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Copper(I) complexes of *N*-alkyl-substituted *N*-Heterocyclic carbenes☆

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ABSTRACT

We report herein the synthetic routes to and spectroscopic and structural characterization of a variety of copper complexes bearing small alkyl-substituted *N*-heterocyclic carbene (NHC) ligands. Complexes of the type [Cu(NHC)(X)] and $[Cu(NHC)_2(X)]$ (X = Cl) were readily synthesized by reaction of Cu(I)Cl with a variety of the carbenes. The molecular structures of the [Cu(NHC)(X)] complexes all show two-coordinate Cu(I) atoms in nearly linear arrangements with $C_{(NHC)}$—Cu—Cl angles very close to 180°. Utilizing the smallest alkyl carbene, Me_2Im (= 1,3-di-methyl-imidazolin-2-ylidene), the compound adopts an ionic structure featuring a $[Cu(Me_2Im)_2]^+$ cation and a $[CuCl_2]^-$ anion. The reaction of copper(I) chloride with two equivalents of some NHCs (NHC = Me_2Im, $^iPr_2Im$, $^iPr_2ImMe_2$ [= 1,3-di-*iso*-propyl-4,5-dimethylimidazolin-2-ylidene]) afforded complexes of the type $[Cu(NHC)_2(X)]$, which show a trigonal planar geometry with a propeller-like arrangement of the NHC ligands. Furthermore, complexes of the type [Cu(NHC)(OR)] (OR = OAc, OtBu, acac [= acetylacetonato], DBM [= dibenzoylmethanato]), were synthesized starting from $[Cu(^iPr_2Im)(X)]$ ($^iPr_2Im$ = 1,3-di-*iso*-propylimidazolin-2-ylidene), and characterized. The molecular structure of [Cu(NHC)(DBM)] clearly reveals the typical bidentate binding mode of the DBM ligand. The compounds reported represent very useful starting points for the investigation of NHC copper(I) chemistry.

1. Introduction

In 2009, we published a facile route for the synthesis of aryl boronates from aryl halides using a copper(I) catalyst and diboron(4) reagents as the boron source [1]. The borylation system consists of 1.5 equivalents of B_2pin_2 and potassium *tert*-butoxide as a base, the substrate (aryl iodides or bromides), 10 mol% of copper(I) iodide, and 13 mol% of $^nBu_3P$. The reaction was carried out over 17 h at room temperature to obtain isolated yields that were good to almost quantitative for a wide variety of substrates. At a temperature of 60 °C, the system gave 100% conversion within 2.5 h with catalyst loadings as low as 3 mol%. It was also possible to use bis(neopentylglycolato)diboron as the boron reagent to form the corresponding boronates. Based on the stoichiometric reaction of a structurally characterized NHC-copper(I) boryl complex [2] (NHC = *N*-Heterocyclic Carbene) with an aryl iodide, and other stoichiometric and well-known/studied copper(I) reactions, a catalytic cycle was proposed. These mechanistic investigations were undertaken using the corresponding NHC complexes, which were less reactive than the phosphine analogues, and the proposed mechanism was supported by DFT calculations [1]. The potential of this system was also demonstrated for the borylation of primary and secondary alkyl halides (iodides, bromides and chlorides) and pseudohalides [3]. Many synthetically important functional groups including alcohol, ester, cyano, ketone, ether, olefin, amide, ketal, and silyl ether groups were well tolerated with moderate to very good yields. Furthermore, good reactivity was observed when arene- and heterocycle-containing compounds were used as substrates. This methodology made it possible to obtain many desired organoboronates in a robust synthesis with high functional group tolerance and without production of any toxic metal residues.

Similarly, carbon-carbon bond forming cross-coupling reactions of organocopper reagents with alkyl halides are, next to Grignard or organolithium reagents, among the most important in organic synthesis [4]. However, one major drawback was low atom efficiency (for example, only one alkyl group could be transferred from

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☆ Dedicated to Professor Richard J. Puddephatt on the occasion of his 75th birthday.

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a cuprate), which led to the development of copper-catalyzed alkylation reactions of Grignard reagents [5]. These catalytic reactions are much easier to carry out and are significantly less expensive. Recent research has focused on replacing the Grignard reagents with organoboron reagents, which have a higher functional group tolerance, are commercially available and easier to synthesize, store and purify [6]. As copper-catalyzed borylation [7–9] and cross-coupling are useful reactions we decided to explore the synthesis of a variety of NHC-stabilized copper(I) complexes, such as chlorides, alkoxides, alkyls, aryls, in some detail, especially for *N*-alkyl-substituted NHCs, with which we have much experience in the chemistry of iron [10], cobalt [11] and nickel [12] complexes.

2. Results and discussion

We report herein mainly on the synthesis and characterization of a number of complexes of the type [Cu(NHC)(X)] and [Cu(NHC)(OR)]. Such complexes are valuable starting materials for the investigation of NHC copper(I) chemistry, due to their ease of synthesis using various routes and the stability of (some of) the complexes to air, water and light [13]. The broad scope and effectiveness of NHC-copper(I) complexes of the type [Cu(NHC)(halide)] in catalytic transformations has been demonstrated on several occasions [14]. One of the most common routes to Lewis base-stabilized copper(I) chlorides is the reaction of CuX with the Lewis-base, often using an *in situ* formed NHC [13]. However, there are several disadvantages to this route, for example the use of strong bases *in situ* and the need for exact stoichiometry to prevent the formation of undesired side products such as [Cu(I)(base)] or [Cu(NHC)(base)]. A more convenient way to synthesize [Cu(NHC)(halide)] complexes is the reaction of copper(I) oxide with the corresponding halide salt of the imidazolium precursor [15]. This route is effective for many NHCs, often results in good to excellent yields, and it can be performed in technical grade solvents such as CH_2Cl_2, toluene or even water.

The syntheses of [Cu(NHC)(X)] complexes we were investigating started with isolated small N-alkyl-substituted NHCs and copper(I) chloride. The equimolar reaction, at low temperature, of free carbenes with copper(I) chloride yielded solids which are sensitive to both light and air (Scheme 1).

The reaction of copper(I) chloride with 1,3-di-*tert*-butylimidazolin-2-ylidene ($^t\mathrm{Bu_2Im}$), 1,3-di-*iso*-propylimidazolin-2-ylidene ($^i\mathrm{Pr_2Im}$), 1,3-di-*iso*-propyl-4,5-dimethylimidazolin-2-ylidene ($^i\mathrm{Pr_2ImMe_2}$) and 1,3,4,5-tetramethylimidazolin-2-ylidene ($\mathrm{Me_4Im}$) provided the corresponding mono NHC-stabilized [Cu(NHC)(Cl)] complexes **1**–**4** in 66%–87% yield on a gram-scale at low temperature. In the case of complexes **1** and **2**, the NMR data match those previously reported by the groups of Nolan and Chang [16], who provided access to these complexes by different routes. Chang *et al.* prepared [Cu($^i\mathrm{Pr_2Im}$)(Cl)] **2** from the reaction of the imidazolium salt with an excess of base ($\mathrm{NaO}^t\mathrm{Bu}$) at ambient temperature generating the free carbene *in situ*. This pathway suffers from low yields of only 23%, possibly due to the formation of the corresponding copper alkoxides in the presence of an excess of base. Furthermore, they also characterized **2** by X-ray diffraction (which provided data similar to ours), but did not confirm the purity by elemental analysis [16b]. Complexes **3** and **4** are novel compounds and the NMR data obtained for the NHC ligands are in the expected range. The characteristic carbene-carbon atom shifts are all within 5.2 ppm of one another in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra (**1**: 174.1 ppm, **2**: 174.5 ppm, **3**: 170.0 ppm, **4**: 175.2 ppm). Complexes **1**–**4** were fully characterized and the molecular structures of these complexes are shown in Fig. 1.

