

Nanoparticles

Direct Synthesis of N-Heterocyclic Carbene-Stabilized Copper Nanoparticles from an N-Heterocyclic Carbene–Borane

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Abstract: N-Heterocyclic carbene (NHC)-stabilized copper nanoparticles (NPs) were synthesized from an NHC–borane adduct and mesitylcopper(I) under thermal conditions (refluxing toluene for 2.5 h). NPs with a size distribution of 11.6 ± 1.8 nm were obtained. The interaction between Cu NPs and NHC ligands was probed by X-ray photoelectron

spectroscopy, which showed covalent binding of the NHC to the surface of the NPs. Mechanistic studies suggested that NHC–borane plays two roles: contributing to the reduction of $[\text{CuMes}]_2$ to release Cu^0 species and providing NHC ligands to stabilize the copper NPs.

Introduction

N-heterocyclic carbenes (NHCs) are considered to be a versatile family of compounds in modern chemistry, and accordingly they have attracted attention in various fields since the early 1990s.^[1,2] The taming of these compounds has unlocked a wide range of new applications from academia to industry, in organometallic chemistry, organocatalysis, surface chemistry, and nanoparticles synthesis.^[3,4] Although metallic nanoparticles (NPs) have a promising range of applications, depending on the physical and chemical properties of the metal, examples of NHC-stabilized nanoparticles are still limited to few metals (Scheme 1, left).^[4,5] Common strategies for their preparation rely on the reduction of an organometallic precursor (isolated

or generated in situ)^[6–11] or ligand exchange.^[11–13] In spite of numerous works concerning their syntheses and applications,^[14] Cu NPs are still challenging to prepare as a colloidal solution that is resistant to aggregation over time and with a metal surface that is neither oxidized nor hydroxylated as long as it is kept under inert atmosphere.^[15] Their stabilization with NHCs has only been reported recently, whereby NHCs were used as additional ligands on supported preformed nanoparticles to tune the catalytic activity for the hydrogenation of alkynes.^[16,17] Before this recent work, the interaction of copper surfaces with NHCs was mostly probed on self-assembled monolayers on flat surfaces,^[18,19] and also on supported Cu NPs post-grafted with IMes NHC [1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene].^[17] Because NHC–borane adducts combine both the potential roles of stabilizing-ligand source and reducing agent,^[20] we envisioned them as good candidates for the synthesis of NHC-stabilized Cu NPs.

Results and Discussion

Previous works dealing with the synthesis of NHC-capped Au NPs showed superior stabilization of NPs with long alkyl chains ($n\text{-C}_{12}\text{H}_{25}$ or $n\text{-C}_{14}\text{H}_{29}$) on the NHC compared to shorter-chain analogues.^[6,11,13,21] Thus, we started our investigations with an NHC–borane with $n\text{-C}_{12}\text{H}_{25}$ aliphatic chains on the N atoms of the NHC core. $[\text{CuMes}]_n$ was previously used for the synthesis of colloidal Cu NPs.^[22–27] In this study, copper NPs were generated under inert atmosphere from a solution of $[\text{CuMes}]_n$ in toluene, to which NHC– BH_3 was added (1–5 equiv). The solution was heated to reflux in toluene for 2.5 h to give a deep red suspension (Scheme 1, right). In contact with air, the final red suspension of NPs was quickly oxidized and took on a blue color.


To narrow the size distribution of the NPs, reaction conditions were screened (metal/NHC–borane ratio and concentration; see Supporting Information, Tables S1 and S2, Figure S1).

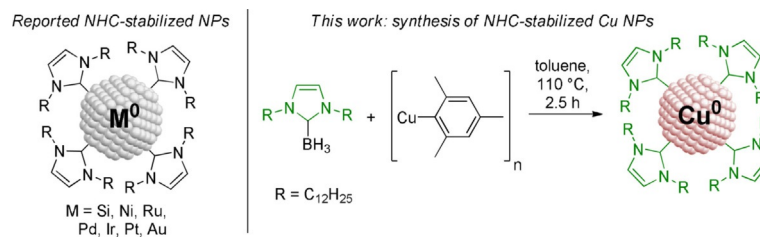
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<https://doi.org/10.1002/chem.201901534>



Scheme 1. Left: Metal(loid) NPs stabilized by NHC.^[4] Right: proposed synthetic pathway using NHC–BH₃ adducts for direct formation of Cu NPs stabilized by NHC.

