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

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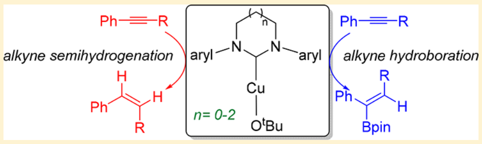
Supporting Information

**ABSTRACT:** A series of two-coordinate copper *tert*-butoxide complexes bearing five-, six-, and seven-membered ring N-heterocyclic carbenes, prepared by protonolysis of (NHC)CuMes with $^t$BuOH, have been used as catalytic precursors in the semihydrogenation of alkynes with silanes/$^t$BuOH and the hydroboration of alkynes with HBPin. Both processes proceed with high regioselectivity and show enhancements with six- and seven-membered ring carbenes.



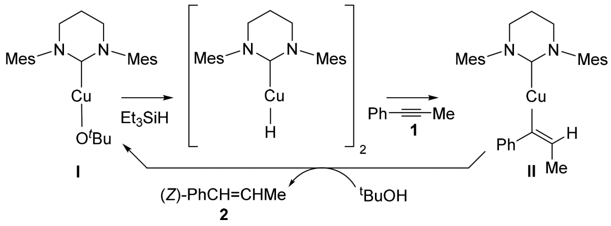
## INTRODUCTION

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 original[1] Arduengo-type unsaturated/saturated five-membered ring N-heterocyclic carbenes (NHCs),[2,3] in particular, cyclic alkyl amino carbenes (CAACs),[4] abnormal/mesoionic carbenes,[5] 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 that of their five-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 toward 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 focused on Pd,[10] together with a smaller number of reports employing Ru,[11] Rh,[12] Ir,[13] Ni,[14] Pt,[15] Cu,[16] and Au.[17] The paucity of work is somewhat surprising given that, in the vast majority of direct comparisons between RE-NHCs (most commonly, six- and seven-membered ring systems) and imidazolidin-2-ylidenes, 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$^t$Bu (**I**) with silanes, we found that the combination of **I** and Et$_3$SiH in the presence of $\mathrm{PhC{\equiv}CMe}$ (**1**) and $^t$BuOH at room temperature led to semihydrogenation of the alkyne to give just the *Z*-isomer of $\mathrm{PhCH{=}CHMe}$ (**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**, Et$_3$SiH, and **1**.

**Scheme 1. Semihydrogenation of $\mathrm{PhC{\equiv}CMe}$ (1) by (6-Mes)CuO$^t$Bu (I)**



Recent years have witnessed a number of reports on homogeneous alkyne semihydrogenation catalysts, with 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] Co,[24] and Ni.[25] Copper complexes[26] 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 five-membered ring NHC precursor (IPr)CuO$^t$Bu,[26a,b] we now describe a catalytic investigation with a series of (NHC)CuO$^t$Bu complexes that

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Organometallics XXXX, XXX, XXX−XXX

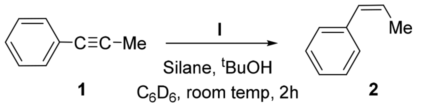
differ both in ring size (five-, six-, and seven-membered ring carbenes) and N-substituents. In the course of investigating the influence of other variables (reductant, substrate, and alcohol) on catalytic activity, we have established that this same range of (NHC)CuO$^t$Bu complexes catalyze the $\alpha$-hydroboration of internal alkynes. In both catalytic processes, the presence of RE-NHC ligands leads to activity higher than that found with the five-membered ring analogues.

## ■ RESULTS AND DISCUSSION

The preliminary catalytic study shown in Scheme 1 employed 5 mol % of **I**, 1.1 equiv of Et$_3$SiH, and 1.1 equiv of $^t$BuOH.[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 increasing 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, Et$_3$SiH has been shown to be a relatively unreactive silane for semireduction reactions.[23b,26a,b] Indeed, upon trialling a range of other trialkyl and mixed aryl/alkyl silanes for the semireduction 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 Semihydrogenation 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 |

[a]Conditions: **1** (0.22 mmol), **I** (1 or 5 mol %), 1.1 equiv of silane, 1.1 equiv of $^t$BuOH, C$_6$D$_6$ (0.5 mL), 25 °C, 2 h. [b]Yield of **2** determined by $^1$H NMR spectroscopy using 1,3,5-(MeO)$_3$C$_6$H$_3$ as an internal standard. [c]Reaction 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$^t$Bu complexes using the method employed previously for **I**, namely, incorporation of free RE-NHC into polynuclear [Cu(Mes)]$_n$ to give (RE-NHC)CuMes (Supporting Information), followed by protonolysis with $^t$BuOH. 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$^t$Bu 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]

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−C$_{\mathrm{NHC}}$/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 (%$V_{\mathrm{bur}}$) using the Samb*V*ca program.[28] There is a fairly steady increase in steric profile of the six-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 that of **III**−**VIII** for the semireduction 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 8−10). 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 and 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 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 $^t$BuOH to EtOH or $^i$PrOH, which afforded product yields of 52 and 31%, respectively, after 2 h (2 mol % loading).[29] Activity increased further with $^i$PrOH 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)CuO$^i$Pr 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 semihydrogenation 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 were deposited as 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 (Supporting Information). 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 conversion over 24 h. The same behavior was observed upon incorporation of functionalized substituents onto an aryl ring (**15**).[32]

**Catalytic Hydroboration of Alkynes.** Given the central role of [(NHC)CuH]$_2$ in the catalytic semihydrogenation, the activity of **I** was tested with other E−H substrates besides