Compounds **1**–**4** reveal two-coordinate Cu(I) atoms in nearly linear arrangements with $\mathrm{C_{(NHC)}}$–Cu–Cl angles very close to 180°. Only compound **2** differs significantly from linearity with an angle of 170.95(5)°, which is in accordance with the literature [16b]. The $\mathrm{C_{(NHC)}}$–Cu and the Cu–Cl bond lengths lie in the range of 1.88 to

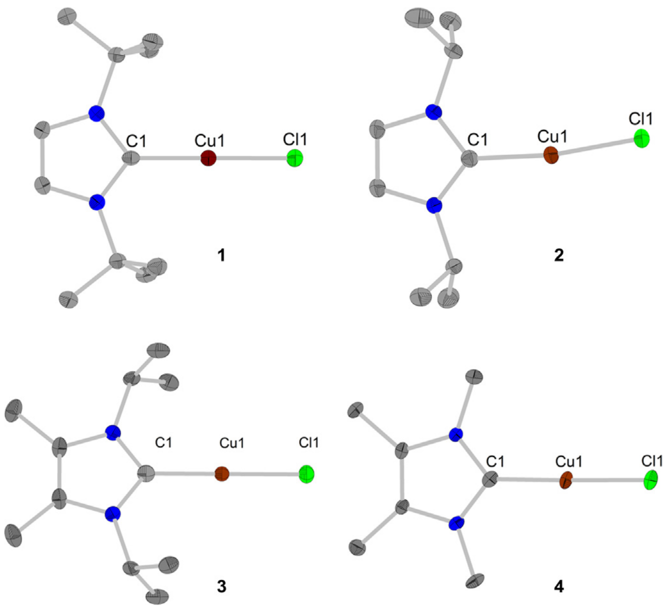
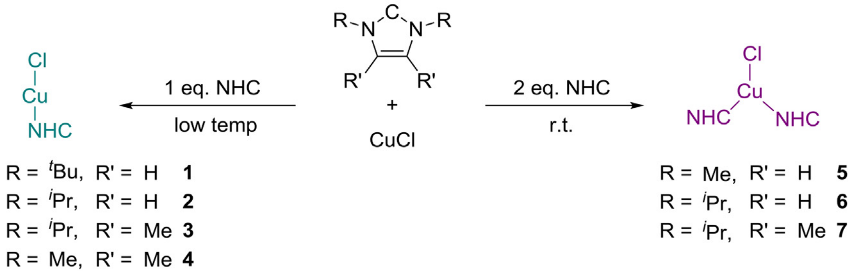


Fig. 1. Element (color): carbon (grey), nitrogen (blue), copper (maroon), chlorine (green). Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability. Top left: Molecular structure of [Cu($^t\mathrm{Bu_2Im}$)(Cl)] **1**. Selected bond lengths (Å) and angles (deg): Cu–C1 1.879(2), Cu–Cl 2.0937(7), C1–Cu–Cl 180.00(0)°. Top right: Molecular structure of [Cu($^i\mathrm{Pr_2Im}$)(Cl)] **2**. Selected bond lengths (Å) and angles (deg): Cu–C1 1.8781(14), Cu–Cl 2.1055(4), C1–Cu–Cl 170.95(5)°. Bottom left: Molecular structure of [Cu($^i\mathrm{Pr_2ImMe_2}$)(Cl)] **3**. Selected bond lengths (Å) and angles (deg): Cu1–C1 1.886(3), Cu1–Cl 2.1056(9), C1–Cu1–Cl1 180.00(0)°. Bottom right: Molecular structure of [Cu($\mathrm{Me_4Im}$)(Cl)] **4**. Selected bond lengths (Å) and angles (deg): Cu1–C1 1.878(2), Cu1–Cl1 2.1081(5), C1–Cu1–Cl1 177.93(7)°. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Scheme 1. Synthesis of [Cu(NHC)(Cl)] and [$\mathrm{Cu(NHC)_2(Cl)}$] complexes.

1.89 Å and 2.09 to 2.11 Å, respectively. In general, complexes **1**–**4** show smaller $C_{(NHC)}$–Cu distances compared to [Cu(NHC)(Cl)] complexes with sterically more demanding NHCs, ([Cu(Cy_2Im)(Cl)] $C_{(NHC)}$–Cu 2.114(11) Å, Cu–Cl 2.136(4) Å; [Cu(Mes_2Im)(Cl)] $C_{(NHC)}$–Cu 1.956(10) Å, Cu–Cl 2.091(2) Å; [Cu($Dipp_2$Im)(Cl)] $C_{(NHC)}$–Cu 1.953(8) Å, Cu–Cl 2.089(3) Å) [14f,16,17], while the Cu–Cl distances are in the same range (mean $C_{(NHC)}$–Cu 1.880 Å, Cu–Cl 2.1032 Å).

From the reaction of copper(I) chloride with two equivalents of 1,3-di-methylimidazolin-2-ylidene (Me_2Im), $^iPr_2$Im and $^iPr_2ImMe_2$ at room temperature the bis–NHC–stabilized [Cu(NHC)$_2$(Cl)] complexes **5**–**7** were obtained in 56%–70% yield. In addition to NMR spectroscopy and HRMS, complex **6** was further characterized by X-ray diffraction (Fig. 2), whereas for complex **7** only crystals of poor quality were obtained which led to a preliminary X-ray structure (see SI Fig. S26). In the $^{13}C\{^1H\}$ NMR spectra the carbene-carbon atoms of **5**–**7** were detected between 183.8 and 184.7 ppm and thus show a downfield shift compared to their mono–NHC–stabilized analogues.

The bis–NHC–stabilized complex **6** adopts a distorted trigonal planar geometry with the sum of the angles around the Cu-center being exactly 360°. The carbene heterocycles are twisted out of the trigonal coordination plane, which results in a propeller-like structure. The observed geometry is consistent with that of a bis–NHC–copper iodide complex reported by Albrecht and co-workers [18]. The Cu-halide bond in **6** (Cu–Cl 2.3668(11) Å) is considerably shorter than that in the analogous Cu-iodide complex (Cu–I 2.7623(7) Å) [18].

The 1:1 reaction of the smallest alkyl carbene, Me_2Im, with copper(I) chloride yielded **8** as a grey powder in 85% yield. Layering a saturated THF solution of compound **8** with hexane at 6 °C yielded crystals suitable for X-ray diffraction. The molecular structure is shown in Fig. 3. The molecular structure of **8** reveals that this complex is an ionic compound featuring a $[Cu(Me_2Im)_2]^+$ cation and a $[CuCl_2]^-$ anion. In addition to Cu1 and Cu2 sitting on two crystallographic inversion centers, both lie, together with C1 and Cl1, respectively, on a crystallographic twofold axis and on a mirror plane. X-ray powder diffraction (see SI Fig. S25) confirms this ionic structure $[Cu(Me_2Im)_2]^+[CuCl_2]^-$ for the bulk material. The ^{1}H NMR spectrum of **8** in solution displays one singlet for six protons with a chemical shift of 2.70 ppm for the methyl groups and one singlet with a shift of 5.52 ppm for the protons of the backbone of the NHC ligand. The $^{13}C\{^1H\}$ NMR spectrum shows three signals at 38.5 ppm, 123.1 ppm and 177.8 ppm for the NHC ligand. Thus, the NMR spectrum recorded in solution gives no evidence for a possible equilibrium in solution with a second species such as the neutral NHC copper chloride [Cu(Me_2Im)(Cl)].

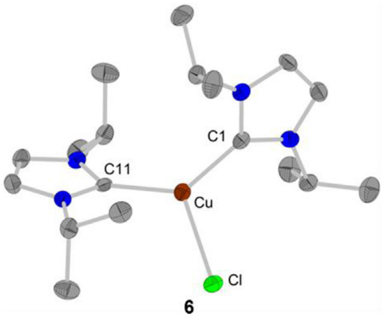


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Fig. 2. Molecular structure of [Cu($^iPr_2Im)_2$(Cl)] **6**. Element (color): carbon (grey), nitrogen (blue), copper (maroon), chlorine (green). Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Cu–C1 1.921(4), Cu–C11 1.938(4), Cu–Cl 2.3668(11), C1–Cu–Cl 112.6(1), C11–Cu–Cl 113.9(1), C1–Cu–C11 133.5(2). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

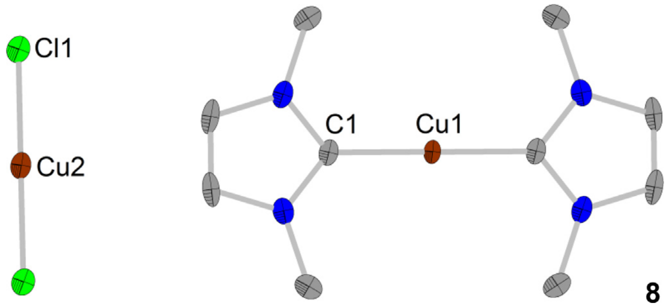

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Fig. 3. Molecular structure of $[Cu(Me_2Im)_2]^+[CuCl_2]^-$ **8**. Element (color): carbon (grey), nitrogen (blue), copper (maroon), chlorine (green). Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Cu–C1 1.889(8), Cu2–Cl 1.1150(8), C1–Cu–C 180.00(0)°. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1 gives a comparison of the $^{13}C\{^1H\}$ NMR chemical shifts of the carbene-carbon atoms and the key bond distances and angles found in the crystal structures of the mono- and bis-NHC copper(I) chloride complexes **1**–**8**.

The bis-NHC complexes **5**–**6** have slightly longer $C_{(NHC)}$–Cu as well as much longer Cl–Cu bond lengths than the analogous mono-NHC complexes **1**–**4**. For the *N*-isopropyl-substituted compounds, the resonance of the carbene-carbon atom in the $^{13}C\{^1H\}$ NMR spectrum is shifted downfield by 10–14 ppm for [Cu(NHC)$_2$(Cl)] compared to those of the mono-substituted analogues. While complex **8**, with an unmethylated backbone, has an ionic composition, complex **4** with a methylated backbone is neutral.