A concentration of 100 mM for the Cu precursor and a 1:3 ratio of [CuMes]_n to NHC–BH₃ were selected as the best conditions to obtain Cu NPs. The NPs were isolated by centrifugation and washed under inert atmosphere to remove any soluble molecular complexes or clusters. TEM indicated a diameter distribution of 11.6 ± 1.8 nm (Figure 1A).

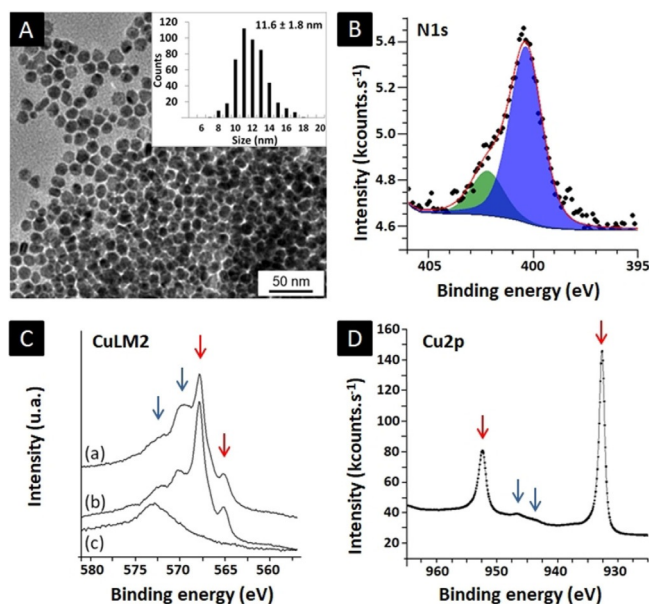


Figure 1. A) TEM image and size distribution of the isolated NPs; B) N 1s XPS spectrum of Cu NPs and decomposition: blue: resulting from covalent bonding; green: resulting from imidazolium contamination. C) Cu LM2 Auger spectra of a) Cu NPs, b) bulk copper metal reference, and c) [CuMes]_n. D) Cu 2p XPS spectrum.

Due to the very high oxygen sensitivity of these Cu NPs, we were unable to characterize their surfaces by routine thermogravimetric and IR analysis. We instead used X-ray photoelectron spectroscopy (XPS) to probe the surface species without exposing the powder to air.^[28] The XPS measurements also give access to the Auger contributions of copper. XPS was performed on Cu NPs powder, the NHC–BH₃ precursor, and [CuMes]_n (Figure 1B–D).

We first confirmed that copper was essentially in a metallic state in the Cu NPs powder. Figure 1C shows the Cu LM2 Auger spectrum obtained for the Cu NPs (spectrum a). Because of the intrinsically complex shape of Auger Cu spectra, it was compared to those of a bulk copper metal reference (spec-

trum b) and the [CuMes]_n precursor (spectrum c). The spectrum of the Cu NPs shows the same four main transitions as that of the Cu metal reference (the two major ones are indicated by red arrows), which clearly indicate metallic character of the Cu NPs. The peaks under the blue arrows are mostly contributed by the copper metal, but also have another contribution, as their intensity in spectrum a is higher than in spectrum b. The presence of the [CuMes]_n precursor can be totally excluded by comparison with reference spectrum c. To further identify the unknown contribution, the Cu 2p photopeaks were analyzed (Figure 1D). They show characteristic Cu 2p_{3/2} and Cu 2p_{1/2} components of copper metal at 932.6 and 952.3 eV, respectively (Figure 1D, red arrows). This confirms the metallic character of copper, as observed on the Cu LM2 Auger spectrum, according to Biesinger.^[29] The presence of two weak peaks at 944 and 947 eV indicates electronically depleted copper centers (Figure 1D, blue arrows) and could be correlated with the additional contribution observed for the Auger peaks.