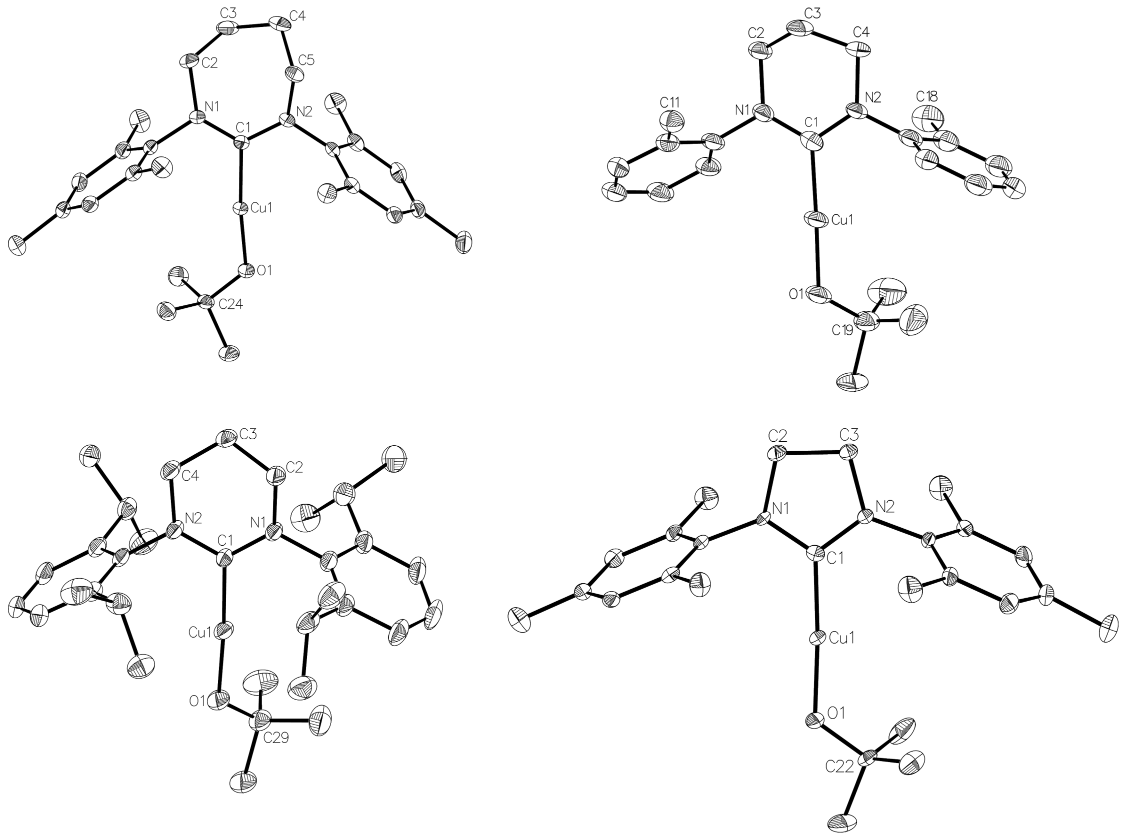


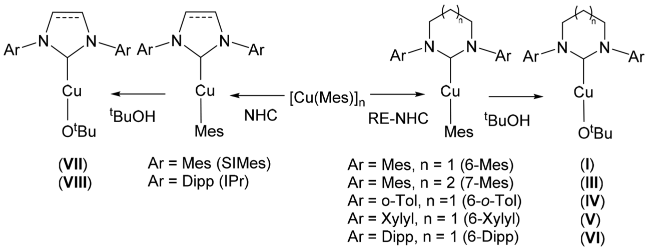
**Figure 1.** Molecular structures of **III**, **IV**, **VI**, and **VII**, with ellipsoids shown at the 30% probability level. In all cases, hydrogen atoms have been omitted for clarity. Also omitted for **IV** is the minor disordered component of C11. For **VI**, only one of the two molecules present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

**Table 2. Structural Comparison of (NHC)CuO$^t$Bu Complexes**

| entry | (NHC)CuO$^t$Bu | $r$(Cu−C$_{\mathrm{NHC}}$) (Å) | $r$(Cu−O) (Å) | N−C−N (deg) | %$V_{\mathrm{bur}}$[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) |

[a] Value calculated at M−C$_{\mathrm{NHC}}$ 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.

**Scheme 2. Synthesis of (NHC)CuO$^t$Bu Complexes**



silanes (Scheme 1). Although $NH_3{\cdot}BH_3$ 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 $\alpha$- and $\beta$-vinylboronate products **27** and **28**.[34,35] The preferential formation of the $\alpha$-product **27** is consistent with a hydrocupration pathway.[33] Indeed, a low-temperature $^1$H NMR spectrum following addition of HBPin to **I** confirmed generation of [(6-Mes)CuH]$_2$.[20d,36] As with semihydrogenation, the use of Cu catalysts for hydroboration has received considerable interest. Although many of the studies (including some with NHC ligands) have focused on terminal alkynes,[37] there are far fewer examples of Cu-catalyzed hydroboration of more challenging internal alkynes.[38]

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 compared to that of **I** (entry 4). In comparison to **I**, both **IV** and **VI** again gave poor yields. In addition, both of the five-membered ring NHC complexes **VII** and **VIII** now also showed poor activity, whereas the 7-Mes complex **III** proved to be the most active (entry 5).

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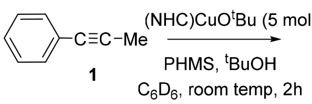
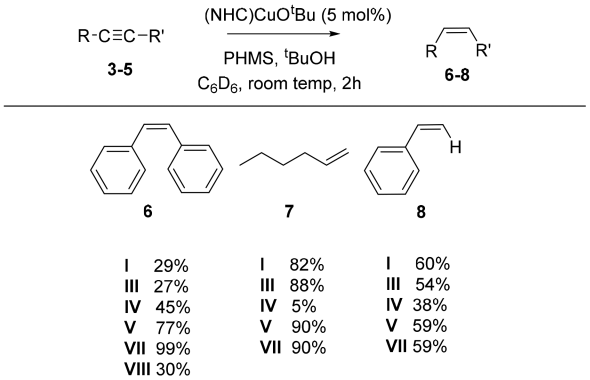
### Table 3. Catalytic Semihydrogenation of PhC≡CMe by (NHC)CuO$^t$Bu[a]



| 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 |

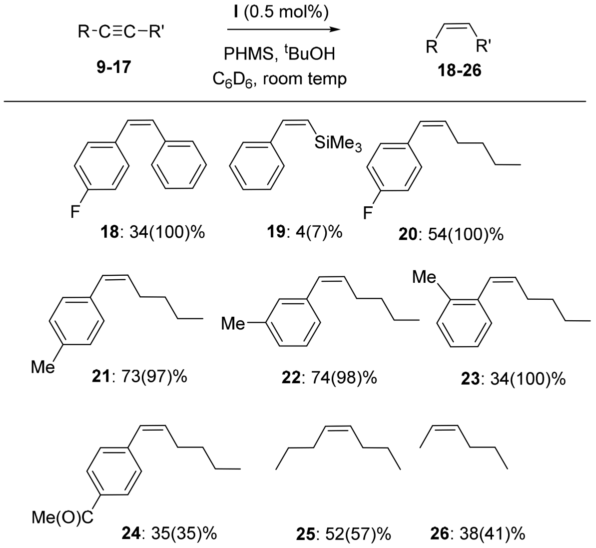
[a] Conditions: **1** (0.22 mmol), (NHC)CuO$^t$Bu (5 mol %), 1.1 equiv of PHMS, 1.1 equiv of $^t$BuOH, $C_6D_6$ (0.5 mL), 25 °C, 2 h. [b] Yield of **2** determined by $^1$H NMR spectroscopy using 1,3,5-$(MeO)_3C_6H_3$ as an internal standard. [c] 2 mol % (NHC)CuO$^t$Bu.

### Scheme 3. Semihydrogenation Activity of (NHC)CuO$^t$Bu as a Function of Alkyne[a]



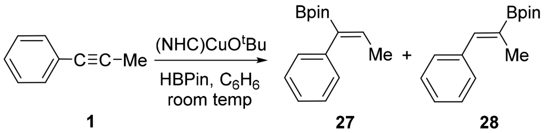
[a] Conditions as given in Table 3.

### Scheme 4. Substrate Scope for Semihydrogenation with I, Showing Conversions after 3 h and (in Parentheses) 24 h[a]



[a] Conditions: RC≡CR′ (0.22 mmol), **I** (0.5 mol %), 2 equiv of PHMS, 2 equiv of $^t$BuOH, $C_6D_6$ (0.5 mL), 25 °C. Product yields determined by $^1$H NMR spectroscopy using 1,3,5-$(MeO)_3C_6H_3$ as an internal standard.

