Xylyl (prepared in-situ from [6-Xylyl-H]BF₄ (500 mg, 1.22 mmol) and KHMDS (269 mg, 1.34 mmol)) with Cu(Mes)_n (223 mg, 1.22 mmol), followed by reaction with ^tBuOH. The product was recrystallized from THF/hexane to yield **V** as an off-white solid. Yield 122 mg (23 %) ¹H NMR (500 MHz, C₆D₆): δ 6.99 (t, *J* = 7.7 Hz, 2H, Ar), 6.92 (d, *J* = 7.7 Hz, 4H, Ar), 2.41 (m, 4H, NCH₂), 2.13 (s, 12H, CH₃), 1.28 (m, 2H, NCH₂CH₂), 1.21 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 202.7 (s, NCN), 145.2 (s), 135.1 (s), 129.4 (s), 68.4 (s), 43.6 (s), 37.0 (s), 20.7 (s), 18.1 (s). Anal. calcd for C₂₄H₃₃N₂O₂Cu: C, 67.18; H, 7.75; N, 6.53; found C, 66.78; H, 7.75; N, 6.55.

(6-Dipp)CuO^tBu (VI). Prepared as for **III** by reaction of 6-Dipp (prepared in-situ from [6-Dipp-H]Br (300 mg, 0.62 mmol) and KHMDS (136 mg, 0.68 mmol)) with Cu(Mes)_n (113 mg, 0.62 mmol) followed by reaction with ^tBuOH to afford **VI** as an off-white solid. Crystalline material was obtained from benzene/hexane. Yield 110 mg (33%). NMR data matched those in the literature.^{20d}

(SiMes)CuO^tBu (VII). Prepared as for **III** by reaction of SiMes (made in-situ from [SiMes-H]Cl (563 mg, 1.64 mmol) and KHMDS (330 mg, 1.6 mmol)) with Cu(Mes)_n (300 mg, 1.64 mmol) followed by reaction with ^tBuOH to give **VII** as an off-white solid. Crystalline material was obtained from toluene/pentane at -30°C. Yield 520 mg (72 %). ¹H NMR data matched those in the literature.²⁷ ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 204.9 (s, NCN), 138.3 (s), 136.1 (s), 135.8 (s), 129.9 (s), 68.0 (s), 50.4 (s), 34.4 (s), 21.0 (s), 18.0 (s). The extreme air-sensitivity of **VII** precluded all attempts to measure CHN microanalysis data.

(IPr)CuO^tBu (VIII). Prepared as for **III** by reaction of IPr (400 mg, 1.03 mmol) with Cu(Mes)_n (188 mg, 1.03 mmol) in C₆H₆ (5 mL), followed by reaction with ^tBuOH (1 mL) in C₆H₆ to give **VIII** as an off-white solid. Yield 268 mg (49 %). ¹H NMR data matched those in the literature.⁴¹

Typical Catalytic Procedures. (i) *Alkyne semi-hydrogenation:* To a flame dried J. Youngs NMR tube was added 1-phenylpropyne (0.22 mmol), PMHS (0.24 mmol), 1,3,5-(MeO)₃C₆H₃ (0.022 mmol, internal standard) and 500 μL of 2.2 × 10⁻³ M C₆D₆ stock solution of **1**. Catalysis was initiated by addition of ^tBuOH (0.24 mmol) and reactions followed by ¹H NMR spectroscopy. After the desired reaction time, solutions were filtered through a silica plug (hexane as eluent) and the filtrate reduced to dryness using a flow of N₂. The residue was dissolved in minimal CHCl₃ and washed through a silica plug with hexane to afford alkene products. (ii) *Alkyne hydroboration:* To a flame dried J. Young's resealable NMR tube was added 1-phenylpropyne (66.5 μL, 0.51 mmol), 1,3,5-(MeO)₃C₆H₃ (100 μL from a 0.2 M stock solution in C₆D₆, internal standard) and **1** (400 μL from a 0.025 × 10⁻³ M stock solution in C₆D₆). HBPIn (81.2 μL, 0.560 mmol, 1.1 equiv) was added to initiate the reaction. The solution was shaken at room temperature for 3 h at which point the clear yellow solution was flushed through a silica plug with CH₂Cl₂. The resulting solution was reduced to dryness and analysed by GC.

X-ray crystallography. Data for **III**, **IV** and **VI** were collected using a Rigaku SuperNova instrument and a Cu-Kα source while those for **VIII**, (7-Mes)CuMes (ESI), (6-Xylyl)CuMes (ESI), (6-Dipp)CuMes (ESI) and **IX** (ESI) were obtained using a Rigaku Xcalibur instrument equipped with Mo-Kα radiation. All experiments were conducted at 150 K, with the exception of that for **III**, which was implemented at 210 K. Structures were solved using Olex-2⁴² and refined using SHELXL.⁴³ Refinements were generally straightforward with a few notable exceptions which follow herein.

The data pertaining to **IV** are representative of a small single crystal obtained after cardinal efforts to extract a suitable sample from a batch of very twinned material. The result is an unequivocal testimony to an excellent modern diffractometer and area detector. The methyl group based on C11, in the compound, was seen to be disordered in a 80:20 ratio. C-C distances involving the two components of this atom were restrained to being similar in order to assist convergence. The motif in

VI was seen to consist of two molecules and the proximity of a hydrogen atom attached to the apical NHC carbon (C3) in one moiety is suggestive of a C-H...O interaction with the ^tBu oxygen (O2) in the other molecule [H3A-O2, 2.29 Å; O2-C3, 3.075(4) Å; C3-H3A-O2; 138.0°]. The asymmetric unit in **VII** was seen to contain half of a benzene molecule, proximate to a crystallographic inversion center, in addition to one molecule of the copper complex. Data integration and subsequent refinement of the model take account of the fact that the crystal was a twinned by a 180° rotation, in direct space, about 1 0 0.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1845505-1845512 for **III**, **IV**, **VI**, **VIII**, (7-Mes)CuMes, (6-Xylyl)CuMes, (6-Dipp)CuMes and **IX**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax(+44) 1223 336033), e-mail: deposit@ccdc.cam.ac.uk.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Multinuclear NMR spectra of (RE-NHC)CuMes, **I-VIII**, alkynes, semi-hydrogenation and hydroboration products. X-ray structures of (RE-NHC)CuMes and **IX**.

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Notes

The authors declare no competing financial interest.

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