We propose that these weak transitions are related to the surface copper atoms that interact with the NHC ligand. To verify this hypothesis, we analyzed the C 1s and N 1s regions. The C 1s photopeak was dominated by the alkyl chain signal, supposedly from the NHC, and this prevented detection of the characteristic component of the C–M covalent bond (see Supporting Information, Figure S2A). However, the N 1s photopeak clearly shows two distinct components, characteristic of specific chemical environments (Figure 1B). The major component at 400.3 eV was already observed in a previous study on NHC-stabilized Au NPs and is characteristic of covalent binding of the NHC ligand to the metal NP through its N–C–N carbon atom.^[21] Hence, in the present case, it was attributed to covalent binding of the NHC to the copper metal NPs. We suggest that the surface Cu atoms bound to the NHC, rather than a copper oxide/hydroxide impurity, are responsible for the additional components observed in the Cu LM2 Auger peak and Cu 2p peaks, because the reaction and analysis were performed under oxygen-free conditions. The atomic composition estimated by XPS gave an NHC/Cu ratio of approximately 1/20, corresponding to an apparent ratio of one NHC to two surface copper atoms. However, the precise determination of ligand coverage by XPS is not possible because, owing to the inelastic mean free path of photoelectrons, the depth of analysis is less than 5 nm. Thus, only a fraction of the NP is probed by XPS, and this prevents quantitative assessment. On the basis of a previous study on Au NPs prepared by using an imidazolium precursor, the minor component (ca. 20%) observed at

402.4 eV in the N 1s region was tentatively attributed to contamination with imidazolium species.^[21] Indeed, the $[\text{CuMes}]_n$ commercial precursor contains significant amounts of Cl and Br impurities from its synthesis^[30] (0.6 and 2.3 wt% with respect to Cu, respectively), which remain in the reaction medium and are precipitated with the NPs. Because of the presence of the Br impurity, the B 1s region of the XP spectrum could not be interpreted, due to the overlap of B 1s and Br 3p peaks (see Supporting Information, Figure S2B).

Altogether, we can now provide a fairly complete description of the Cu NPs: they are metallic and have NHC ligands at their surface as the major stabilizing species. The NHC results from dissociation of the NHC–borane into NHC and BH_3 , which is likely liberated to the gas phase as B_2H_6 , in the presence of the copper surface, as schematized in Scheme 2 (bottom). One central question remained: what is the pathway for formation of the Cu^0 species from $[\text{CuMes}]_n$? To answer this, the early stages of NP formation were investigated.

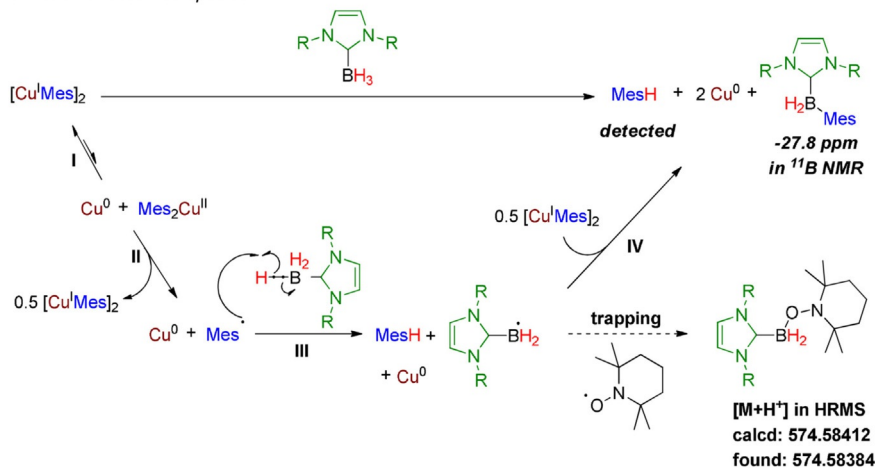
First, we monitored the reaction between $[\text{CuMes}]_n$ and NHC-BH_3 (3 equiv), as performed above, by $^1\text{H}\{^{11}\text{B}\}$ and ^{11}B NMR spectroscopy in $[\text{D}_8]\text{toluene}$. The $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of the crude mixture revealed that all the initial $[\text{CuMes}]_n$ had reacted after 2.5 h at reflux. However, 90% of the initial NHC-BH_3 remained unconverted while the remaining 10% was converted to the $\text{NHC-BH}_2\text{Mes}$ adduct, as evaluated by comparing the ^{11}B NMR spectra of the mixture before and after heating. The latter species was identified from the triplet at -27.8 ppm in the ^{11}B NMR spectrum and from singlets at -27.8 ppm (ArH, 2H), 2.83 ppm ($\text{MesBH}_2\text{-NHC}$, 2H), 2.46 ppm (o -