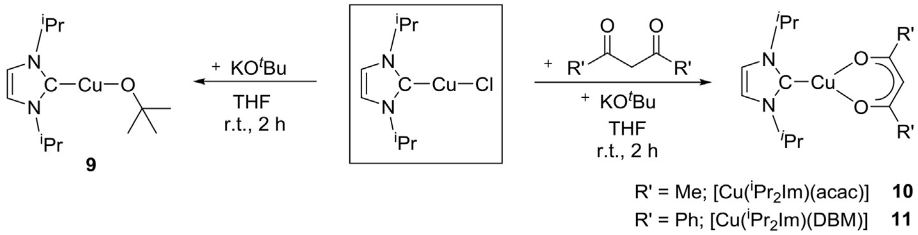
The complexes [Cu($^iPr_2$Im)(Cl)] **2** and [Cu($^iPr_2ImMe_2$)(Cl)] **3** show similar $C_{(NHC)}$–Cu and Cu–Cl distances, but the $C_{(NHC)}$–Cu–Cl angles as well as the $^{13}C\{^1H\}$ NMR chemical shifts of the carbene-carbon atom show some deviation (170.95° and 180.0°; 169.7 ppm and 174.5 ppm). In the previously reported complexes [Cu(Mes_2Im)(Cl)] and [Cu(Mes_2ImMe_2)(Cl)] ($C_{(NHC)}$–Cu: 1.956(10) and 1.921(11); Cu–Cl: 2.091(2) and 2.124(5)), the $C_{(NHC)}$–Cu and Cu–Cl bond distances differ more, while the $C_{(NHC)}$–Cu–Cl angles are much closer (180.000(1)° and 179.5(4)°) [16,17]. These conflicting trends leave the influence of the methylated NHC backbone on these structural parameters unclear. The $[Cu(NHC)_2]^+$ cation found in complex **8** is known for other '*in situ*' formed copper(I) complexes [16].

3. Synthesis of NHC-stabilized copper(I) derivatives

As copper(I) alkoxides, acetates and acetylacetones are very important precatalysts, intermediates or reactive species, we were interested to synthesize these types of complexes stabilized by the small NHC ligand $^iPr_2$Im. In most cases, the complex [Cu($^iPr_2$Im)(Cl)] **2** is a suitable starting material for this purpose (see Scheme 2). Analogous to a procedure reported by Sadighi *et al.* [19] for the Cu(I)-alkoxide complex [Cu($Dipp_2$Im)(O^{t}Bu)] bearing a sterically more demanding NHC ligand, the complex [Cu($^iPr_2$Im)(O^{t}Bu)] **9** can be prepared readily by adding one equivalent of freshly sublimed KO^{t}Bu to a THF solution of **2**. Compound **9** was fully characterized. Compared to the initial complex **2**, the ^{1}H NMR spectrum of compound **9** displays one additional singlet at 1.79 ppm arising from the protons of the *tert*-butyl group. The resonance of the carbene-carbon atom in the $^{13}C\{^1H\}$ NMR spectrum is shifted slightly downfield to 177.5 ppm compared to that of the starting compound **2** (174.5 ppm).

Table 1
$^{13}C\{^1H\}$ NMR chemical shifts and key bond distances and angles found in the crystal structures of the mono- and bis-NHC copper(I) chloride complexes **1**–**8**.

	$^{13}C\{^1H\}$ NMR: C_q [ppm]	Distance $C_{(NHC)}$–Cu [Å]	Distance Cl–Cu [Å]	Angle $C_{(NHC)}$–Cu–Cl [°]	Angle $C_{(NHC)}$–Cu–$C_{(NHC)}$ [°]
[Cu(^{t}Bu$_2$Im)(Cl)] **1**	174.1	1.879(2)	2.0937(7)	180(0)	-
[Cu(^{i}Pr$_2$Im)(Cl)] **2**	174.5	1.8781(14)	2.1055(4)	170.95(5)	-
[Cu(^{i}Pr$_2$ImMe$_2$)(Cl)] **3**	170.0	1.886(3)	2.1056(9)	180(0)	-
[Cu(Me$_4$Im)(Cl)] **4**	175.2	1.878(2)	2.1081(5)	177.93(7)	-
[Cu(Me$_2$Im)$_2$(Cl)] **5**	183.8	-	-	-	-
[Cu(^{i}Pr$_2$Im)$_2$(Cl)] **6**	184.7	1.921(4) 1.938(4)	2.3668(11)	113.9(1) 112.6(1)	133.5(2)
[Cu(^{i}Pr$_2$ImMe$_2$)$_2$(Cl)] **7**	183.9	-	-	-	-
[Cu(Me$_2$Im)$_2$]$^+$[Cu(Cl)$_2$]$^-$ **8**	177.8	1.889(8)	1.1150(8)	-	-



Scheme 2. Synthesis of the NHC-stabilized copper(I) complexes **9**, **10** and **11**.

Alternatively, chelating coligands which are often applied in catalysis are the acetylacetonato (acac) or dibenzoylmethanato (DBM) ligands. These ligands have a lower basicity compared to alkoxides due to the delocalization of the negative charge. Furthermore, the bidentate coordination mode could be useful in chelating the substrate and the metal atom or reacting with a boron center to produce a very stable, neutral (acac)B(OR)$_2$ 4-coordinate boron compound. Indeed, Rh-acac complexes have proven to be very useful catalyst precursors for several catalytic borylation reactions [20]. The syntheses of [Cu(^{i}Pr$_2$Im)(acac)] **10** and [Cu(^{i}Pr$_2$Im)(DBM)] **11** were performed using an approach similar to one which was previously reported [21], starting from [Cu(NHC)(Cl)], KO^{t}Bu and the respective dione (Scheme 2). The products were characterized by elemental analysis, NMR spectroscopy and HRMS, and complex **11** was characterized in addition by X-ray diffraction (Fig. 4).

The ^{1}H NMR spectra for **10** and **11** display a singlet for the proton in between the two carbonyl-moieties with chemical shifts of 5.57 ppm and 6.95 ppm, respectively. The carbene-carbon atoms were detected at 180.4 ppm and 178.8 ppm in the $^{13}C\{^1H\}$ NMR spectra, whereas the carbonyl-carbon atoms show broadened signals at 189.5 ppm and 184.8 ppm, respectively.

The molecular structure of **11** clearly reveals the typical bidentate binding mode of the DBM ligand in the solid state. The sums of the angles around the trigonal planar metal center are 358.15°–360°. Compared to copper(I) base complexes of monodentate ligands such as [Cu(^{i}Pr$_2$Im)(OAc)] **12** (1.8698 Å, see below), the Cu–O bond lengths found in the copper(I) DBM complex **11** are significantly longer (average: 1.9930 Å).

Metal acetates can also be effective in transmetalation reactions involving Ar-B(OR)$_2$ and (RO)$_2$B–B(OR)$_2$ systems due to the formation of a six-membered ring transition state [22]. As such, and given the lower basicity of acetate compared with alkoxides, these may prove useful in both stoichiometric model reactions as well as catalytic processes.

The complexes of the sterically more hindered carbenes [Cu(Dipp$_2$Im)(OAc)] and [Cu(Mes$_2$Im)(OAc)] are known [23]. For the small NHC ^{i}Pr$_2$Im, we have found it advantageous to synthesize [Cu(^{i}Pr$_2$Im)(OAc)] **12** from copper(I) acetate (Scheme 3).

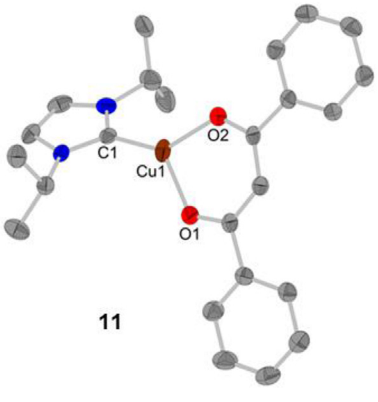
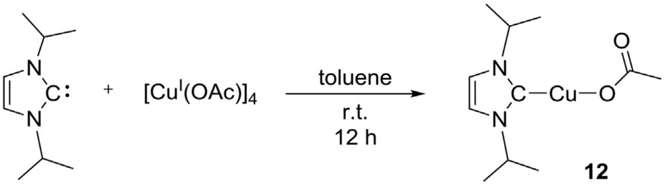


Fig. 4. Molecular structure of [Cu(^{i}Pr$_2$Im)(DBM)] **11**. Element (color): carbon (grey), nitrogen (blue), copper (maroon), oxygen (red). Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability. Only one of the three molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): C1–Cu1 1.862(2), 1.875(2), 1.862(3), Cu1–O1 1.9945(19), 1.9774(17), 1.9968(19), Cu1–O2 1.9706(18), 2.0064(18), 2.0121(19), C1–Cu1–O1 130.33(9), 128.60(9), 131.39(10), C1–Cu1–O2 139.15(9), 140.16(9), 138.37(11), O1–Cu1–O2 90.43(7), 90.93(7), 90.17(8), NC1N-O1Cu1O2 47.96(14), 73.34(16), 36.51(15). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The reaction of ^{i}Pr$_2$Im with copper(I) acetate afforded an off-white powder **12** in 32% yield. The ^{1}H NMR spectrum shows, in



Scheme 3. Synthesis of [Cu(^{i}Pr$_2$Im)(OAc)] **12**.

addition to the sharp signals for the protons attached to the NHC ligand, a broadened resonance for the acetate protons, which is indicative of a dynamic process, presumably the exchange of the coordinating oxygen atoms within the acetate moiety. The $^{13}C\{^{1}H\}$ NMR spectrum also reveals sharp resonances for the NHC ligand and a broadened signal at 176.1 ppm for the carbonyl carbon atom. The methyl carbon atoms of the acetate group were detected in a 2D-NMR spectrum at 23.1 ppm. The exact nature and energetics of this dynamic process could not be determined by ^{1}H VT-NMR in a range between −39 °C and 70 °C. However, in addition to NMR spectroscopy, compound **12** was further characterized using elemental analysis, HRMS, and X-ray diffraction (Fig. 5).

