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# Ring-Expanded N-Heterocyclic Copper(I) Boryl Complexes: The Structures of [(6-Dipp)CuBcat], [(6-Dipp)CuBneop], and [(6-Dipp)CuBhex]

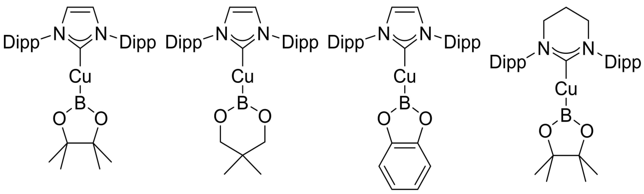
Dawid J. Babula,[a, b] Rex S. C. Charman,[a] Thomas H. Jerome,[a] Thomas M. Horsley Downie,[a] Mary F. Mahon,*[a, c] and David J. Liptrot*[a]

σ-Bond metathesis reactions between [(6-Dipp)CuOtBu] (6-Dipp = :C({Dipp}NCH$_2$)$_2$CH$_2$, Dipp = 2,6-iPr$_2$–C$_6$H$_3$) and three diboranes gave access to three new copper(I) boryl complexes [(6-Dipp)CuBcat], [(6-Dipp)CuBneop], and [(6-Dipp)CuBhex] (cat = 1,2-O$_2$C$_6$H$_4$; neop = (OCH$_2$)$_2$C(CH$_3$)$_2$; hex = OC(CH$_3$)HCH$_2$C-(CH$_3$)$_2$O). Whilst [(6-Dipp)CuBcat] and [(6-Dipp)CuBneop] formed rapidly in toluene, access to [(6-Dipp)CuBhex] required heating to 60 °C for days. The complexes were characterised by single-crystal X-ray crystallography which showed in all three cases that the systems were monomers and distorted-linear at the copper atom. The stability of [(6-Dipp)CuBneop] was found to be comparable to that of [(IPr*)Cu-Bneop] (IPr* = 1,3-bis(2,6-(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene); it persisted in solution for days with no sign of decomposition. [(6-Dipp)CuBhex] is a rare crystallographically characterised example of a complex containing a boryl anion supported by the hexylene glycolato ligand.

## Introduction

The great utility of C–B bonds in selective functionalisation has spurred on significant interest in the installation of boryl groups. Whilst hydroboration is the most widely applied classical route to C–B bonds, the last two decades have seen significant progress in the development of nucleophilic boron fragments which are competent at creating new C–B bonds with carbon electrophiles. Boryl anions bonded to groups 1,[1] 2,[2–7] and a range of transition metals[8–9] are now known. Copper(I) boryls have seen particular interest owing to their exploitation under catalytically relevant conditions.[10] This interest has also resulted in the isolation and structural characterisation of an ever growing range of copper(I) boryls,[11–13] aided by the ease of their synthesis. With a few notable exceptions,[13–15] copper(I) boryl bonds are made via a Cu–O/B–B σ-bond metathesis between a ligated copper alkoxide and a diborane.[16] The N-heterocyclic carbene (NHC) class of ligands has contributed significantly, a consequence of the readily tuneable electronic and steric properties of these ligands. Tuneability proves to be particularly important in the case of species of the form (NHC)CuBX$_2$ (X$_2$ = diolate, diamide, amidolate) whose stability is often limited; many of these compounds readily decompose to copper metal, free carbene and diborane. Nevertheless, significant progress has been made in the isolation and structural characterisation of NHC-copper(I) boryls. Sadighi and co-workers reported [(IPr)CuBpin] in 2005,[17] and a close analogue, [(Cl$_2$IPr)CuBpin], was reported by Tsuji and co-workers in 2013.[18] Variations of substitution at the boron centre have also been reported, with the diol derivatives [(IPr)CuBcat] and [(IPr)CuBneop] having been reported by Kleeberg[19] and Sadighi[20] respectively (Figure 1).