CH_3 , 6H), and 2.33 ppm (p - CH_3 , 3H) in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (see Supporting Information, Figures S3–S5). Heating NHC-BH_3 in refluxing toluene does not alter it at all, as shown by ^1H and ^{11}B NMR spectroscopy. Mesitylene was also identified as a side product [singlets at 6.65 (ArH, 3H) and 2.13 ppm (CH_3 , 9H)]. Surprisingly, in this reaction, less than one hydrido group per Cu atom was required for complete reaction of the Cu precursor. This means that NHC-BH_3 did not act as a stoichiometric reactant for the reduction of Cu^{I} species to Cu^0 . Hence, the hydridic character of NHC-BH_3 does not seem to be involved in the main pathway leading to Cu^0 species.

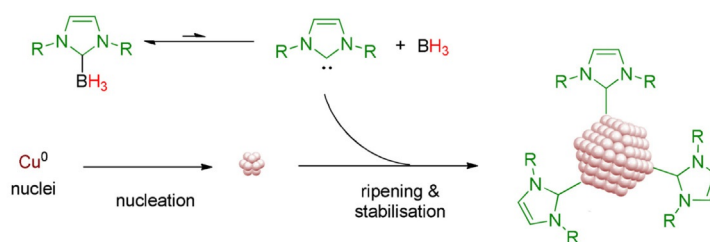
We investigated the reaction mechanism in greater depth using complementary experiments. First, $[\text{CuMes}]_n$ was heated at 110°C for 2.5 h in the absence of NHC-BH_3 . This resulted in conversion of most of the $[\text{CuMes}]_5$ to $[\text{CuMes}]_2^{[31]}$ with only traces of degradation products (see Supporting Information, Figure S6). By TEM, a few small and ill-defined nano-objects were observed, probably resulting from the degradation of the sensitive copper precursor (Supporting Information, Figure S8B). This indicated that NHC-BH_3 was required for complete transformation of $[\text{CuMes}]_n$ into Cu NPs.

NHC–boranes are known to form NHC–boryl radicals in the presence of a radical initiator.^[32–34] In a second experiment, the possibility of a radical mechanism was thus explored by using TEMPO as a radical scavenger. In the presence of 2 equiv of TEMPO with respect to Cu and 3 equiv of NHC-BH_3 with respect to Cu in the reaction medium, after 2.5 h, $[\text{CuMes}]_n$ had only partially reacted with the formation of NPs and mesitylene. However, $\text{NHC-BH}_2\text{Mes}$ was no longer detected by NMR

Formation of observed species



Growth and stabilisation of the nanoparticles



Scheme 2. Top: Proposed mechanistic pathway for the formation of Cu^0 species and observed side products. Bottom: proposed pathway from Cu^0 species to NHC-stabilized NPs.

spectroscopy (see Supporting Information, Figures S6 and S7). Interestingly, the NPs had the same morphologies as in the experiment with a 1:1 ratio between $[\text{CuMes}]_n$ and NHC-BH_3 (Supporting Information, Figure S8D). This was highly suggestive that 2 equiv of TEMPO are able to scavenge 2 equiv of NHC-boryl radical. Besides, NHC was essential to the stabilization of the NPs, as the reaction conducted with 2 equiv of TEMPO but without NHC-BH_3 produced few nanoparticles with ill-defined shapes (Supporting Information, Figures S6 and S8C). Whereas NMR spectroscopy was neither sensitive nor discriminative enough, HRMS revealed new species: on using 4 equiv of TEMPO, the NHC-boryl radical/TEMPO adduct could be detected $[\text{C}_{36}\text{H}_{72}\text{N}_3\text{OB}+\text{H}]^+$, calcd: 574.58412, found: 574.58384; Supporting Information, Figures S9–S12).^[35] Therefore, the presence of a radical species (TEMPO) affected the ability of the NHC-borane to react with the copper precursor and to stabilize the nanoparticles.