Compound **12** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit with slightly different bond lengths and angles. The distance from the carbonyl oxygen O2 to the copper atom is 2.7628(15) Å [2.8243(16) Å] with a carbon-oxygen distance of 1.236(3) Å [1.236(3) Å]. The coordination around the copper atom is close to linear with a C1—Cu—O1 angle of 177.30(8)° [176.02(7)°]. The bond lengths are 1.8700(18) Å [1.8731(18) Å] for C1—Cu and 1.8683(13) Å [1.8713(14) Å] for Cu—O1. The crystal structure reveals a monodentate acetate ligand. A literature search showed that, in crystal structures of phosphine-stabilized copper(I) acetate complexes, the bidentate binding mode is predominant, but in NHC-stabilized analogues only the monodentate binding mode is found [23]. DFT calculations on a very similar complex ([Cu(Me$_2$Im)(OAc)]) performed by Sadighi *et al.* showed that the bidentate binding mode is more stable by just 1.1 kcal/mol with an uncertainty of ±5 kcal/mol. With both binding modes at almost the same energy and both optimized structures not fitting the bond lengths and angles found in the crystal structure of [Cu(Dipp$_2$Im)(OAc)], they suggest attractive intermolecular interactions between the carbonyl oxygen atom and the backbone proton of a second NHC (2.238 and 2.347 Å for [Cu(Dipp$_2$Im)(OAc)]) [23a]. With an intermolecular O—H bond length of 2.2931(14) and 2.2433(13) Å, complex **12** also shows short distances, possibly explaining the monodentate binding mode.

4. Conclusion

We have synthesized a series of NHC-stabilized copper complexes of the type [Cu(NHC)(Cl)], [Cu(NHC)$_2$(Cl)] and [Cu(NHC)(OR)] (OR = OAc, O^{t}Bu, acac, DBM). The synthetic route starts from copper(I) chloride and the isolated NHC, to suppress the formation of sideproducts caused by the use of strong bases for the *in situ* deprotonation of the NHC ligand. All of the compounds obtained were fully characterized, and the majority of them were further analyzed using X-ray diffraction. In the case of the equimolar reaction of the smallest alkyl NHC with copper(I) chloride, the structure obtained revealed an ionic compound, consisting of a $[Cu(Me_2Im)_2]^+$ cation and a $[CuCl_2]^-$ anion.

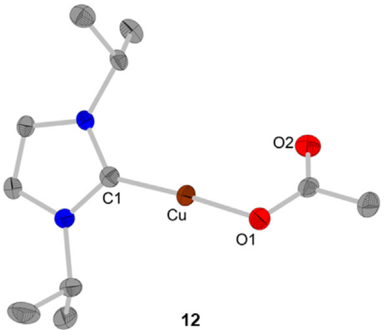


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Fig. 5. Molecular structure of [Cu(^{i}Pr$_2$Im)(OAc)] **12**. Element (color): carbon (grey), nitrogen (blue), oxygen (red), copper (maroon). Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability. Only one of the two molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): C1—Cu 1.8700(18) [1.8731(18)], Cu—O1 1.8683(13) [1.8713(14)], C1—Cu—O1 177.30(8)° [176.02(7)°]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

5. Experimental section

5.1. General considerations

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques. NMR spectra were recorded on a Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) Avance 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) and Avance 200 (^{1}H, 200 MHz), using C_6D_6. ^{13}C NMR spectra are broad-band proton-decoupled ($^{13}C\{^{1}H\}$). Assignment of the ^{13}C NMR data was supported by $^{13}C,^{1}H$ correlation experiments. Chemical shifts are listed in parts per million (ppm) and were determined relative to internal C_6D_5H (^{1}H, $\delta = 7.16$) and natural-abundance carbon resonances of C_6D_6 (^{13}C, $\delta = 128.06$). Coupling constants are quoted in Hertz. High resolution mass spectra were measured on a Thermo Scientific Exactive Plus mass spectrometer, equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C.

The NHC ligands were prepared according to literature procedures: ^{i}Pr$_2$Im [24], Me$_2$Im [24], ^{t}Bu$_2$Im [25], ^{i}Pr$_2$ImMe$_2$ [26], Me$_4$Im [26]. All other reagents were obtained from commercial sources and were used as received.

5.2. Synthesis and characterization of new compounds

5.2.1. [Cu(^{t}Bu$_2$Im)(Cl)] 1

A Schlenk tube containing copper(I) chloride (2.91 g, 29.4 mmol) and 1,3-di-*tert*-butylimidazolin-2-ylidene (5.25 g, 29.4 mmol) was cooled to −110 °C. THF (20 mL) was added slowly down the side of the cooled Schlenk tube. The mixture was slowly warmed to room temperature and stirred for 30 min before being heated to 50 °C for 1 h. The solvent of the yellow suspension was removed under reduced pressure. The crude product was washed with 20 mL of *n*-hexane and dried *in vacuo* to obtain a colorless solid. **Yield:** 6.90 g (24.7 mmol, 84%) of a colorless solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for [$C_{11}H_{20}ClCuN_2$] [403.74 g/mol]: Calc. (obs.) C 47.31 (47.14), H 7.22 (7.64), N 10.03 (9.98). **^{1}H-NMR** (300 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.41 (s, 18 H, C*H*$_3$), 6.47 (s, 2 H, C*H*C*H*). **^{13}C{^{1}H}-NMR** (75 MHz, 25 °C, C_6D_6): δ_C/ppm = 31.9 (*C*H$_3$), 57.7 (*C*$_q$), 116.6 (*C*H*C*H), 174.1 (N*C*N). **HRMS-ASAP** (*m*/*z*): $[M]^+$ calc. for $C_{11}H_{20}ClCuN_2$, 278.0606 found, 278.0603.

5.2.2. [Cu(^{i}Pr$_2$Im)(Cl)] 2

A Schlenk tube containing copper(I) chloride (3.00 g, 10.1 mmol) and THF (25 mL) was cooled to −110 °C. Via syringe, 1,3-di-*iso*-propylimidazolin-2-ylidene (4.61 g, 30.3 mmol, 4.61 mL) was added dropwise. The mixture was slowly warmed to room temperature and stirred for 12 h. The solvent of the grey suspension was removed under reduced pressure. The crude product was washed with 20 mL of *n*-hexane and dried *in vacuo* to obtain a grey solid. **Yield:** 6.60 g (26.3 mmol, 87%) of a solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for [$C_9H_{16}ClCuN_2$] [251.24 g/mol]: Calc. (obs.) C 43.03 (42.77), H 6.42 (6.11), N 11.15 (11.00). **^{1}H-NMR** (300 MHz, 25 °C, C_6D_6): δ_H/ppm = 0.93 (d, 12 H, $^{3}J_{HH}$ = 7 Hz, CHC*H*$_3$), 4.34 (sept, 2 H, $^{3}J_{HH}$ = 7 Hz, C*H*CH$_3$), 6.25 (s, 2 H, C*H*C*H*). **^{13}C{^{1}H}-NMR** (75 MHz, 25 °C, C_6D_6): δ_C/ppm = 23.5 (CH*C*H$_3$), 53.6 (*C*HCH$_3$), 117.0 (*C*H*C*H), 174.5 (N*C*N). **HRMS-ASAP** (*m*/

z): $[2\,M]^+$ calc. for $C_9H_{16}ClCuN_2$, 502.0572 found 502.0554.