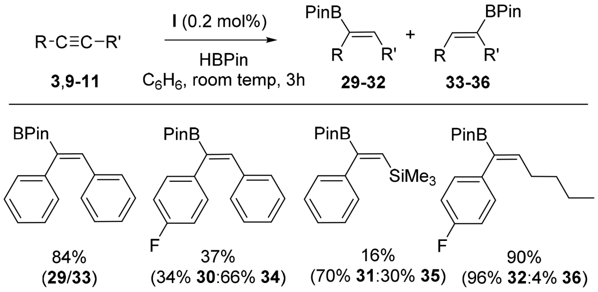
### Table 4. (NHC)CuO$^t$Bu-Catalyzed Hydroboration of PhC≡CMe (1) with HBPin[a]



| 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 |

[a] Conditions: (NHC)CuO$^t$Bu, 1.1 equiv of HBPin, $C_6H_6$ (0.5 mL), room temperature. Values are the average of two runs. [b] Determined by GC using 1,3,5-$(MeO)_3C_6H_3$ as an internal standard. [c] **II** = (6-Mes)CuC(Ph)=CH(Me).

### Scheme 5. Yield and *α* (29−32) and *β* (33−36) Ratio (in Parentheses) of Hydroboration Products Catalyzed by I



A preliminary probe of the activity of **I** toward a series of internal alkynes with different substituents (Scheme 5) revealed similarities to the results of semihydrogenation, such as reduced activity of ArC≡CSiMe$_3$ relative to ArC≡CMe and ArC≡C(butyl).

A recent DFT study of (NHC)Cu-catalyzed alkyne hydroboration[39] 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 $^1$H NMR spectroscopy, $[(6\text{-Mes})CuH]_2$ 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$^t$Bu complexes bearing five-, six-, and seven-membered ring N-heterocyclic carbene ligands have been prepared and investigated as precursors for the semihydrogenation and hydroboration of alkynes with silanes and pinacolborane, respectively. Both reactions take place with high selectivity to afford ($Z$)-alkenes and $\alpha$-hydroboration products, respectively, through a common hydrocupration pathway.

The enhancement of catalysis by six- and seven-membered ring NHCs compared to their five-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, $Et_2O$) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene, THF). $C_6D_6$ and THF-$d_8$ were vacuum transferred from potassium. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 400/500 MHz and Agilent 500 MHz NMR spectrometers and referenced to solvent signals as follows: benzene ($^1$H, $\delta$ 7.16; $^{13}$C{$^1$H}, $\delta$ 128.0), THF ($^1$H, $\delta$ 3.58; $^{13}$C{$^1$H}, $\delta$ 67.2; $^{19}$F, externally to $CFCl_3$ ($\delta$ 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$^t$Bu (I),[19a] 6-$o$-Tol,[7] 6-Xylyl,[7] 6-Dipp,[7] and 7-Mes.[7]

**(7-Mes)CuO$^t$Bu (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 Young resealable ampule and stirred for 1 h. The resulting solution was concentrated, and pentane was added to yield a near 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 $^t$BuOH (1 mL) was added. After being stirred for 2 h at room temperature, the solution was reduced to dryness, and the residue was redissolved in a minimum amount of $C_6H_6$ and then reprecipitated 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%). $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ 6.75 (s, 4H, Ar), 3.05 (m, 4H, $NCH_2CH_2$), 2.24 (s, 12H, $CH_3$), 2.10 (s, 6H, $CH_3$), 1.49 (quint, $^3J_{HH}$ = 3.0 Hz, 4H, $NCH_2CH_2$), 1.18 (s, 9H, $C(CH_3)_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$): $\delta$ 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 $C_{27}H_{39}N_2OCu$: C, 68.83; H, 8.34; N, 5.95. Found: C, 68.96; H, 8.34; N, 5.84.

**(6-$o$-Tol)CuO$^t$Bu (IV).** Compound **IV** was prepared as for **III** by reaction of 6-$o$-Tol (prepared in situ from [6-$o$-Tol·H]$BF_4$ (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 $^t$BuOH to yield **IV** as an off-white solid. Yield 95 mg (17%). Crystalline material was obtained from benzene/hexane. $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ 7.16−6.94 (m, 8H, Ar), 2.62−2.46 (m, 4H, $NCH_2$),$^{‡*}$ 2.13 (s, 6H, $CH_3$), 1.28 (m, 2H, $NCH_2CH_2$), 1.26 (s, 9H, $C(CH_3)_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$): $\delta$ 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 (Supporting Information), which we assign to major ($^‡$) and minor (*) conformers.[18a] Anal. Calcd for $C_{22}H_{29}N_2OCu$: C, 65.89; H, 7.29; N, 6.99. Found: C, 65.85; H, 7.27; N, 6.68.

**(6-Xylyl)CuO$^t$Bu (V).** Compound **V** was prepared as for **III** by reaction of 6-Xylyl (prepared in situ from [6-Xylyl·H]$BF_4$ (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 $^t$BuOH. The product was recrystallized from THF/hexane to yield **V** as an off-white solid. Yield 122 mg (23%). $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ 6.99 (t, $J_{HH}$ = 7.7 Hz, 2H, Ar), 6.92 (d, $J_{HH}$ = 7.7 Hz, 4H, Ar), 2.41 (m, 4H, $NCH_2$), 2.13 (s, 12H, $CH_3$), 1.28 (m, 2H, $NCH_2CH_2$), 1.21 (s, 9H, $C(CH_3)_3$). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$): $\delta$ 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 $C_{24}H_{33}N_2OCu$: C, 67.18; H, 7.75; N, 6.53; Found: C, 66.78; H, 7.75; N, 6.55.

**(6-Dipp)CuO$^t$Bu (VI).** Compound **VI** was 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 $^t$BuOH 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$^t$Bu (VII).** Compound **VII** was 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 $^t$BuOH to give **VII** as an off-white solid. Crystalline material was obtained from toluene/pentane at −30 °C. Yield 520 mg (72%). $^1$H NMR data matched those in the literature.[27] $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$): $\delta$ 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$^t$Bu (VIII).** Compound **VIII** was prepared as for **III** by reaction of IPr (400 mg, 1.03 mmol) with Cu(Mes)$_n$ (188 mg, 1.03 mmol) in $C_6H_6$ (5 mL), followed by reaction with $^t$BuOH (1 mL) in $C_6H_6$ to give **VIII** as an off-white solid. Yield 268 mg (49%). $^1$H NMR data matched those in the literature.[41]

**Typical Catalytic Procedures.** *Alkyne Semihydrogenation:* To a flame-dried J. Youngs NMR tube were added 1-phenylpropyne (0.22 mmol), PMHS (0.24 mmol), 1,3,5-$(MeO)_3C_6H_3$ (0.022 mmol, internal standard), and 500 $\mu$L of 2.2 × $10^{-3}$ M $C_6D_6$ stock solution of **I**. Catalysis was initiated by addition of $^t$BuOH (0.24 mmol) and reactions followed by $^1$H NMR spectroscopy. After the desired reaction time, solutions were filtered through a silica plug (hexane as eluent), and the filtrate was reduced to dryness using a flow of $N_2$. The residue was dissolved in minimal $CHCl_3$ and washed through a silica plug with hexane to afford alkene products.