The steric demands of the ancillary ligands both bonded to copper and around the boron centre have been shown to significantly influence the structure of copper boryls. Kleeberg reported that with smaller carbenes, the (NHC)CuBpin (NHC = :C(N{tBu}CH)$_2$, :C(N{iPr}C{CH$_3$})$_2$) systems formed boron bridged



(IPr)CuBpin (IPr)CuBneop (IPr)CuBcat (6-Dipp)CuBpin

**Figure 1.** A selection of previously reported NHC-copper boryls.

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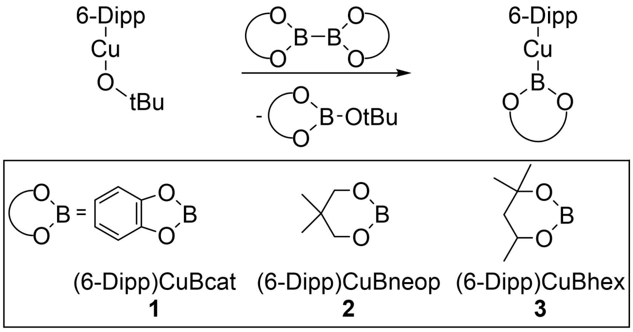
dimers with short Cu···Cu distances.[21] NHC steric demand also affects the stability of the resultant complexes; whilst [(IPr)CuBneop] could be crystallographically characterised, Kleeberg and co-workers found it showed poor stability relative to [(IDipp*)CuBneop] supported by the extremely bulky 5-membered NHC, IDipp* (1,3-bis(2,6-(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene).[22]

We reported that ring-expanded NHCs (RE-NHCs) could also confer additional stability on copper boryl systems; the electronic and steric divergence of 6-Dipp from its five-membered cousin, IPr, allowed us to isolate [(6-Dipp)CuBpin] which persisted in solution for weeks at room temperature. In contrast, [(IPr)CuBpin] decomposes within hours.[23] Diaminoborane derivatives have also been extensively explored by Kleeberg and co-workers who reported a range of NHC-copper diaminoboryls where the varying substitution on both the NHC and boron resulted in either monomeric or, in the case of smaller substituents, dimeric μ-boryl systems.[21,24] Following the significant effects on stability introduced by the relatively minor substitution of the IPr for 6-Dipp ligand in a (NHC)CuBpin complex that we recently reported, we set out to investigate whether the 6-Dipp ligand could support a wider range of dialkoxyboryl fragments at copper.



**Scheme 1.** The synthetic approach used to access compounds **1**–**3**.

## Results and Discussion

We synthesised three new copper boryls, (NHC)Cu-Bcat, -Bneop, and -Bhex (compounds **1**, **2** and **3** respectively) via the reaction of [(6-Dipp)CuOtBu][25] with the appropriate diborane (Scheme 1). In the case of compound **1**, reaction in toluene followed by filtration, rapid removal of solvent *in vacuo* and isolation from the byproduct, tBuOBcat, by washing with hexane was required to evade Lewis acid-mediated decomposition[19] allowing access to **1** in 37% yield. Compound **2** was synthesised in toluene at −40 °C overnight, and diffusion of hexane into the resultant solution afforded **2** in 28% yield. Compound **3** was prepared via the reaction of [(6-Dipp)CuOtBu] and $B_2hex_2$ in toluene for one day at 60 °C. Removal of the solvent *in vacuo* followed by extraction into hexane, filtration, and cooling to ca. −40 °C furnished **3** in 51% yield but contaminated with [(6-Dipp)CuOBhex]. The synthesis of compounds **1**–**3** was generally found to be extremely sensitive to air, resulting in, at times complete, formation of [(6-Dipp)CuOBR$_2$] from ingress of even very small amounts of adventitious air. Crystals suitable for characterisation via SCXRD, characterisations were obtained, for compounds **1** and **2** by vapour diffusion of hexane into a saturated toluene solution, whilst X-ray quality material of **3** was acquired by layering hexane over a saturated toluene solution. The structures of compounds **1**–**3** are shown in Figure 2.

All compounds crystallise as monomeric complexes containing a distorted-linear geometry at the copper centre (C1–Cu1–B1: **1**, 177.27(13); **2**, 171.35(7); **3**, 163.40(7)°). In compounds **1**–**3** the N1–C1–N2 angles pertaining to the carbene carbon atom are similar and close to 117° implying