5.2.3. $[Cu(^iPr_2ImMe_2)(Cl)]$ 3

A Schlenk tube containing copper(I) chloride (297 mg, 3.00 mmol) and 1,3-di-*iso*-propyl-4,5-dimethylimidazolin-2-ylidene (540 mg, 3.00 mmol) was cooled to −110 °C. THF (5 mL) was added slowly down the side of the cooled Schlenk tube. The mixture was slowly warmed to room temperature and stirred for 16 h. The solvent of the brownish suspension was removed under reduced pressure. The crude product was washed with 10 mL of *n*-hexane and dried *in vacuo* to obtain a colorless solid. **Yield:** 630 mg (2.25 mmol, 75%) of an off-white solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for $[C_{11}H_{20}CuN_4Cl]$ [279.29 g/mol]: Calc. (obs.) C 47.31 (47.10), H 7.22 (7.52), N 10.03 (9.71). **^{1}H-NMR** (200 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.33 (d, 12 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$), 1.37 (s, 6 H, C_qCH_3), 3.86 (sept, 2 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$). **^{13}C{^{1}H}-NMR** (100 MHz, 25 °C, C_6D_6): δ_C/ppm = 8.7 (C_qCH_3), 24.3 ($CHCH_3$), 50.2 ($CHCH_3$), 123.4 (C_qC_q), 170.0 (NCN). **HRMS-ASAP** (*m*/*z*): $[M-Cl]^+$ calc. for $C_{11}H_{20}CuN_2$, 243.0917 found, 243.0915.

5.2.4. $[Cu(Me_4Im)(Cl)]$ 4

A Schlenk tube containing copper(I) chloride (198 mg, 2.00 mmol) and 1,3,4,5-tetramethylimidazolin-2-ylidene (248 mg, 2.00 mmol) was cooled to −110 °C. THF (5 mL) was added slowly down the side of the cooled Schlenk tube glass. The mixture was slowly warmed to room temperature and stirred for 16 h. The solvent of the white suspension was removed under reduced pressure. The crude product was washed with 10 mL of *n*-hexane and dried *in vacuo* to obtain a colorless solid. **Yield:** 295 mg (1.32 mmol, 66%) of an off-white solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for $[C_7H_{12}CuN_2Cl]$ [223.18 g/mol]: Calc. (obs.) C 37.67 (38.04), H 5.42 (5.47), N 12.55 (12.70). **^{1}H-NMR** (200 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.17 (s, 6 H, C_qCH_3), 2.83 (s, 6 H, NCH_3). **^{13}C {^{1}H}-NMR** (100 MHz, 25 °C, C_6D_6): δ_C/ppm = 8.2 (C_qCH_3), 34.9 (NCH_3), 124.4 (C_qC_q), 175.2 (NCN). **HRMS-ASAP** (*m*/*z*): $[M-Cl]^+$ calc. for $C_7H_{12}CuN_2$, 187.0291 found, 187.0285.

5.2.5. $[Cu(Me_2Im)_2(Cl)]$ 5

1,3-Dimethylimidazolin-2-ylidene (485 mg, 5.05 mmol, 485 μL) was added to a suspension of copper(I) chloride (250 mg, 2.52 mmol) in THF (7 mL), via syringe. The yellow reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the crude product was washed with 10 mL of *n*-hexane and dried *in vacuo* to obtain a light grey powder. **Yield:** 413 mg (1.42 mmol, 56%) of a grey powder which is susceptible to oxidation and hydrolysis. **Elemental analysis** for $[C_{10}H_{16}ClCuN_4]$ [291.26 g/mol]: Calc. (obs.) C 41.24 (40.96), H 5.54 (5.67), N 19.24 (18.67). **^{1}H-NMR** (300 MHz, 25 °C, CD_3CN): δ_H/ppm = 3.80 (s, 6 H, CH_3), 7.01 (s, 2 H, $CHCH$). **^{13}C{^{1}H}-NMR** (75 MHz, 25 °C, CD_3CN): δ_C/ppm = 38.1 (CH_3), 122.3 ($CHCH$), 183.8 (NCN). **HRMS-ASAP** (*m*/*z*): $[M]^+$ calc. for $C_{10}H_{16}CuN_4Cl$, 290.0354 found, 290.0344.

5.2.6. $[Cu(^iPr_2Im)_2(Cl)]$ 6

1,3-Di-*iso*-propylimidazolin-2-ylidene (769 mg, 5.05 mmol, 769 μL) was added at room temperature to a suspension of copper(I) chloride (250 mg, 2.52 mmol) in 10 mL of THF. The grey-green reaction mixture was stirred for 1.5 h at room temperature before the solvent was removed under reduced pressure. The crude product was washed with 10 mL of *n*-hexane and dried *in vacuo* to obtain a light grey powder. **Yield:** 665 mg (1.65 mmol, 65%) of a light grey solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for $[C_{18}H_{32}ClCuN_4]$ [403.74 g/mol]: Calc. (obs.) C 53.58 (54.21), H 7.99 (8.02), N 13.89 (13.97). **^{1}H-NMR** (300 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.23 (d, 24 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$), 5.36 (sept, 4 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$), 6.46 (s, 4 H, $CHCH$). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, C_6D_6): δ_C/ppm = 23.7 ($CHCH_3$), 52.2 ($CHCH_3$), 115.5 ($CHCH$), 184.7 (NCN). **HRMS-ASAP** (*m*/*z*): $[M]^+$ calc. for $C_{18}H_{32}CuN_4Cl$, 402.1606 found, 402.1593.

5.2.7. $[Cu(^iPr_2ImMe_2)_2(Cl)]$ 7

THF (5 mL) was added at room temperature to a Schlenk tube containing copper(I) chloride (99.0 mg, 1.00 mmol) and 1,3-di-*iso*-propyl-4,5-dimethylimidazolin-2-ylidene (360 mg, 2.00 mmol). The mixture was stirred for 16 h. The solvent of the brownish suspension was removed under reduced pressure. The crude product was washed with 10 mL of *n*-hexane and dried *in vacuo* to obtain a colorless solid. **Yield:** 320 mg (0.70 mmol, 70%) of an off-white solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for $[C_{22}H_{40}CuN_4Cl]$ [459.59 g/mol]: Calc. (obs.) C 57.50 (57.23), H 8.77 (8.62), N 12.19 (12.05). **^{1}H-NMR** (200 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.50 (d, 24 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$), 1.68 (s, 12 H, (C_qCH_3), 5.17 (br, 4 H, $CHCH_3$). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C_6D_6): δ_C/ppm = 9.6 (C_qCH_3), 23.3 ($CHCH_3$), 51.8 ($CHCH_3$), 123.0 (C_qC_q), 183.9 (NCN). **HRMS-ASAP** (*m*/*z*): $[M-Cl]^+$ calc. for $C_{22}H_{40}CuN_4$, 423.2543 found, 423.2539.

5.2.8. $[Cu(Me_2Im)_2]^+[CuCl_2]^-$ 8

1,3-Dimethylimidazolin-2-ylidene (970 mg, 10.1 mmol, 970 μL) was added dropwise to a Schlenk tube containing copper(I) chloride (1.00 g, 10.1 mmol) and THF (25 mL), which was cooled to −110 °C. The mixture was slowly warmed to room temperature and stirred for 12 h. The solvent of the grey suspension was removed under reduced pressure. The crude product was washed with 20 mL of *n*-hexane and dried *in vacuo* to obtain a grey solid. **Yield:** 1.68 g (8.61 mmol, 85%) of a grey powder which is susceptible to oxidation and hydrolysis. **Elemental analysis** for $[C_5H_8ClCuN_2]$ [195.13 g/mol]: Calc. (obs.) C 30.78 (31.54), H 4.13 (4.46), N 14.36 (14.66). **^{1}H-NMR** (300 MHz, 25 °C, CD_3CN): δ_H/ppm = 3.77 (s, 6 H, CH_3), 7.05 (s, 2 H, $CHCH$). **^{13}C{^{1}H}-NMR** (75 MHZ, 25 °C, CD_3CN): δ_C/ppm = 38.5 (CH_3), 123.1 ($CHCH$), 177.8 (NCN). **HRMS-ASAP** (*m*/*z*): $[M]^+$ calc. for $C_{10}H_{16}CuN_4$, 255.0665 found, 255.0662. **HRMS-ASAP** (*m*/*z*): $[M]^-$ calc. for $CuCl_2$,132.8668 found, 132.8668.

5.2.9. $[Cu(^iPr_2Im)(O^tBu)]$ 9

THF (10 mL) was added to a mixture of $[Cu(^iPr_2Im)(Cl)]$ (200 mg, 796 μmol) and KO^tBu (90 mg, 796 μmol) and the yellow reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure. Toluene (10 mL) was added and the suspension filtered through Celite®. The solvent was removed under reduced pressure and the crude product was washed with 10 mL of *n*-hexane. The resulting yellow solid was dried *in vacuo*. **Yield:** 58 mg (231 mmol, 29%) of a yellow solid. **Elemental analysis** for $[C_{13}H_{25}CuN_2O]$ [288.90 g/mol]: Calc. (obs.) C 54.05 (54.55), H 8.72 (8.59), N 9.70 (9.34). **^{1}H-NMR** (200 MHz, 25 °C, C_6D_6): δ_H/ppm = 0.99 (d, 12 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$), 1.79 (s, 9 H, $C(CH_3)_3$), 4.66 (sept, 2 H, $^3J_{HH}$ = 7 Hz, $CHCH_3$), 6.25 (s, 2 H, $CHCH$). **^{13}C{^{1}H} NMR** (50 MHz, 25 °C, C_6D_6): δ_C/ppm = 23.4 ($CHCH_3$), 36.6 ($C(CH_3)_3$), 53.2 ($CHCH_3$), 69.1 (OC_q), 116.3 ($CHCH$), 177.5 (NCN). **HRMS-ASAP** (*m*/*z*): $[M+H]^+$ calc. for $C_{13}H_{25}CuN_2O$, 289.1336 found, 289.1333.