To reconcile all these observations, we propose the radical pathway depicted in Scheme 2. After dismutation of $[\text{CuMes}]_2$ into Cu^0 and Cu^{2+} species (step I),^[36–38] the latter undergoes one Cu-C homoleptic bond cleavage leading to the generation of mesityl radical and regeneration of a mesitylcopper(I) complex (step II).^[39] This mesityl radical is keen to perform hydrogen abstraction from the initial NHC-BH_3 ,^[40] forming a NHC-boryl radical and mesitylene as byproduct (step III). Reaction of the NHC-boryl radical with mesitylcopper(I) complex, either by single-electron transfer or by homolytic substitution, would lead to the formation of the $\text{NHC-BH}_2\text{Mes}$ adduct and Cu^0 (step IV).^[43] In the presence of TEMPO initially introduced into the reaction medium, the NHC-boryl adduct was successfully trapped and detected by HRMS, and this is strong support for formation of the NHC-boryl radical. Although this mechanism rationalizes formation of both the NHC-mesitylborane adduct and mesitylene, the fact that the final experimental ratio of 3:7 between these byproducts is not 1:1 seems to indicate that the mesityl radical reacted with another hydrogen source or that a second pathway could also be responsible for the formation of NPs. Once Cu^0 species are generated in solution, they aggregate into NPs, which are stabilized by NHC ligands originating from the dissociation of NHC-borane adduct at 110°C , possibly catalyzed by the nascent Cu^0 NPs. Few NHC ligands are actually required to stabilize the Cu NPs. Indeed, with a diameter of 11.6 nm, they have about 10–15% of their Cu atoms on the surface. With an initial $\text{NHC-BH}_3/\text{Cu}$ ratio of three and assuming one NHC ligand for two surface copper atoms, only 1–3% of the initially introduced NHC-BH_3 must be converted to NHC, a minute amount, the disappearance of which is difficult to probe by ^1H or ^{11}B NMR spectroscopy.

Conclusion

We have reported the first example of colloidal synthesis of NHC-stabilized Cu NPs. These were straightforwardly prepared by using NHC-boranes as NHC source and mesitylcopper(I) as metal precursor. The role of the borane in NHC-BH_3 seems to be trapping of the mesityl radical, which releases Cu^0 species. The identification of the side products of the reaction suggests

that the formation of Cu^0 species involves a radical pathway. The nature of the metal–ligand bond at the NP surface was characterized by XPS, which showed that the interaction between the NPs and the carbene moiety is covalent. Functional Cu NPs are now available from this one-step synthetic route thanks to the rich modularity of NHCs. Furthermore, we expect this methodology to be suitable for the synthesis of NHC-stabilized nanoparticles of other transition metals.

Experimental Section

Unless stated otherwise, all syntheses and procedures were carried under inert gas (N_2 or Ar) in a glovebox (H_2O : ≤ 0.5 ppm, O_2 : ≤ 0.5 ppm) or on a Schlenk line in oven-dried glassware.

1,3-Didodecylimidazolium bromide

1,3-Didodecylimidazolium bromide was prepared according to a modified literature procedure.^[41] Imidazole (500 mg, 7.4 mmol) was dissolved in THF (5 mL) and the solution was added to a solution of sodium hydride (60% w/w, 324 mg, 8.1 mmol) in THF (5 mL) at 0°C . The ice bath was removed and the mixture was stirred for 1 h at room temperature. After dropwise addition of 1-bromododecane (3.5 mL, 14.7 mmol), the mixture was stirred at room temperature for at least 1 h before being heated at 70°C until completion of the reaction (at least 24 h). The solvent of the mixture was evaporated under reduced pressure. The residue was dissolved in dichloromethane and the solution filtered. The filtrate was evaporated under reduced pressure, the residue dissolved in diethyl ether, and the solution left at 4°C for 2 h. After collection by filtration, the precipitate was dried in vacuo to give the product as a white powder (2.75 g, 5.7 mmol). Yield: 77%. ^1H NMR (400 MHz, CDCl_3): δ = 10.88 (t, J = 1.3 Hz, 1H, N=CHN), 7.20 (d, J = 1.3 Hz, 2H, NCH=CHN), 4.36 (t, J = 7.4 Hz, 4H, N-CH_2), 1.92 (quint, J = 7.4 Hz, 4H, $\text{NCH}_2\text{CH}_2\text{C}$), 1.35–1.25 (m, 36H, aliphatic chain), 0.88 (t, J = 6.5 Hz, 6H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 137.70, 121.78, 50.29, 32.00, 30.44, 29.70, 29.60, 29.49, 29.43, 29.11, 26.37, 22.78, 14.22; HRMS calcd for $\text{C}_{27}\text{H}_{53}\text{N}_2^+$: m/z 405.4203; found: 405.4197.