*Alkyne Hydroboration:* To a flame-dried J. Youngs resealable NMR tube were added 1-phenylpropyne (66.5 $\mu$L, 0.51 mmol), 1,3,5-$(MeO)_3C_6H_3$ (100 $\mu$L from a 0.2 M stock solution in $C_6D_6$, internal standard), and **I** (400 $\mu$L from a 0.025 × $10^{-3}$ M stock solution in $C_6D_6$). HBPin (81.2 $\mu$L, 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 $CH_2Cl_2$. The resulting solution was reduced to dryness and analyzed by GC.

**X-ray Crystallography.** Data for **III**, **IV**, and **VI** were collected using a Rigaku SuperNova instrument and a Cu K$\alpha$ source, and those for **VIII**, (7-Mes)CuMes (Supporting Information), (6-Xylyl)CuMes (Supporting Information), (6-Dipp)CuMes (Supporting Information), and **IX** (Supporting Information) were obtained using a Rigaku Xcalibur instrument equipped with Mo K$\alpha$ 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-2[42] 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 an 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 $^t$Bu oxygen (O2) in the other molecule [H3A−O2, 2.29 Å; O2−C3,

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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.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00467.

> Multinuclear NMR spectra of (RE-NHC)CuMes, **I**–**VIII**, alkynes, semihydrogenation, and hydroboration products; X-ray structures of (RE-NHC)CuMes and **IX** (PDF)

### Accession Codes

CCDC 1845505−1845512 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

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

(2) (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006. (b) *N-Heterocyclic Carbenes in Transition Metal Catalysis* (Topics in Organometallic Chemistry); Glorius, F., Ed.; Springer: Berlin, 2007. (c) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; Díez-González, S., Ed.; RSC: Cambridge, 2011. (d) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Cazin, C. S. J., Ed.; Springer: Dordrecht, 2011. (e) *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2014. (f) Huynh, H. V. *The Organometallic Chemistry of N-Heterocyclic Carbenes*; Wiley-VCH: Weinheim, 2017. (g) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, 2nd ed.; Díez-González, S., Ed.; RSC: Cambridge, 2017.

(3) (a) Hahn, F. E.; Jahnke, M. C. Heterocyclic Carbenes: Synthesis and Coordination Chemistry. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172. (b) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*, 3612−3676. (c) Dröge, T.; Glorius, F. The Measure of All Rings - N-Heterocyclic Carbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940−6952. (d) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination. *Chem. Rev.* **2018**, DOI: 10.1021/acs.chemrev.8b00067.

(4) (a) Rao, B.; Tang, H.; Zeng, X.; Liu, L.; Melaimi, M.; Bertrand, G. Cyclic (Amino)(aryl)carbenes (CAACs) as Strong $\sigma$-Donating and $\pi$-Accepting Ligands for Transition Metals. *Angew. Chem., Int. Ed.* **2015**, *54*, 14915−14919. (b) Soleilhavoup, M.; Bertrand, G. Cyclic (Alkyl)(amino)carbenes (CAACs): Stable Carbenes on the Rise. *Acc. Chem. Res.* **2015**, *48*, 256−266. (c) Melaimi, M.; Jazzar, R.; Soleilhavoup, M.; Bertrand, G. Cyclic (Alkyl)(amino)carbenes (CAACs): Recent Developments. *Angew. Chem., Int. Ed.* **2017**, *56*, 10046−10068.

(5) (a) Albrecht, M. C4-Bound Imidazolylidenes: From Curiosities to High-Impact Carbene Ligands. *Chem. Commun.* **2008**, 3601−3610. (b) Schuster, O.; Yang, L. R.; Raubenheimer, H. G.; Albrecht, M. Beyond Conventional N-Heterocyclic Carbenes: Abnormal, Remote, and Other Classes of NHC Ligands with Reduced Heteroatom Stabilization. *Chem. Rev.* **2009**, *109*, 3445−3478. (c) Nasr, A.; Winkler, A.; Tamm, M. Anionic N-Heterocyclic Carbenes: Synthesis, Coordination Chemistry and Applications in Homogeneous Catalysis. *Coord. Chem. Rev.* **2016**, *316*, 68−124.

(6) (a) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. Sterically Demanding, Bioxazoline-Derived N-Heterocyclic Carbene Ligands with Restricted Flexibility for Catalysis. *J. Am. Chem. Soc.* **2004**, *126*, 15195−15201. (b) Wurtz, S.; Glorius, F. Surveying Sterically Demanding N-Heterocyclic Carbene Ligands with Restricted Flexibility for Palladium-Catalyzed Cross-Coupling Reactions. *Acc. Chem. Res.* **2008**, *41*, 1523−1533.

(7) Iglesias, M.; Beetstra, D. J.; Knight, J. C.; Ooi, L.-L.; Stasch, A.; Coles, S.; Male, L.; Hursthouse, M. B.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. Novel Expanded Ring N-Heterocyclic Carbenes: Free Carbenes, Silver Complexes, And Structures. *Organometallics* **2008**, *27*, 3279−3289.

(8) Li, J.; Shen, W. X.; Li, X. R. Recent Developments of Expanded Ring N-Heterocyclic Carbenes. *Curr. Org. Chem.* **2012**, *16*, 2879−2891.

(9) (a) Poulten, R. C.; Page, M. J.; Algarra, A. G.; Le Roy, J. J.; López, I.; Carter, E.; Llobet, A.; Macgregor, S. A.; Mahon, M. F.; Murphy, D. M.; Murugesu, M.; Whittlesey, M. K. Synthesis, Electronic Structure, and Magnetism of $[Ni(6\text{-}Mes)_2]^+$: A Two-Coordinate Nickel(I) Complex Stabilized by Bulky N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2013**, *135*, 13640−13643. (b) Phillips, N.; Dodson, T.; Tirfoin, R.; Bates, J. I.; Aldridge, S. Expanded-Ring N-Heterocyclic Carbenes for the Stabilization of Highly Electrophilic Gold(I) Cations. *Chem. - Eur. J.* **2014**, *20*, 16721−16731. (c) Ellul, C. E.; Lowe, J. P.; Mahon, M. F.; Raithby, P. R.; Whittlesey, M. K. $[Ru_3(6\text{-}NHC)(CO)_{10}]$: Synthesis, Characterization and Reactivity of Rare 46-Electron Tri-Ruthenium Clusters. *Dalton Trans.* **2018**, *47*, 4518−4523.