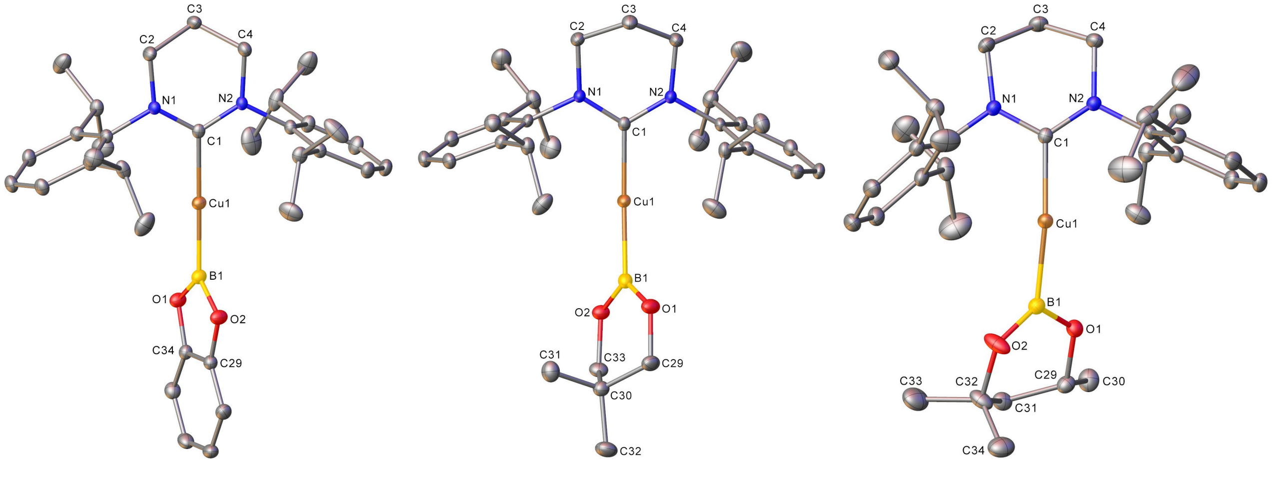


**Figure 2.** Molecular structures of compounds **1**–**3** (left to right). Only one of the two molecules present in each of **1** and **2** are shown. Minor disordered components (**2** and **3**) and all hydrogen atoms have been omitted, for clarity. Ellipsoids are represented at 30% probability. Key bond lengths (Å) and angles (°): **1**; C1–Cu1, 1.947(2); Cu1–B1, 1.974(3); B1–O1, 1.423(4); B1–O2, 1.428(4); C1–Cu1–B1, 177.27(13). **2**; C1–Cu1, 1.9446(15); Cu1–B1, 1.999(2); B1–O1, 1.393(2); B1–O2, 1.386(2); C1–Cu1–B1, 171.35(7); O1–B1–O1, 117.58(16); N1–C1–N2, 116.56(13). **3**: C1–Cu1, 1.9528(15) ; Cu1–B1, 2.0041(18); B1–O1, 1.381(3); B1–O2, 1.364(2); C1–Cu1–B1, 163.40(7); O1–B1–O1, 117.07(16); N1–C1–N2, 117.48(13).

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that the electronic nature of the carbene ligand is essentially unchanged by variation in the substitution at the boron atom. As the steric demand of the diolate ligand on boron increases, the Cu–B bond distances also show a tendency towards increase whilst the Cu–C bond lengths remain essentially unchanged (C1–Cu1: **1**, 1.947(2); **2**, 1.9446(15); **3**, 1.9528(15). Cu1–B1: **1**, 1.974(3); **2**, 1.999(2); **3**, 2.0041(18) Å). This expansion in boryl steric bulk is associated with a compression of the C–Cu–B angle (C1–Cu1–B1: **1**, 177.27(13); **2**, 171.35(7); **3**, 163.40(7)°). Such deviations could reflect the effect of London dispersion force interactions between the 6-Dipp ligand and boryl fragment. Interrogation of the structures, however, does not show a significant number of short intramolecular C–H···H–C contacts.[26] Instead, crystalline packing effects may induce this trend, with larger substituents being more affected by this phenomenon owing to an increased exposed area of the substituents at boron to the solid-state environment. In addition, intramolecular contacts may contribute to this deviation from linearity. For example, in compound **2**, the O and B atoms in the Bneop fragment approach a methyl substituent of one of the flanking Dipp groups in the 6-Dipp ligand.

Compound **3** shows a similar close approach of the O and B atoms to methyl substituents on both flanking rings. The presence of these short contacts may imply that ligand-boryl interactions contribute to the decrease in the C–Cu-B angle, or may instead simply reflect the consequence of forcing this angle away from linearity which must, by its nature, bring the carbene and boryl ligands closer together. Such close approaches are absent in the structure of compound **1**, but equivalent intramolecular contacts are present in our previously reported structure of [(6-Dipp)CuBpin].[23] The metric parameters of the C–Cu-B core of this compound ([(6-Dipp)CuBpin]: C1–Cu1 1.9587(12); Cu1–B1 2.0017(15) Å; C1–Cu1–B1 164.24(6)°) were similar to those of **3** suggesting that the Bhex and Bpin ligands share a similar steric demand despite their divergent O–B–O angles (O1–B1–O2: **3**, 117.58(16); [(6-Dipp)CuBpin], 108.32(11)°).