5.2.10. Synthesis of $[Cu(^iPr_2Im)(acac)]$ 10

To a Schlenk tube charged with $[Cu(^iPr_2Im)(Cl)]$ (125 mg, 498 μmol) and KO^tBu (56 mg, 498 μmol), 5 mL of THF was added, before acetylacetone (47 mg, 498 μmol, 52 μL) was added via syringe. After 1 h at room temperature, the yellow reaction mixture was filtered through Celite®. The solvent was removed under reduced pressure and the product was dried *in vacuo*. **Yield**: 85 mg

(270 μmol, 54%) of a yellow solid. **Elemental analysis** for [$C_{14}H_{23}CuN_2O_2$] [314.90 g/mol]: Calc. (obs.) C 53.40 (53.82), H 7.36 (7.29), N 8.90 (9.18). **^{1}H-NMR** (200 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.03 (d, 12 H, $^3J_{HH} = 7$ Hz, $CHCH_3$), 2.12 (s, 6 H, C_qCH_3), 4.88 (sept, 2 H, $^3J_{HH} = 7$ Hz, $CHCH_3$), 5.57 (s, 1 H, C_qCHC_q), 6.21 (s, 2 H, CHCH). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C_6D_6): δ_C/ppm = 23.5, 28.8, 52.9, 99.6, 115.6, 180.4 (NCN), 189.5 (OC_q). **HRMS-ASAP** (*m*/*z*): [M + H]$^+$ calc. for $C_{14}H_{24}CuN_2O_2$, 315.1128 found, 315.1123.

5.2.11. Synthesis of [Cu(^{i}Pr$_2$Im)(DBM)] 11

To a Schlenk tube charged with [Cu(^{i}Pr$_2$Im)(Cl)] (125 mg, 498 μmol) and KO^{t}Bu (56 mg, 498 μmol) and dibenzoylmethane (112 mg, 498 μmol) THF (5 mL) was added. After 1 h at room temperature, the bright orange reaction mixture was filtered through Celite®. The solvent was removed under reduced pressure and the product was dried *in vacuo*. **Yield**: 30 mg (68 μmol, 14%) of an orange fluffy solid. **Elemental analysis** for [$C_{24}H_{27}CuN_2O_2$] [439.04 g/mol]: Calc. (obs.) C 65.66 (65.68), H 6.20 (6.07), N 6.38 (6.54). **^{1}H-NMR** (200 MHz, 25 °C, C_6D_6): δ_H/ppm = 1.06 (d, 12 H, $^3J_{HH} = 7$ Hz, $CHCH_3$), 4.82 (sept, 2 H, $^3J_{HH} = 7$ Hz, $CHCH_3$), 6.34 (s, 2 H, CHCH), 6.95 (s, 1 H, C_qCHC_q) 7.18–7.28 (m, 6 H, $_{aryl}CH$), 8.19–8.22 (m, 4 H, $_{aryl}CH$). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, C_6D_6): δ_C/ppm = 23.5, 53.1, 93.8, 116.2, 127.7, 128.3, 129.8, 143.9, 178.8 (NCN), 184.8 (OC_q). **HRMS-ASAP** (*m*/*z*): [M + H]$^+$ calc. for $C_{24}H_{27}CuN_2O_2$, 439.1441 found, 439.1437.

5.2.12. Synthesis of [Cu(^{i}Pr$_2$Im)(OAc)] 12

Copper(I) acetate (150 mg, 1.22 mmol) was suspended in toluene (10 mL) and 1,3-di-*iso*-propyl-imidazolin-2-ylidene (186 mg, 1.22 mmol, 186 μL) was added. The red reaction mixture was stirred for 12 h before it was filtered through Celite®. Afterwards, the solvent was removed under reduced pressure. The crude product was washed with *n*-hexane and dried *in vacuo* to obtain a beige solid. **Yield:** 106 mg (0.39 mmol, 32%) of a beige solid which is susceptible to oxidation and hydrolysis. **Elemental analysis** for [$C_{11}H_{19}CuN_2O_2$] [274.83 g/mol]: Calc. (obs.) C 48.07 (48.52), H 6.97 (6.94), N 10.19 (9.73). **^{1}H-NMR** (400 MHz, 25 °C, C_6D_6): δ_H/ppm = 0.94 (d, 12 H, $^3J_{HH} = 7$ Hz, $CHCH_3$), 2.51 (br, 3 H, O_2CCH_3), 4.48 (sept, 2 H, $^3J_{HH} = 7$ Hz, $CHCH_3$), 6.14 (s, 2 H, CHCH). **^{13}C{^{1}H}-NMR** (100 MHz, 25 °C, C_6D_6): δ_C/ppm = 23.5 (C_qCH_3), 23.3 ($CHCH_3$), 53.5 ($CHCH_3$), 117.0 (CHCH), 174.6 (NCN), 176.1 (br, C_qCH_3). **HRMS-ASAP** (*m*/*z*): [M+H]$^+$ calc. for $C_{11}H_{19}CuN_2O_2$, 275.0815 found, 275.0806.

5.3. Crystallographic details

Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Bruker X8 Apex-2 diffractometer, with CCD area detector and mirror-monochromated Mo- $K_\propto$ radiation, equipped with an Oxford Cryosystems low temperature device. Data were collected at 100 K. The images were processed with the Bruker software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions and refined using a riding model. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package [27]. All non-hydrogen atoms were refined anisotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 1873529–1873536 (compounds **1–4, 6, 8, 11, 12**). Copies of the data can be obtained free of charge on application to the CSD.

Crystal data of **[Cu(^{t}Bu$_2$Im)(Cl)] 1**: (CCDC 1873529), $C_{11}H_{20}ClCuN_2$, $M_r = 279.28$, monoclinic space group $C2/c$, $a = 10.8229(9)$ Å, $b = 11.6435(11)$ Å, $c = 11.0027(9)$ Å, $\beta = 107.335(2)$ °, $\alpha = \gamma = 90°$, $V = 1323.5(2)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd.} = 1.402$ g cm^{-3}, $\mu = 1.824$ mm^{-1}, $F(000) = 584$, 4386 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $2.64° < \theta < 27.02°$, 4493 independent reflections, 1246 observed reflections ($I > 2\sigma(I)$), 73 parameters, 0 restraints; *all data:* $R_1 = 0.0311$ and w$R_2 = 0.1003$, $I > 2\sigma(I)$: $R_1 = 0.0266$ and w$R_2 = 0.0926$, *Goof* 0.812, largest difference peak/hole 0.658/-0.396 e·Å^{-3}.

Crystal data of **[Cu(^{i}Pr$_2$Im)(Cl)] 2**: (CCDC 1873530), $C_9H_{16}ClCuN_2$, $M_r = 251.23$, monoclinic space group $P2_1/c$, $a = 10.2944(5)$ Å, $b = 9.8798(5)$ Å, $c = 12.1082(6)$ Å, $\beta = 109.8560(10)$ °, $\alpha = \gamma = 90°$, $V = 1158.27(10)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd.} = 1.441$ g cm^{-3}, $\mu = 2.076$ mm^{-1}, $F(000) = 520$, 14729 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $2.10° < \theta < 26.07$, 2298 independent reflections, 2189 observed reflections ($I > 2\sigma(I)$), 122 parameters, 0 restraints; *all data:* $R_1 = 0.0218$ and w$R_2 = 0.0550$, $I > 2\sigma(I)$: $R_1 = 0.0203$ and w$R_2 = 0.0550$, *Goof* 1.066, largest difference peak/hole 0.375/-0.233e·Å^{-3}.

Crystal data of **[Cu(^{i}Pr$_2$ImMe$_2$)(Cl)] 3**: (CCDC 1873533), $C_{11}H_{20}ClCuN_2$, $M_r = 279.28$, tetragonal space group $P4_32_12$, $a = 7.9930(17)$ Å, $b = 7.9930(17)$ Å, $c = 20.607(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1316.5(6)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd.} = 1.409$ g cm^{-3}, $\mu = 1.834$ mm^{-1}, $F(000) = 584$, 13329 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $2.733° < \theta < 26.091°$, 1304 independent reflections, 1227 observed reflections ($I > 2\sigma(I)$), 74 parameters, 0 restraints; *all data:* $R_1 = 0.0320$ and w$R_2 = 0.0829$, $I > 2\sigma(I)$: $R_1 = 0.0304$ and w$R_2 = 0.0822$, *Goof* 1.107, largest difference peak/hole 0.352/-0.782 e·Å^{-3}.