(10) (a) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. 1,3-Dialkyl- and 1,3-Diaryl-3,4,5,6-tetrahydropyrimidin-2-ylidene Rhodium(I) and Palladium(II) Complexes: Synthesis, Structure, and Reactivity. *Chem. - Eur. J.* **2004**, *10*, 1256−1266. (b) Rogers, M. M.; Wendlandt, J. E.; Guzei, I. A.; Stahl, S. S. Aerobic Intramolecular Oxidative Amination of Alkenes Catalyzed by NHC-Coordinated Palladium Complexes. *Org. Lett.* **2006**, *8*, 2257−2260. (c) Dunsford, J. J.; Cavell, K. J. Expanded Ring N-Heterocyclic Carbenes: A Comparative Study of Ring Size in Palladium(0) Catalyzed Mizoroki-Heck Coupling. *Dalton Trans.* **2011**, *40*, 9131−9135. (d) Spallek, M. J.; Riedel, D.; Rominger, F.; Hashmi, A. S. K.; Trapp, O. Six-Membered, Chiral NHCs Derived from Camphor: Structure-Reactivity Relationship in Asymmetric Oxindole Synthesis. *Organometallics* **2012**, *31*, 1127−1132. (e) Siemeling, U.; Färber, C.; Bruhn, C.; Fürmeier, S.; Schulz, T.; Kurlemann, M.; Tripp, S. Group 10 Metal Complexes of a Ferrocene-Based N-Heterocyclic Carbene: Syntheses, Structures and Catalytic Applications. *Eur. J. Inorg. Chem.* **2012**, 1413−1422. (f) Hauwert, P.; Dunsford, J. J.; Tromp, D. S.; Weigand, J. J.; Lutz, M.; Cavell, K. J.; Elsevier, C. J. Zerovalent $[Pd(NHC)(Alkene)_{1,2}]$ Complexes Bearing Expanded-Ring N-Heterocyclic Carbene Ligands in Transfer Hydrogenation of Alkynes.

*Organometallics* **2013**, *32*, 131−140. (g) Kolychev, E. L.; Asachenko, A. F.; Dzhevakov, P. B.; Bush, A. A.; Shuntikov, V. V.; Khrustalev, V. N.; Nechaev, M. S. Expanded Ring Diaminocarbene Palladium Complexes: Synthesis, Structure and Suzuki-Miyaura Cross-Coupling of Heteroaryl Chlorides in Water. *Dalton Trans.* **2013**, *42*, 6859−6866. (h) Dunsford, J. J.; Cavell, K. J. P-PEPPSI-Type Expanded Ring N-Heterocyclic Carbene Complexes: Synthesis, Characterization, and Catalytic Activity in Suzuki-Miyaura Cross-Coupling. *Organometallics* **2014**, *33*, 2902−2905. (i) Yang, L.; Zhang, X.; Mao, P.; Xiao, Y.; Bian, H.; Yuan, J.; Mai, W.; Qu, L. NCN Pincer Palladium Complexes Based on 1,3-Dipicolyl-3,4,5,6-Tetrahydropyrimidin-2-ylidenes: Synthesis, Characterization and Catalytic Activities. *RSC Adv.* **2015**, *5*, 25723−25729. (j) Topchiy, M. A.; Dzhevakov, P. B.; Rubina, M. S.; Morozov, O. S.; Asachenko, A. F.; Nechaev, M. S. Solvent-Free Buchwald-Hartwig (Hetero)arylation of Anilines, Diarylamines, and Dialkylamines Mediated by Expanded-Ring N-Heterocyclic Carbene Palladium Complexes. *Eur. J. Org. Chem.* **2016**, 1908−1914. (k) Karaca, E. Ö.; Akkoc, M.; Nawaz Tahir, M.; Arici, C.; Imik, F.; Gürbüz, N.; Yaşar, Y.; Özdemir, I. A Novel Ditopic Ring-Expanded N-Heterocyclic Carbene Ligand-Assisted Suzuki-Miyaura Coupling Reaction in Aqueous Media. *Tetrahedron Lett.* **2017**, *58*, 3529−3532. (l) Gribanov, P. S.; Chesnokov, G. A.; Topchiy, M. A.; Asachenko, A. F.; Nechaev, M. S. A General Method of Suzuki-Miyaura Cross-Coupling for 4- and 5-Halo-1,2,3-Triazoles in Water. *Org. Biomol. Chem.* **2017**, *15*, 9575−9578. (m) Chesnokov, G. A.; Gribanov, P. S.; Topchiy, M. A.; Minaeva, L. I.; Asachenko, A. F.; Nechaev, M. S.; Bermesheva, E. V.; Bermeshev, M. V. Solvent-Free Buchwald-Hartwig Amination with Low Palladium Loadings. *Mendeleev Commun.* **2017**, *27*, 618−620. (n) Zhou, B.-H.; Wu, C.; Chen, W.-X.; Huang, H.-X.; Li, L.-L.; Fan, Li.-M.; Li, J. New $C_2$-Symmetric Six-Membered Carbene Ligands Incorporating Two Hydroxyl Groups for Palladium-Catalyzed Deprotonative-Cross-Coupling Processes (DCCP) of sp$^3$ C-H Bonds in Diarylmethanes. *Tetrahedron Lett.* **2017**, *58*, 4157−4161.

(11) (a) Yang, L.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. Novel Metathesis Catalysts Based on Ruthenium 1,3-Dimesityl-3,4,5,6-tetrahydropyrmidin-2-ylidenes: Synthesis, Structure, Immobilization and Catalytic Activity. *Chem. - Eur. J.* **2004**, *10*, 5761−5770. (b) Yun, J.; Marinez, E. R.; Grubbs, R. H. A New Ruthenium-Based Olefin Metathesis Catalyst Coordinated with 1,3-Dimesityl-1,4,5,6-tetrahydropyrimidin-2-ylidene: Synthesis, X-ray Structure and Reactivity. *Organometallics* **2004**, *23*, 4172−4173. (c) Kumar, P. S.; Wurst, K.; Buchmeiser, M. R. Ru-Alkylidene Metathesis Catalysts Based on 1,3-Dimesityl-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidenes: Synthesis, Structure, and Activity. *Organometallics* **2009**, *28*, 1785−1790.

(12) (a) Imlinger, N.; Mayr, M.; Wang, D.; Wurst, K.; Buchmeiser, M. R. Arylation of Carbonyl Compounds Catalyzed by Rhodium and Iridium 1,3-R$_2$-Tetrahydropyrimidin-2-ylidenes: Structure-Activity Correlations. *Adv. Synth. Catal.* **2004**, *346*, 1836−1843. (b) Binobaid, A.; Iglesias, M.; Beetstra, D. J.; Kariuki, B.; Dervisi, A.; Fallis, I. A.; Cavell, K. J. Expanded Ring and Functionalized Expanded Ring N-Heterocyclic Carbenes as Ligands in Catalysis. *Dalton Trans.* **2009**, 7099−7112. (c) Newman, P. D.; Cavell, K. J.; Hallett, A. J.; Kariuki, B. M. Rhodium and Iridium Complexes of an Asymmetric Bicyclic NHC Bearing Secondary Pyridyl Donors. *Dalton Trans.* **2011**, *40*, 8807−8813. (d) Zhang, J.; Qin, X.; Fu, J.; Wang, X.; Su, X.; Hu, F.; Jiao, J.; Shi, M. Fine-Tuneable 3,4-Dihydroquinazol-2ylidene Carbenes: Synthesis, Rhodium(I) Complexes, and Reactivity. *Organometallics* **2012**, *31*, 8275−8282. (e) Dunsford, J. J.; Tromp, D. S.; Cavell, K. J.; Elsevier, C. J.; Kariuki, B. M. N-Alkyl Functionalized Expanded Ring N-Heterocyclic Carbene Complexes of Rhodium(I) and Iridium(I): Structural Investigations and Preliminary Catalytic Evaluation. *Dalton Trans.* **2013**, *42*, 7318−7329.