The structures of IPr analogues of compounds **1** and **2** were reported by Kleeberg and co-workers.[19,22] The metric parameters of **1** (**1**: C1–Cu1, 1.948(3); Cu1–B1, 1.974(3) Å; C1–Cu1–B1, 177.35(13); O1–B1–O1, 106.7(2)°) and its analogue, [(IPr)CuBcat],[19] are similar ([(IPr)CuBcat]: C1–Cu1, 1.9309(15); B1–Cu1, 1.978(2) Å; C1–Cu1–B1, 174.22(7); O1–B1–O2, 106.96(13)°). Similarly, the C–Cu–B core of **2** (**2**: C1–Cu1, 1.9446(15); Cu1–B1, 1.999(2); B1–O1, 1.393(2); B1–O2, 1.386(2) Å; C1–Cu1–B1, 171.35(7); O1–B1–O1, 117.58(16); N1–C1–N2, 116.56(13)°) and the comparative metrics for [(IPr)CuBneop][22] deviated little, but these two compounds showed vast differences in stability. [(IPr)CuBneop] decomposed within hours at room temperature to IPr, neop$_2$B$_2$, copper metal, and a number of more remarkable products including [(IPr)$_6$Cu$_{55}$] and [(IPr)$_{12}$Cu$_{179}$].[22] By contrast, **2** (and in fact **1** and **3** also) persisted in solution for days with limited evidence of decomposition (see Supporting Information), a feature shared with [(IPr*)CuBneop], which also exhibited similar metric parameters ([(IPr*)CuBneop]: C1–Cu1, 1.935(2); B1–Cu1, 2.020(2) Å; B1–Cu1–C1, 171.36(8); O1–B1–O2 117.16(16)°).[22] Collectively, these data imply that, despite the potential effect of NHC ring-expansion on the electronic nature of the carbene carbon and thus the Cu–C bond, the dominant difference between IPr and 6-Dipp in the case of copper(I) boryls is in their steric demand. The 6-membered ring of 6-Dipp forces the flanking aryl groups closer to the copper centre, evidently resulting in a local steric environment similar to that induced by the extremely bulky 2,6-(diphenylmethyl)-4-methylphenyl flanking arenes in IPr*. Although a fully elucidated mechanism of copper boryl decomposition remains elusive, the elegant work of the Kleeberg group, and these results suggest an agglomerative mechanism whereby two or more Cu–B bonds come together to eventually generate Cu(0) and a diborane species. Thus, ligands that protect the copper centre from such associative steps result in stable [(NHC)CuBR$_2$] systems even where the substituents at boron are relatively small.

Compound **3**, on the other hand, constitutes the first example of a copper complex of the Bhex system. Hill and co-workers reported sole other crystallographically characterised Bhex anion, [LMg(DMAP)Bhex] (L = ({Dipp}NC(CH$_3$))$_2$CH; DMAP = 4-dimethylaminopyridine).[4] Despite the significant differences between magnesium and copper that preclude a meaningful comparison of the metric parameters at the metal centre, the O–B–O angles in **3** and LMg(DMAP)Bhex are similar (O–B–O: **3**, 117.07(16); [LMg(DMAP)Bhex], 117.2(4)°).[4]

## Conclusion

Reaction of [(6-Dipp)CuOtBu] with diboranes allows access to three new copper(I) boryls bonded to a ring-expanded NHC. X-ray crystallography on [(6-Dipp)CuBcat] (**1**) and [(6-Dipp)CuBneop] (**2**) show that the metric parameters of the C–Cu–B core are similar compared to their 5-membered NHC (IPr) analogues. Despite these structural similarities, compound **2** is profoundly more stable than [(IPr)CuBneop], an attribute shared with [(IPr*)CuBneop]. Given the trivial synthesis of the 6-Dipp ligand, and the high solubility of the resultant complex, we expect **2** will show utility as a readily accessible, isolable source of the Cu-Bneop fragment. Finally, we synthesised and characterised [(6-Dipp)CuBhex] (**3**), a copper complex of a sparsely reported hexylene glycol ligated boryl. Careful interrogation of the structures of **2** and **3** show an increasing deviation from linearity of copper boryls as the size of the boron substituents increases. This deviation increases access to one face of Cu–B bond and may provide a route to highly reactive [(NHC)CuBR$_2$] systems. We have, thus, shown that the 6-Dipp ligand system has excellent properties to support a range of copper(I) boryl moieties, expanded the range of copper(I) boryls thus known and, in doing so, provided some additional insight into the structure, possible bonding, and potential reactivity of these important synthons.