Crystal data of **[Cu(Me$_4$Im)(Cl)] 4**: (CCDC 1873536), $C_7H_{12}ClCuN_2$, $M_r = 233.18$, monoclinic space group $P2_1/c$, $a = 8.2580(8)$ Å, $b = 15.8530(11)$ Å, $c = 7.7508(5)$ Å, $\beta = 115.996(2)°$, $\alpha = \gamma = 90°$, $V = 912.03(12)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd.} = 1.625$ g cm^{-3}, $\mu = 2.625$ mm^{-1}, $F(000) = 456$, 11651 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $2.570° < \theta < 26.024°$, 1799 independent reflections, 1633 observed reflections ($I > 2\sigma(I)$), 104 parameters, 0 restraints; *all data:* $R_1 = 0.0264$ and w$R_2 = 0.0586$, $I > 2\sigma(I)$: $R_1 = 0.0227$ and w$R_2 = 0.0570$, *Goof* 1.083, largest difference peak/hole 0.400/-0.292 e·Å^{-3}.

Crystal data of **[Cu(^{i}Pr$_2$Im)$_2$(Cl)] 6**: (CCDC 1873532), $C_{18}H_{32}ClCuN_4$, $M_r = 403.47$, orthorhombic space group $P2_12_12_1$, $a = 9.3953(19)$ Å, $b = 10.1716(18)$ Å, $c = 21.326(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2038.1(7)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd.} = 1.315$ g cm^{-3}, $\mu = 1.210$ mm^{-1}, $F(000) = 856$, 12480 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $1.91° < \theta < 26.85°$, 4277 independent reflections, 3064 observed reflections ($I > 2\sigma(I)$), 225 parameters, 0 restraints; *all data:* $R_1 = 0.0766$ and w$R_2 = 0.0901$, $I > 2\sigma(I)$: $R_1 = 0.0455$ and w$R_2 = 0.0799$, *Goof* 0.974, largest difference peak/hole 0.490/-0.360 e·Å^{-3}.

Crystal data of **[Cu(Me$_2$Im)$_2$]$^+$[CuCl$_2$]$^-$ 8**: (CCDC 1873535), $C_{10}H_{16}Cl_2CuN_4$, $M_r = 390.25$, monoclinic space group $C2/m$, $a = 14.996(3)$ Å, $b = 6.2266(15)$ Å, $c = 8.0416(19)$ Å, $\beta = 111.107(6)°$, $\alpha = \gamma = 90°$, $V = 700.5(3)$ Å^3, $T = 100$ K, $Z = 2$, $\rho_{calcd.} = 1.850$ g cm^{-3}, $\mu = 3.403$ mm^{-1}, $F(000) = 392$, 4578 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $2.72° < \theta < 26.87°$, 820 independent reflections, 773 observed reflections ($I > 2\sigma(I)$), 59 parameters, 0 restraints; *all data:* $R_1 = 0.0229$ and w$R_2 = 0.0555$, $I > 2\sigma(I)$: $R_1 = 0.0213$ and w$R_2 = 0.0551$, *Goof* 1.793, largest difference peak/hole 0.357/-0.263 e·Å^{-3}.

Crystal data of **[Cu(^{i}Pr$_2$Im)(DBM)] 11:** (CCDC 1873531), $C_{24}H_{27}CuN_2O_2$, $M_r = 439.01$, monoclinic space group $P2_1/c$,

$a = 17.1889(12)$ Å, $b = 10.5700(7)$ Å, $c = 36.668(3)$ Å, $\beta = 96.129(2)$ °, $\alpha = \gamma = 90°$, $V = 6624.1(8)$ Å^3, $T = 100$ K, $Z = 12$, $\rho_{calcd.} = 1.321$ g cm^{-3}, $\mu = 1.010$ mm^{-1}, $F(000) = 2760$, 66500 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $1.718° < \theta < 26.432°$, 13597 independent reflections, 11202 observed reflections ($I > 2\sigma(I)$), 152 parameters, 0 restraints; *all data:* $R_1 = 0.0399$ and w$R_2 = 0.0767$, $I > 2\sigma(I)$: $R_1 = 0.0348$ and w$R_2 = 0.0743$, *Goof* 0.839, largest difference peak/hole 0.680/−0.839 e·Å^{-3}.

Crystal data of **[Cu(^{i}Pr$_2$Im)(OAc)] 12**: (CCDC 1873534), $C_{11}H_{19}CuN_2O_2$, $M_r = 274.82$, triclinic space group P-1, $a = 9.3560(5)$ Å, $b = 12.0931(6)$ Å, $c = 12.1272(6)$ Å, $\alpha = 76.550(4)$ °, $\beta = 88.732(2)$ °, $\gamma = 84.509(2)$ °, $V = 1328.35(12)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd.} = 1.374$ g cm^{-3}, $\mu = 1.633$ mm^{-1}, $F(000) = 576$, 23911 reflections in $h(-8/8)$, $k(0/18)$, $l(0/19)$ measured in the range $1.73° < \theta < 26.11°$, 5250 independent reflections, 4364 observed reflections ($I > 2\sigma(I)$), 299 parameters, 0 restraints; *all data:* $R_1 = 0.0374$ and w$R_2 = 0.0619$, $I > 2\sigma(I)$: $R_1 = 0.0249$ and w$R_2 = 0.0567$, *Goof* 1.021, largest difference peak/hole 0.334/-0.273 e·Å^{-3}.

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Appendix A. Supplementary data

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References

[1] C. Kleeberg, L. Dang, Z. Lin, T.B. Marder, Angew. Chem. Int. Ed. 48 (2009) 5350–5354.

[2] (a) D.S. Laitar, P. Müller, J.P. Sadighi, J. Am. Chem. Soc. 127 (2005) 17196–17197;
(b) K. Semba, M. Shinomiya, T. Fujihara, J. Terao, Y. Tsuji, Chem. Eur J. 19 (2013) 7125–7132;
(c) J. Plotzitzka, C. Kleeberg, Inorg. Chem. 55 (2016) 4813–4823;
(d) C. Borner, L. Anders, K. Brandhorst, C. Kleeberg, Organometallics 36 (2017) 4687–4690;
(e) C. Kleeberg, C. Borner, Organometallics 37 (2018) 4136–4146, https://doi.org/10.1021/acs.organomet.8b00672.

[3] C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P.G. Steel, T.B. Marder, L. Liu, Angew. Chem. Int. Ed. 51 (2012) 528–532.

[4] (a) G.H. Posner, Org. React. 22 (1975) 253;
(b) B.H. Lipshutz, S. Sengupta, Org. React. 40 (1992) 641;
(c) E. Erdik, Tetrahedron 40 (1984) 641–657.

[5] (see for example) (a) G. Cahiez, C. Chaboche, M. Jézéquel, Tetrahedron 56 (2000) 2733–2737;
(b) J. Terao, A. Ikumi, H. Kuniyasu, N. Kambe, J. Am. Chem. Soc. 125 (2003) 5646–5647;
(c) J. Terao, H. Todo, S.A. Begum, H. Kuniyasu, N. Kambe, Angew. Chem. 119 (2007) 2132–2135;
(d) G. Cahiez, O. Gager, J. Buendia, Angew. Chem. Int. Ed. 49 (2010) 1278–1281;
(e) D.H. Burns, J.D. Miller, H.-K. Chan, M.O. Delaney, J. Am. Chem. Soc. 119 (1997) 2125–2133;
(f) G. Cahiez, O. Gager, J. Buendia, Synlett (2010) 299–303;
(g) R. Shen, T. Iwasaki, J. Terao, N. Kambe, Chem. Commun. 48 (2012) 9313–9315.

[6] (see for example) (a) M.B. Thathagar, J. Beckers, G. Rothenberg, J. Am. Chem. Soc. 124 (2002) 11858–11859;
(b) J. Mao, J. Guo, F. Fang, S.-J. Ji, Tetrahedron 64 (2008) 3905–3911;
(c) S. Wang, M. Wang, L. Wang, B. Wang, P. Li, J. Yang, Tetrahedron 67 (2011) 4800–4806;
(d) J. Liu, F. Dai, Z. Yang, S. Wang, K. Xie, A. Wang, X. Chen, Z. Tan, Tetrahedron Lett. 53 (2012) 5678–5683;
(e) J.-H. Li, D.-P. Wang, Eur. J. Org Chem. 2006 (2006) 2063–2066;
(f) Y.-M. Ye, B.-B. Wang, D. Ma, L.-X. Shao, J.-M. Lu, Catal. Lett. 139 (2010) 141–144;
(g) C.-T. Yang, Z.-Q. Zhang, Y.-C. Liu, L. Liu, Angew. Chem. Int. Ed. 50 (2011) 3904–3907;
(h) S.K. Gurung, S. Thapa, A. Kafle, D.A. Dickie, R. Giri, Org. Lett. 16 (2014) 1264–1267;
(i) Y. Zhou, W. You, K.B. Smith, M.K. Brown, Angew. Chem. Int. Ed. 53 (2014) 3475–3479.