(13) Binobaid, A.; Iglesias, M.; Beetstra, D. J.; Dervisi, A.; Fallis, I.; Cavell, K. J. Donor-Functionalized Expanded Ring N-Heterocyclic Carbenes: Highly Effective Ligands in Ir-Catalyzed Transfer Hydrogenation. *Eur. J. Inorg. Chem.* **2010**, 5426−5431.

(14) (a) Davies, C. E. J.; Page, M. J.; Ellul, C. E.; Mahon, M. F.; Whittlesey, M. K. Ni(I) and Ni(II) Ring-Expanded N-Heterocyclic Carbene Complexes: C-H Activation, Indole Formation and Catalytic Hydrodehalogenation. *Chem. Commun.* **2010**, *46*, 5151−5153. (b) Page, M. J.; Lu, W. Y.; Poulten, R. C.; Carter, E.; Algarra, A. G.; Kariuki, B. M.; Macgregor, S. A.; Mahon, M. F.; Cavell, K. J.; Murphy, D. M.; Whittlesey, M. K. Three-Coordinate Nickel(I) Complexes Stabilized by Six, Seven and Eight Membered Ring N-Hetereocyclic Carbenes: Synthesis, EPR/DFT Studies and Catalytic Activity. *Chem. - Eur. J.* **2013**, *19*, 2158−2167. (c) Banach, Ł; Guńka, P. A.; Buchowicz, W. Half-Sandwich Nickel Complexes with Ring-Expanded NHC Ligands - Synthesis, Structure and Catalytic Activity in Kumada-Tamao-Corriu Coupling. *Dalton Trans.* **2016**, *45*, 8688−8692. (d) Sabater, S.; Page, M. J.; Mahon, M. F.; Whittlesey, M. K. Stoichiometric and Catalytic Reactivity of Ni(6-Mes)(PPh$_3$)$_2$. *Organometallics* **2017**, *36*, 1776−1783.

(15) Dunsford, J. J.; Cavell, K. J.; Kariuki, B. M. Expanded Ring N-Heterocyclic Carbene Complexes of Zero Valent Platinum Dvtms (Divinyltetramethyldisiloxane): Highly Efficient Hydrosilylation Catalysts. *J. Organomet. Chem.* **2011**, *696*, 188−194.

(16) (a) Bantu, B.; Wang, D.; Wurst, K.; Buchmeiser, M. R. Coper(I) 1,3-R$_2$-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-propyl): Synthesis. X-ray Structures, Immobilization and Catalytic Activity. *Tetrahedron* **2005**, *61*, 12145−12152. (b) Park, J. K.; Lackey, H. H.; Rexford, M. D.; Kovnir, K.; Shatruk, M.; McQuade, D. T. A Chiral 6-Membered N-Heterocyclic Carbene Copper(I) Complex That Induces High Stereoselectivity. *Org. Lett.* **2010**, *12*, 5008−5011. (c) Park, J. K.; Lackey, H. H.; Ondrusek, B. A.; McQuade, D. T. Stereoconvergent Synthesis of Chiral Allylboronates from an *E/Z* Mixture of Allylic Aryl Ethers Using a 6-NHC-Cu(I) Catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 2410−2413. (d) Park, J. K.; Ondrusek, B. A.; McQuade, D. T. Regioselective Catalytic Hydroboration of Propargylic Species Using Cu(I)-NHC Complexes. *Org. Lett.* **2012**, *14*, 4790−4793. (e) Park, J. K.; McQuade, D. T. Iterative Asymmetric Allylic Substitutions: *syn-* and *anti-*1,2-Diols through Catalyst Control. *Angew. Chem., Int. Ed.* **2012**, *51*, 2717−2721. (f) Park, J. K.; McQuade, D. T. Chiral 6-NHC Ligand and Copper Complex: Properties, Application, and Mechanism. *Synthesis* **2012**, *44*, 1485−1490. (g) Collins, L. R.; Rookes, T. M.; Mahon, M. F.; Riddlestone, I. M.; Whittlesey, M. K. Use of Ring-Expanded Diamino- and Diamidocarbene Ligands in Copper Catalyzed Azide-Alkyne "Click" Reactions. *Organometallics* **2014**, *33*, 5882−5887. (h) Li, J.; Xu, L. Novel $C_2$-Symmetric Six-Membered NHCs for Asymmetric Copper-Catalyzed Conjugate Addition of Grignard Reagents to 3-Methylhexenone. *Tetrahedron* **2015**, *71*, 2858−2862. (i) Chesnokov, G. A.; Topchiy, M. A.; Dzhevakov, P. B.; Gribanov, P. S.; Tukov, A. A.; Khrustalev, V. N.; Asachenko, A. F.; Nechaev, M. S. Eight-Membered-Ring Diaminocarbenes Bearing Naphthalene Moiety in the Backbone: DFT Studies, Synthesis of Amidinium Salts, Generation of Free Carbene, Metal Complexes, and Solvent-Free Copper Catalyzed Azide−Alkyne Cycloaddition (CuAAC) Reaction. *Dalton Trans.* **2017**, *46*, 4331−4345. (j) Sebest, F.; Dunsford, J. J.; Adams, M.; Pivot, J.; Newman, P. D.; Díez-González, S. Ring-Expanded N-Heterocyclic Carbenes for Copper-Mediated Azide-Alkyne Click Cycloaddition Reactions. *ChemCatChem* **2018**, *10*, 2041−2045.

(17) (a) Dunsford, J. J.; Cavell, K. J.; Kariuki, B. M. Gold(I) Complexes Bearing Sterically Imposing, Saturated Six- and Seven-Membered Expanded Ring N-Heterocyclic Carbene Ligands. *Organometallics* **2012**, *31*, 4118−4121. (b) Morozov, O. S.; Lunchev, A. V.; Bush, A. A.; Tukov, A. A.; Asachenko, A. F.; Khrustalev, V. N.; Zalesskiy, S. S.; Ananikov, V. P.; Nechaev, M. S. Expanded-Ring N-Heterocyclic Carbenes Efficiently Stabilize Gold(I) Cations, Leading to High Activity in $\pi$-Acid-Catalyzed Cyclizations. *Chem. - Eur. J.* **2014**, *20*, 6162−6170. (c) Morozov, O. S.; Gribanov, P. S.; Asachenko, A. F.; Dorovatovskii, P. V.; Khrustalev, V. N.; Rybakov, V. B.; Nechaev, M. S. Hydrohydrazination of Arylalkynes Catalyzed by an Expanded Ring N-Heterocyclic (er-NHC) Gold Complex Under Solvent-Free Conditions. *Adv. Synth. Catal.* **2016**, *358*, 1463−1468. (d) Zargaran, P.; Wurm, T.; Zahner, D.; Schiessl, J.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. A Structure-Based Activity Study

of Highly Active Unsymmetrically Substituted NHC Gold(I) Catalysts. *Adv. Synth. Catal.* **2018**, *360*, 106−111.