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## Experimental Section

**General considerations and starting material**: All air and moisture sensitive reactions were performed under argon using standard Schlenk line and glovebox techniques. Toluene, pentane and hexane were obtained commercially and purified using MBraun solvent purification system. $C_6D_6$ was obtained commercially and dried over a potassium mirror before being vacuum transferred into an ampoule and stored in the glovebox under argon. All NMR data was obtained at 298 K on a Bruker Avance II+ instrument for $^1$H (500 MHz), $^{13}$C{$^1$H}, (126 MHz) and $^{11}$B (160 MHz), and a Bruker Avance 400 instrument for $^1$H (400 MHz), $^{13}$C{$^1$H}, (101 MHz) and $^{11}$B (128 MHz). $^1$H and $^{13}$C NMR spectra were referenced using residual $C_6D_6$ solvent resonances. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, U.K. Bis(catecholato)diboron, bis(hexyleneglycolato)diboron and bis(neopentylglycolate)diboron were all purchased from Sigma Aldrich and used without further purification. [(6-Dipp)CuOtBu] was prepared according to literature procedure.[25]

**Synthesis of compound 1, [(6-Dipp)CuBcat]**: In a vial in the glovebox, [(6-Dipp)CuOtBu] (60 mg, 0.11 mmol) and $B_2cat_2$ (26 mg, 0.11 mmol) were dissolved in toluene (0.5 mL) and the resultant beige solution rapidly deposited a solid. The suspension was filtered immediately, and volatiles were removed *in vacuo* depositing a white powder. The powder was washed with hexane (3× 1 mL) yielding the product, [(6-Dipp)CuBcat] (24.4 mg, 41.6 μmol, 37%).

$^1$H NMR (500 MHz, $C_6D_6$) δ 7.15–7.13 (m, 2H, Ar-*H*), 7.08–7.07 (m, 4H, Ar-*H*), 7.00–6.96 (m, 2H, Ar-*H*), 6.65–6.61 (m, 2H,Ar-*H*), 3.09 (hept, *J*=6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 2.70 (t, *J*=5.9 Hz, 4H, (NC*H*$_2$), 1.59 (d, *J*=6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.51–1.46 (m, 2H, NCH$_2$C*H*$_2$), 1.21 (d, *J*=6.9 Hz, 12H, CH(C*H*$_3$)$_2$); $^{13}$C NMR (126 MHz, $C_6D_6$) δ 204.7 (Cu*C*), 149.8 (Ar-*C*), 145.8 (Ar-*C*), 141.3 (Ar-*C*), 129.4 (Ar-*C*), 124.7 (Ar-*C*), 120.4 (Ar-*C*), 111.5 (Ar-*C*), 46.0 (N*C*H$_2$), 29.0 (*C*H(CH$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 20.4 (NCH$_2$*C*H$_2$); $^{11}$B NMR (160 MHz, $C_6D_6$) δ 43.3 (FWHM=175 Hz); Analysis calculated for [(6-Dipp)CuBcat] (MW=588.10 g/mol): C, 69.56; H, 7.55; N, 4.77. Found: C, 69.04; H, 7.46; N, 4.52.[27]

**Synthesis of compound 2, [(6-Dipp)CuBneop]**: In a vial in the glovebox, [(6-Dipp)CuOtBu] (100 mg, 185 μmol) was dissolved in toluene (2 mL) forming a pale yellow solution. The solution was cooled to −40 °C for 1 h and $B_2neop_2$ (41.7 mg, 185 μmol) was added. The reaction mixture was kept at −40 °C for 16 h. After 16 h, hexane was allowed to diffuse into the reaction mixture overnight at room temperature. Colourless crystals precipitated out of and were washed with hexane (3×1 mL) yielding the product, [(6-Dipp)CuBneop] (30.5 mg, 52.5 μmol, 28%).