[7] (a) H. Ito, H. Yamanaka, J.-i. Tateiwa, A. Hosomi, Tetrahedron Lett. 41 (2000) 6821–6825;
(b) K. Takahashi, T. Ishiyama, N. Miyaura, J. Organomet. Chem. 625 (2001) 47–53;
(c) D.S. Laitar, E.Y. Tsui, J.P. Sadighi, J. Am. Chem. Soc. 128 (2006) 11036–11037.

[8] (a) H. Zhao, Z. Lin, T.B. Marder, J. Am. Chem. Soc. 128 (2006) 15637–15643;
(b) L. Dang, H. Zhao, Z. Lin, T.B. Marder, Organometallics 26 (2007) 2824–2832;
(c) L. Dang, H. Zhao, Z. Lin, T.B. Marder, Organometallics 27 (2008) 1178–1186;
(d) H. Zhao, L. Dang, T.B. Marder, Z. Lin, J. Am. Chem. Soc. 130 (2008) 5586–5594;
(e) L. Dang, Z. Lin, T.B. Marder, Organometallics 27 (2008) 4443–4454;
(f) M. Gao, S.B. Thorpe, C. Kleeberg, C. Slebodnick, T.B. Marder, W. Santos, J. Org. Chem. 76 (2011) 3997–4007;
(g) C. Kleeberg, M.S. Cheung, Z. Lin, T.B. Marder, J. Am. Chem. Soc. 133 (2011) 19060–19063;
(h) S.K. Bose, S. Brand, H.O. Omoregie, M. Haehnel, J. Maier, G. Bringmann, T.B. Marder, ACS Catal. 6 (2016) 8332–8335;
(i) L. Mao, K. Szabó, T.B. Marder, Org. Lett. 19 (2017) 1204–1207;
(j) L. Mao, R. Bertermann, K. Emmert, K.J. Szabó, T.B. Marder, Org. Lett. 19 (2017) 6586–6589.

[9] (a) L. Dang, Z. Lin, T.B. Marder, Chem. Commun. (2009) 3987–3995;
(b) G. Stavber, Z. Časar, ChemCatChem 6 (2014) 2162–2174;
(c) T. Fujihara, K. Semba, J. Terao, Y. Tsuji, Catal. Sci. Technol. 4 (2014) 1699–1709;
(d) K. Semba, T. Fujihara, J. Terao, Y. Tsuji, Tetrahedron 71 (2015) 2183–2197;
(e) E.C. Neeve, S.J. Geier, I.A.I. Mkhalid, S.A. Westcott, T.B. Marder, Chem. Rev. 116 (2016) 9091–9161;
(f) J.-B. Chen, A. Whiting, Synthesis 50 (2018) 3843–3861;
(g) D. Hemming, R. Fritzemeier, S.A. Westcott, W.L. Santos, P.G. Steel, Chem. Soc. Rev. 47 (2018) 7477–7494.

[10] H. Schneider, D. Schmidt, A. Eichhöfer, M. Radius, F. Weigend, U. Radius, Eur. J. Inorg. Chem. (2017) 2600–2616.

[11] (a) S. Dürr, B. Zarzycki, D. Ertler, I. Ivanović-Burmazović, U. Radius, Organometallics 31 (2012) 1730–1742;
(b) S. Dürr, D. Ertler, U. Radius, Inorg. Chem. 51 (2012) 3904–3909;
(c) F. Hering, J.H.J. Berthel, K. Lubitz, U.S.D. Paul, H. Schneider, M. Haerterich, U. Radius, Organometallics 35 (2016) 2806–2821;
(d) K. Lubitz, V. Sharma, S. Shukla, J.H.J. Berthel, H. Schneider, C. Hoßbach, U. Radius, Organometallics 37 (2018) 1181–1191.

[12] (a) T. Schaub, U. Radius, Chem. Eur J. 11 (2005) 5024–5030;
(b) T. Schaub, C. Doering, U. Radius, Dalton Trans. (2007) 1993–2002;
(c) T. Schaub, M. Backes, O. Plietzsch, U. Radius, Dalton Trans. (2009) 7071–7079;
(d) T. Schaub, U. Radius, Z. Anorg, Allg. Chem. 632 (2006) 981–984;
(e) T. Schaub, M. Backes, U. Radius, Organometallics 25 (2006) 4196–4206;
(f) T. Zell, T. Schaub, K. Radacki, U. Radius, Dalton Trans. 40 (2011) 1852–1854;
(g) D. Schmidt, T. Zell, T. Schaub, U. Radius, Dalton Trans. 43 (2014) 10816–10827;
(h) T. Schaub, M. Backes, U. Radius, Chem. Commun. (2007) 2037–2039;
(i) T. Zell, P. Fischer, D. Schmidt, U. Radius, Organometallics 31 (2012) 5065–5073;
(j) B. Zarzycki, T. Zell, D. Schmidt, U. Radius, Eur. J. Inorg. Chem. (2013) 2051–2058.

[13] S. Díez-González, S.P. Nolan, Synlett 2007 (2007) 2158–2167.

[14] (see for example) (a) A. Welle, S. Díez-González, B. Tinant, S.P. Nolan, O. Riant, Org. Lett. 8 (2006) 6059–6062;
(b) M.R. Fructos, T.R. Belderrain, M.C. Nicasio, S.P. Nolan, H. Kaur, M.M. Díaz-Requejo, P.J. Pérez, J. Am. Chem. Soc. 126 (2004) 10846–10847;
(c) C. Munro-Leighton, S.A. Delp, E.D. Blue, T.B. Gunnoe, Organometallics 26 (2007) 1483–1493;
(d) S. Díez-González, E.D. Stevens, N.M. Scott, J.L. Petersen, S.P. Nolan, Chem. Eur J. 14 (2008) 158–168;
(e) G.G. Dubinina, H. Furutachi, D.A. Vicic, J. Am. Chem. Soc. 130 (2008) 8600–8601;
(f) S. Díez-González, H. Kaur, F.K. Zinn, E.D. Stevens, S.P. Nolan, J. Org. Chem. 70 (2005) 4784–4796;
(g) S. Díez-González, A. Correa, L. Cavallo, S.P. Nolan, Chem. Eur J. 12 (2006) 7558–7564;
(h) S. Díez-González, S.P. Nolan, Angew. Chem. Int. Ed. 47 (2008) 8881–8884;
(i) S. Diez-Gonzalez, E.D. Stevens, S.P. Nolan, Chem. Commun. (2008) 4747–4749.

[15] C.A. Citadelle, E.L. Nouy, F. Bisaro, A.M.Z. Slawin, C.S.J. Cazin, Dalton Trans. 39 (2010) 4489–4491.

[16] (a) S. Diez-Gonzalez, E.C. Escudero-Adan, J. Benet-Buchholz, E.D. Stevens, A.M.Z. Slawin, S.P. Nolan, Dalton Trans. 39 (2010) 7595–7606;
(b) W. Xie, S. Chang, Angew. Chem. Int. Ed. 55 (2016) 1876–1880.

[17] (a) K. Semba, M. Shinomiya, T. Fujihara, J. Terao, Y. Tsuji, Chem. Eur J. 19

(2013) 7125–7132;
(b) H. Kaur, F.K. Zinn, E.D. Stevens, S.P. Nolan, Organometallics 23 (2004) 1157–1160.

[18] G. Venkatachalam, M. Heckenroth, A. Neels, M. Albrecht, Helv. Chim. Acta 92 (2009) 1034–1045.

[19] N.P. Mankad, D.S. Laitar, J.P. Sadighi, Organometallics 23 (2004) 3369–3371.

[20] (a) S.A. Westcott, H.P. Blom, T.B. Marder, R.T. Baker, J. Am. Chem. Soc. 114 (1992) 8863–8869;
(b) C. Dai, E.G. Robins, A.J. Scott, W. Clegg, D.S. Yufit, J.A.K. Howard, T.B. Marder, Chem. Commun. (1998) 1983–1984.

[21] A. Welle, S. Díez-González, B. Tinant, S.P. Nolan, O. Riant, Org. Lett. 8 (2006) 6059–6062.

[22] T. Ishiyama, M. Murata, N. Miyaura, J. Org. Chem. 60 (1995) 7508–7510.

[23] (a) N.P. Mankad, T.G. Gray, D.S. Laitar, J.P. Sadighi, Organometallics 23 (2004) 1191–1193;
(b) L.A. Goj, E.D. Blue, S.A. Delp, T.B. Gunnoe, T.R. Cundari, J.L. Petersen, Organometallics 25 (2006) 4097–4104.

[24] (a) T. Schaub, M. Backes, U. Radius, Organometallics 25 (2006) 4196–4206;
(b) T. Schaub, U. Radius, A. Brucks, M.P. Choules, M.T. Olsen, T.B. Rauchfuss, Inorg. Synth. 35 (2011) 78–83.

[25] N.M. Scott, R. Dorta, E.D. Stevens, A. Correa, L. Cavallo, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 3516–3526.

[26] N. Kuhn, T. Kratz, Synthesis (1993) 561–562.

[27] G. Sheldrick, Acta Crystallogr. A71 (2015) 3–8.