(18) (a) Poulten, R. C.; López, I.; Llobet, A.; Mahon, M. F.; Whittlesey, M. K. Stereoelectronic Effects in C-H Bond Oxidation Reactions of Ni(I) N-Heterocyclic Carbene Complexes. *Inorg. Chem.* **2014**, *53*, 7160−7169. (b) Pelties, S.; Carter, E.; Folli, A.; Mahon, M. F.; Murphy, D. M.; Whittlesey, M. K.; Wolf, R. Influence of Ring-Expanded N-Heterocyclic Carbenes on the Structures of Half-Sandwich Ni(I) Complexes: An X-Ray, Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR) Study. *Inorg. Chem.* **2016**, *55*, 11006−11017. (c) Blackaby, W. J. M.; Sabater, S.; Poulten, R. C.; Page, M. J.; Folli, A.; Krewald, V.; Mahon, M. F.; Murphy, D. M.; Richards, E.; Whittlesey, M. K. Mono- and Dinuclear Ni(I) Products Formed Upon Bromide Abstraction from the Ni(I) Ring-Expanded NHC Complex [Ni(6-Mes)($PPh_3$)-Br]. *Dalton Trans.* **2018**, *47*, 769−782.

(19) (a) Collins, L. R.; Riddlestone, I. M.; Mahon, M. F.; Whittlesey, M. K. A Comparison of the Stability and Reactivity of Diamido- and Diaminocarbene Copper Alkoxide and Hydride Complexes. *Chem. - Eur. J.* **2015**, *21*, 14075−14084. (b) Collins, L. R.; Rajabi, N. A.; Macgregor, S. A.; Mahon, M. F.; Whittlesey, M. K. Experimental and Comutational Studies of the Copper Borate Complexes [(NHC)Cu-($HBEt_3$)] and [(NHC)Cu($HB(C_6F_5)_3$)]. *Angew. Chem., Int. Ed.* **2016**, *55*, 15539−15543.

(20) As found for all other (NHC)CuH species, (6-Mes)CuH exists as a dimer in solution. (a) Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. Synthesis, Structure, and Alkyne Reactivity of a Dimeric (Carbene) Copper(I) Hydride. *Organometallics* **2004**, *23*, 3369−3371. (b) Frey, G. D.; Donnadieu, B.; Soleilhavoup, M.; Bertrand, G. Synthesis of a Room-Temperature Stable Dimeric Copper(I) Hydride. *Chem. - Asian J.* **2011**, *6*, 402−405. (c) Schmid, S. C.; Van Hoveln, R.; Rigoli, J. W.; Schomaker, J. M. Development of N-Heterocyclic Carbene-Copper Complexes for 1,3-Halogen Migration. *Organometallics* **2015**, *34*, 4164−4173. (d) Jordan, A. J.; Wyss, C. M.; Bacsa, J.; Sadighi, J. P. Synthesis and Reactivity of New Copper(I) Hydride Dimers. *Organometallics* **2016**, *35*, 613−616. (e) Romero, E. A.; Olsen, P. M.; Jazzar, R.; Soleilhavoup, M.; Gembicky, M.; Bertrand, G. Spectroscopic Evidence for a Monomeric Copper(I) Hydride and Crystallographic Characterization of a Monomeric Silver(I) Hydride. *Angew. Chem., Int. Ed.* **2017**, *56*, 4024−4027.

(21) Lindlar, H. Ein Neuer Katalysator für Selektive Hydrierungen. *Helv. Chim. Acta* **1952**, *35*, 446−450.

(22) (a) Brzozowska, A.; Azofra, L. M.; Zubar, V.; Atodiresei, I.; Cavallo, L.; Rueping, M.; El-Sepelgy, O. Highly Chemo- and Stereoselective Transfer Semihydrogenation of Alkynes Catalyzed by a Stable, Well-Defined Manganese(II) Complex. *ACS Catal.* **2018**, *8*, 4103−4109. (b) Zhou, Y.-P.; Mo, Z.; Luecke, M.-P.; Driess, M. Stereoselective Transfer Semi-Hydrogenation of Alkynes to *E*-Olefins with N-Heterocyclic Silylene-Manganese Catalysts. *Chem. - Eur. J.* **2018**, *24*, 4780−4784.

(23) (a) Srimani, D.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. Iron Pincer Complex Catalyzed, Environmentally Benign, *E*-Selective Semihydrogenation of Alkynes. *Angew. Chem., Int. Ed.* **2013**, *52*, 14131−14134. (b) Johnson, C.; Albrecht, M. *Z*-Selective Alkyne Semi-Hydrogenation Catalyzed by Piano-Stool N-Heterocyclic Carbene Iron Complexes. *Catal. Sci. Technol.* **2018**, *8*, 2779−2783.

(24) (a) Fu, S.; Chen, N.-Y.; Liu, X.; Shao, Z.; Luo, S.-P.; Liu, Q. Ligand-Controlled Cobalt-Catalyzed Transfer Hydrogenation of Alkynes: Stereodivergent Synthesis of *Z*- and *E*-Alkenes. *J. Am. Chem. Soc.* **2016**, *138*, 8588−8594. (b) Tokmic, K.; Fout, A. R. Alkyne Semihydrogenation with a Well-Defined Nonclassical Co-$H_2$ Catalyst: A $H_2$ Spin on Isomerization and *E*-Selectivity. *J. Am. Chem. Soc.* **2016**, *138*, 13700−13705. (c) Chen, C.; Huang, Y.; Zhang, Z.; Dong, X.-Q.; Zhang, X. Cobalt-Catalyzed (*Z*)-Selective Semihydrogenation of Alkynes with Molecular Hydrogen. *Chem. Commun.* **2017**, *53*, 4612−4615.

(25) (a) Barrios-Francisco, R.; García, J. Semihydrogenation of Alkynes in the Presence of Ni(0) Catalyst Using Ammonia-Borane and Sodium Borohydride as Hydrogen Sources. *Appl. Catal., A* **2010**, *385*, 108−113. (b) Richmond, E.; Moran, J. Ligand Control of *E*/*Z* Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction. *J. Org. Chem.* **2015**, *80*, 6922−6929.

(26) (a) Semba, K.; Fujihara, T.; Xu, T.; Terao, J.; Tsuji, Y. Copper Catalyzed Highly Selective Semihydrogenation of Non-Polar Carbon-Carbon Multiple Bonds Using a Silane and an Alcohol. *Adv. Synth. Catal.* **2012**, *354*, 1542−1550. (b) Whittaker, A. M.; Lalic, G. Monophasic Catalytic System for the Selective Semireduction of Alkynes. *Org. Lett.* **2013**, *15*, 1112−1115. (c) Cao, H.; Chen, T.; Zhou, Y.; Han, D.; Yin, S.-F.; Han, L.-B. Copper-Catalyzed Selective Semihydrogenation of Terminal Alkynes with Hydrophosphorus Acid. *Adv. Synth. Catal.* **2014**, *356*, 765−769. (d) Wang, G.-H.; Bin, H.-Y.; Sun, M.; Chen, S.-W.; Liu, J.-H.; Zhong, C.-M. Copper-Catalyzed *Z*-Selective Semihydrogenation of Alkynes with Hydrosilane: A Convenient Approach to *cis*-Alkenes. *Tetrahedron* **2014**, *70*, 2175−2179. (e) Semba, K.; Kameyama, R.; Nakao, Y. Copper-Catalyzed Semihydrogenation of Alkynes to *Z*-Alkenes. *Synlett* **2015**, *26*, 318−322. (f) Pape, F.; Thiel, N. O.; Teichert, J. F. *Z*-Selective Copper(I)-Catalyzed Alkyne Semihydrogenation with Tethered Cu-Alkoxide Complexes. *Chem. - Eur. J.* **2015**, *21*, 15934−15938. (g) Wakamatsu, T.; Nagao, K.; Ohmiya, H.; Sawamura, M. Copper-Catalyzed Semihydrogenation of Internal Alkynes with Molecular Hydrogen. *Organometallics* **2016**, *35*, 1354−1357. (h) Suess, A. M.; Lalic, G. Copper-Catalyzed Hydrofunctionalization of Alkynes. *Synlett* **2016**, *27*, 1165−1174.