$^1$H NMR (400 MHz, $C_6D_6$) δ 7.21–7.18 (m, 2H, Ar-*H*), 7.12–7.10 (m, 4H, Ar-*H*), 3.19 (s, 4H, OC*H*$_2$), 3.13 (hept, *J*=6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 2.72–2.69 (m, 4H, NC*H*$_2$), 1.65 (d, *J*=6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.52–1.47 (m, 2H, NCH$_2$C*H*$_2$), 1.23 (d, *J*=6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.59 (s, 6H, C(C*H*$_3$)$_2$); $^{13}$C NMR (126 MHz, $C_6D_6$) δ 206.1 (Cu*C*), 145.9 (Ar-*C*), 141.6 (Ar-*C*), 129.0 (Ar-*C*), 124.5 (Ar-*C*), 70.0 (O*C*H$_2$), 46.1 (N*C*H$_2$), 31.5 (*C*(CH$_3$)$_2$) 29.0 (*C*H(CH$_3$)$_2$, 25.4 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$, 22.9 (C(*C*H$_3$)$_2$, 20.6 (NCH$_2$*C*H$_2$); $^{11}$B NMR (128 MHz, $C_6D_6$) δ 40.9 (FWHM=1037 Hz). Adventitious oxygen precluded EA of **2**, instead analysis calculated for [(6-Dipp)CuOBneop)] (MW=597.13 g/mol): C, 66.38; H, 8.44; N, 4.69. Found: C, 65.98; H, 8.05; N, 4.56.[27]

**Synthesis of compound 3, [(6-Dipp)CuBhex]**: In an ampoule in the glove box, [(6-Dipp)CuOtBu] (100 mg, 185 μmol) and $B_2hex_2$ (46.9 mg, 185 μmol) were dissolved in toluene (2 mL) forming a light yellow solution. The reaction mixture was stirred at 60 °C for 16 h at which point the solution turned dark red and copper deposition was observed at the bottom of the ampoule. The solution was filtered, and volatiles were removed *in vacuo* depositing a red solid. The red solid was washed with hexane (3× 1 mL) yielding the product, [(6-Dipp)CuBhex] (56.9 mg, 95.6 μmol, 51%) with a 26% impurity of (6-Dipp)CuOBhex. Recrystallisation in the minimum hexane at −40 °C improved the purity, [(6-Dipp)CuBhex] (5.7 mg, 9.6 μmol, 5%) with a 7% impurity of (6-Dipp)CuOBhex. Single crystals were obtained by layering a saturated solution in toluene with pentane at −40 °C. During some reactions to synthesise **3**, adventitious oxygen instead provided [(6-Dipp)CuOBhex] which was fully characterised (see Supporting Information).

$^1$H NMR (400 MHz, $C_6D_6$) δ 7.18–7.14 (m, 10H, Ar-*H* and residual benzene solvent), 7.11–7.08 (m, 4H, Ar-*H*), 3.75–3.66 (m, 1H, OC*H*(CH$_3$)), 3.16–3.06 (m, 4H, C*H*(CH$_3$)$_2$), 2.72–2.69 (m, 4H, NC*H*$_2$), 1.62 (d, *J*=6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.54–1.48 (m, 3H, NCH$_2$C*H*$_2$ and impurity of (6-Dipp)CuOBHex), 1.24–1.22 (m, 14H, (CH(C*H*$_3$)$_2$) and (C(CH$_3$)$_2$C*H*$_2$), 1.08 (s, 3H, OC(C*H*$_3$)$_2$), 1.03 (s, 3H, OC(C*H*$_3$)$_2$), 1.01 (d, *J*=6.2 Hz, 3H, (OCH(C*H*$_3$)); $^{13}$C NMR (126 MHz, $C_6D_6$) δ 206.2 (Cu*C*), 145.8 (Ar-*C*), 141.6 (Ar-*C*), 128.9 (Ar-*C*), 124.5 (Ar-*C*), 66.4 (O*C*(CH$_3$)$_2$), 60.9 (O*C*H(CH$_3$)), 47.5 (CH(CH$_3$)*C*H$_2$), 46.1 (N*C*H$_2$), 32.9 (OC(*C*H$_3$)$_2$), 29.6 (OC(*C*H$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)), 24.5 (OCH(*C*H$_3$)), 20.6 (NCH$_2$*C*H$_2$); $^{11}$B NMR (128 MHz, $C_6D_6$) δ 40.9 (FWHM=659 Hz). Excess ligand could not be obviated in repeated elemental analyses, so analysis calculated for [(6-Dipp)CuBhex]·[6-Dipp]. (MW=999.80 g/mol): C, 74.48; H, 9.28; N, 5.60. Found: C, 73.26; H, 8.94; N, 5.25.[27]

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** boron · boryl anion · carbene ligands · copper · ring-expanded N-heterocyclic carbene

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