1,3-Didodecylimidazol-2-ylidene borane (NHC-BH_3)

NHC-BH_3 was prepared according to a modified literature procedure.^[42] 1,3-Didodecylimidazolium bromide (2 g, 4.1 mmol) was dissolved in THF (20 mL) and the solution cooled to -78°C . A solution of potassium bis(trimethylsilyl)amide (1 M in THF, 4.3 mL, 4.3 mmol) was added. The mixture was stirred at -78°C for 1 h before addition of a solution of $\text{BH}_3\cdot\text{THF}$ (1 M in THF, 4.1 mL, 4.1 mmol). The cooling bath was removed and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and the solution filtered. The filtrate was evaporated under reduced pressure. The resulting yellow oil was purified by column chromatography on silica gel (eluent: pentane/dichloromethane 55/45) to give the pure product as a white powder (750 mg, 1.8 mmol). Yield: 44%. ^1H NMR (400 MHz, CDCl_3): δ = 6.79 (s, 2H, NCH=CHN), 4.09 (t, J = 7.6 Hz, 4H, NCH_2), 1.77 (quint, J = 7.6 Hz, 4H, $\text{NCH}_2\text{CH}_2\text{C}$), 1.35–1.15 (m, 36H, aliphatic chain), 0.88 (t, J = 6.5 Hz, 6H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 170.16, 118.80, 48.84, 32.04, 30.26, 29.75, 29.68, 29.62, 29.47, 29.32, 26.65, 22.81, 14.24; ^{11}B NMR (96 MHz, CDCl_3): δ = -37.3 (q, J = 85.7 Hz, BH_3); HRMS calculated for $\text{C}_{27}\text{H}_{52}\text{N}_2\text{BH}_3\text{Na}^+$: m/z 441.4356; found: 441.4347.

Copper NPs

Synthetic procedure for the Cu NPs shown in Figure 1: In a Schlenk tube, 0.3 mL of a 100 mM solution of [CuMes]₂ in toluene (18.3 mg, 0.1 mmol in 1 mL of toluene) was mixed with 0.9 mL of a 100 mM solution of NHC–BH₃ in toluene (43.3 mg, 0.1 mmol in 1 mL of toluene). The resulting solution (1.2 mL total) was stirred at toluene reflux temperature for 2.5 h, after which an aliquot was taken and analyzed by TEM. Additional synthetic details are given in the Supporting Information.

For NMR analysis, the reaction was conducted as follows: In a glovebox, an air-tight NMR tube was successively charged with [CuMes]₂ (5.5 mg, 0.03 mmol), NHC–BH₃ (39 mg, 0.09 mmol), and [D₈]toluene (600 µL). The NMR tube was then heated in an oil bath at reflux for 2.5 h (the solution rapidly turned deep red after few minutes of heating). The starting mixture and the crude mixture obtained after heating were analyzed by ¹H, ¹H{¹¹B}, and ¹¹B NMR spectroscopy.

Acknowledgements

The following partners are acknowledged for funding: Sorbonne Université, CNRS and Collège de France under ANR-10-IDEX-0001-02 PSL*. This work was supported by the LabEx MiChem and the Labex MATHSSE, both parts of French state funds managed by the ANR within the Investissements d'Avenir program under reference ANR-11-IDEX-0004-02. Denis Lesage is acknowledged for his expertise in mass spectrometry.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbene ligands • copper • nanoparticles • radical reactions • reaction mechanisms

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Manuscript received: April 2, 2019

Revised manuscript received: June 7, 2019

Accepted manuscript online: June 17, 2019

Version of record online: August 5, 2019