(27) Dubinina, G. G.; Ogikubo, J.; Vicic, D. A. Structure of Bis(trifluoromethyl)cuprate and Its Role in Trifluoromethylation Reactions. *Organometallics* **2008**, *27*, 6233−6235.

(28) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; ragone, F.; Scarano, V.; Cavallo, L. Samb*V*ca: A Web Application for the Calculation of the Buried Volume of N-Heterocyclic Carbene Ligands. *Eur. J. Inorg. Chem.* **2009**, 1759−1766.

(29) In the case of **I**, the yield of 86% from **1** using $^t$BuOH changed as follows with different alcohols; MeOH (76%), EtOH (87%), $^i$PrOH (89%).

(30) Goj, L. A.; Blue, E. D.; Munro-Leighton, C.; Gunnoe, T. B.; Petersen, J. L. Cleavage of X-H Bonds (X = N, O, or C) by Copper(I) Alkyl Complexes to Form Monomeric Two-Coordinate Copper(I) Systems. *Inorg. Chem.* **2005**, *44*, 8647−8649.

(31) Further support for this argument was provided by the fact that a 69% yield of (*Z*)-stilbene (**6**) was produced after 3 h when **I** was used under more dilute conditions (i.e., 0.5 mol % loading).

(32) For the conversion of **15** to **24**, 1.1 equiv of PHMS and 1.1 equiv of $^t$BuOH were used as product yield decreased with larger amounts of silane and alcohol.

(33) No hydroboration was observed with HBCat.

(34) The $\alpha$- and $\beta$-positions were assigned in accord with those defined in ref 35.

(35) Semba, K.; Fujihara, T.; Terao, J.; Tsuji, Y. Copper-Catalyzed Highly Regio- and Stereoselective Directed Hydroboration of Unsymmetrical Internal Alkynes: Controlling Regioselectivity by Choice of Catalytic Species. *Chem. - Eur. J.* **2012**, *18*, 4179−4184.

(36) Shintani, R.; Nozaki, K. Copper-Catalyzed Hydroboration of Carbon Dioxide. *Organometallics* **2013**, *32*, 2459−2462.

(37) (a) Takahashi, K.; Ishiyama, T.; Miyaura, N. A Borylcopper Species Generated from Bis(pinacolato)diboron and its Additions to $\alpha,\beta$-Unsaturated Carbonyl Compounds and Terminal Alkynes. *J. Organomet. Chem.* **2001**, *625*, 47−53. (b) Lee, Y.; Jang, H.; Hoveyda, A. H. Vicinal Diboronates in High Enantiomeric Purity through Tandem Site-Selective NHC-Cu-Catalyzed Boron-Copper Additions to Terminal Alkynes. *J. Am. Chem. Soc.* **2009**, *131*, 18234−18235. (c) Jang, H.; Zhugralin, A. R.; Lee, Y.; Hoveyda, A. H. Highly Selective Methods for Synthesis of Internal ($\alpha$-) Vinylboronates through Efficient NHC-Cu-Catalyzed Hydroboration of Terminal Alkynes. Utility in Chemical Synthesis and Mechanistic Basis for Selectivity. *J. Am. Chem. Soc.* **2011**, *133*, 7859−7871. (d) Moure, A. L.; Mauleón, P.; Gómez Arrayás, R.; Carretero, J. C. Formal Regiocontrolled Hydroboration of Unbiased Internal Alkynes via Borylation/Allylic Alkylation of Terminal Alkynes. *Org. Lett.* **2013**, *15*,

2054−2057. (e) Yoshida, H.; Takemoto, Y.; Takaki, K. A Masked Diboron in Cu-Catalyzed Borylation Reaction: Highly Regioselective Formal Hydroboration of Alkynes for Synthesis of Branched Alkenylborons. *Chem. Commun.* **2014**, *50*, 8299−8302. (f) Jang, W. J.; Lee, W. L.; Moon, J. H.; Lee, J. Y.; Yun, J. Copper-Catalyzed Trans-Hydroboration of Terminal Aryl Alkynes: Stereodivergent Synthesis of Alkenylboron Compounds. *Org. Lett.* **2016**, *18*, 1390−1393. (g) Bai, T.; Yang, Y.; Han, C. Isolation and Characterization of Hydrocarbon Soluble NHC Copper(I) Phosphoranimide Complex and Catalytic Application for Alkyne Hydroboration Reaction. *Tetrahedron Lett.* **2017**, *58*, 1523−1527.

(38) (a) Jung, H.-Y.; Yun, J. Copper-Catalyzed Double Borylation of Silylacetylenes: Highly Regio- and Stereoselective Synthesis of *Syn*-Vicinal Diboronates. *Org. Lett.* **2012**, *14*, 2606−2609. (b) Bidal, Y. D.; Lazreg, F.; Cazin, C. S. J. Copper-Catalyzed Regioselective Formation of Tri- and Tetrasubstituted Vinylboronates in Air. *ACS Catal.* **2014**, *4*, 1564−1569. (c) Chae, Y. M.; Bae, J. S.; Moon, J. H.; Lee, J. Y.; Yun, J. Copper-Catalyzed Monoborylation of Silylalkynes; Regio- and Stereoselective Synthesis of (*Z*)-*β*-(Borylvinyl)silanes. *Adv. Synth. Catal.* **2014**, *356*, 843−849. (d) Kim, Y. E.; Li, D.; Yun, J. Regioselective Synthesis of Highly Functionalized Alkenylboronates by Cu-Catalyzed Borylation of Propargylic Silylalkynes. *Dalton Trans.* **2015**, *44*, 12091−12093.

(39) Li, Y. Copper(I)-Catalyzed Reaction of Unsymmetrical Alkynes with HB(pin): A Density Functional Theory Study. *J. Phys. Org. Chem.* **2017**, *30*, e3630.

(40) Eriksson, H.; Håkansson, M. Mesitylcopper: Tetrameric and Pentameric. *Organometallics* **1997**, *16*, 4243−4244.

(41) Sakaguchi, H.; Uetake, Y.; Ohashi, M.; Niwa, T.; Ogoshi, S.; Hosoya, T. Copper-Catalyzed Regioselective Monodefluoroborylation of Polyfluoroalkenes en Route to Diverse Fluoroalkenes. *J. Am. Chem. Soc.* **2017**, *139*, 12855−12862.

(42) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.

(43) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *467−473*, A46. Sheldrick, G. M. *SHELXL-97*, a computer program for crystal structure refinement; University of Göttingen, 1997.

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