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Homogeneous oxidation reactions catalysed by in situ-generated triazolylidene copper(I) complexes

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Abstract

Four new Cu complexes bearing triazolylidene ligands 1-(R)-3-methyl-4-phenyl-1H-1,2,3-triazol-3-ium-5-yl: R = phenyl (**2a**), mesitylenyl (**2b**), propyl (**2c**), hexyl (**2d**) (NHC) were synthesised in high yields. Characterisation by spectroscopic and analytical methods confirmed the molecular composition of the complexes as NHC–Cu-I. The complexes **2(a–d)** bearing NHC wingtip variations were tested as in situ-generated catalysts for homogeneous oxidation catalysis with H_2O_2 as oxidant. The in situ technique was adopted for ease of application and to circumvent the poor stability of the complexes in solution. The results showed that the NHC–Cu-I complexes are capable of initiating oxidation reactions, yielding ketones/aldehydes as dominant products for the oxidation of alkanes under optimised reaction conditions, with complexes bearing aliphatic *N*-substituents showing the highest catalytic activities. Oxidation of toluene with **2c** resulted in a mixture of benzaldehyde and benzyl alcohol as the main products. Also, **2c** catalysed the oxidation of *n*-octane, yielding a mixture of mainly C-8 oxidation products with over 75% selectivity for the isomeric octanones. Analysis of regioselectivity indicated that the internal C_{sp^3}–H bonds of *n*-octane [especially C(2)] are more reactive than the terminal ones.

Introduction

The oxidation of saturated substrates via activation of unreactive bonds under mild catalytic conditions is still a challenging global problem to both industry and academia [1]. Over the years, first-row transition metal complexes have emerged as cheap and effective oxidation catalysts that are capable of operating under mild reaction conditions [2]. In particular, copper complexes bearing bulky organic ligands have shown great potential as homogeneous catalysts for the efficient oxidation of a wide range of substrates [3].

With regard to choice of ligand, *N*-heterocyclic carbenes (NHC) have become very prominent in organometallic chemistry and their metal complexes have made important contributions in catalysis. This is due to their ability to form stable covalent metal–ligand bonds and their ease of steric and electronic tuning through variation of the wingtip *N*-substituents of the azole ring [4]. Since the first cationic di-carbene $(NHC)_2$–Cu complex was reported by Arduengo [5] and later application of NHC–Cu complexes in catalysis by Woodward et al. [6], a great deal of catalytic and structural work in this area has continued to build on those foundations [7]. In spite of all the interest, the handling of NHC–Cu complexes is non-trivial, and concerns on the relative stability of "free" NHC–Cu have resulted in the development of in situ catalytic approaches as alternative methods. This technique was first reported in 2001 by Woodward, [6] from which a number of reports soon followed, all signifying that copper salts make better catalysts in the presence of NHC ligands [8–10]. Hence, in this report we present new NHC–Cu^I catalysts generated in situ for the oxidation of a range of substrates under mild reaction conditions.

Results and discussion

Synthesis of the triazolylidene Cu(I) complexes

We adopted the method of Son et al. [11] for the synthesis of the NHC–Cu complexes (**2**, Scheme 1). This is a very simple method akin to the well-established Ag_2O route for

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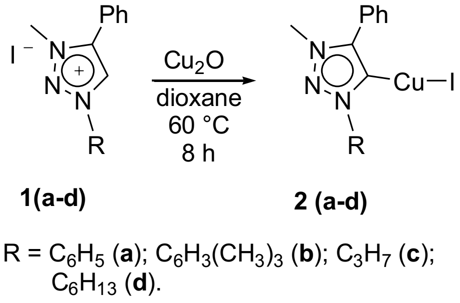


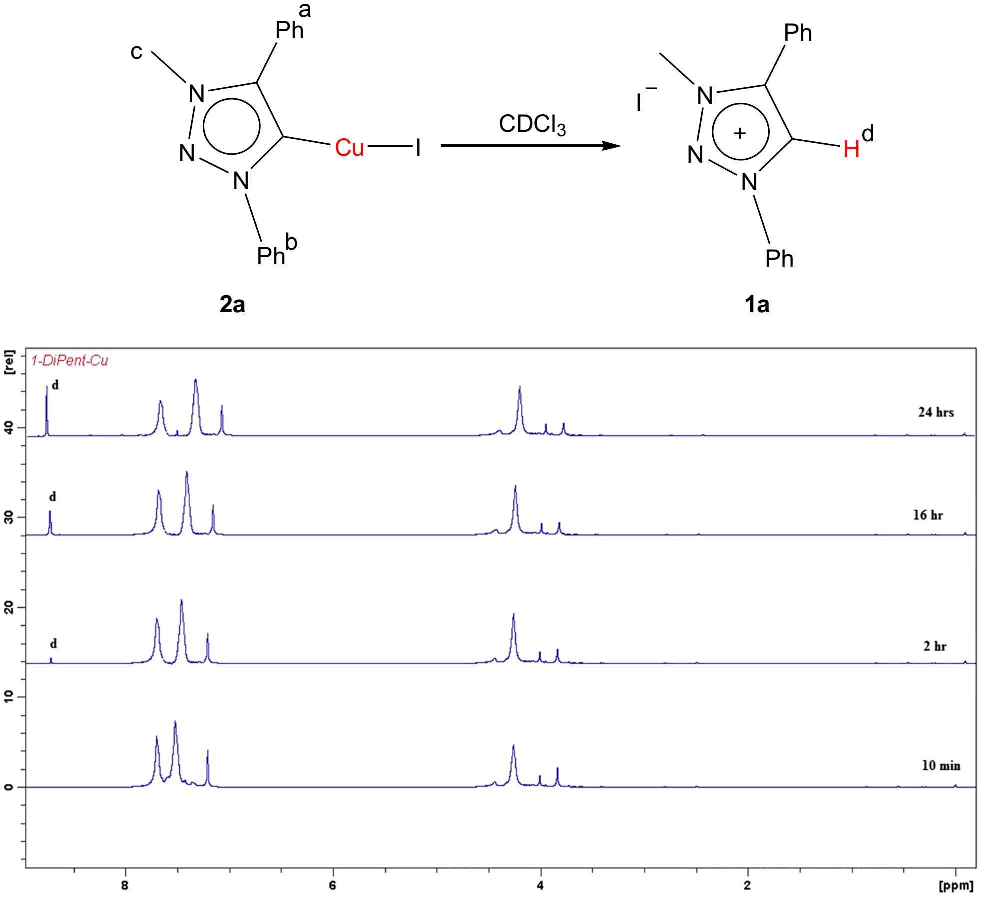
Scheme 1 Synthesis of the NHC–Cu-I complexes (**2a–d**) by the direct reaction of NHC (**1a–d**) with Cu_2O

the synthesis of NHC–metal complexes. Hence, the direct reaction of the proligands **1(a–d)** with Cu_2O in dioxane correspondingly led to the formation of complexes **2(a–d)**. Workup procedure and isolation of the complexes in pure form are also very straightforward and uncomplicated. Hence, at the end of each run, solids (mainly insoluble, unreacted Cu_2O) were simply filtered off and the clear filtrate evaporated to dryness, yielding circa 70% of analytically pure **2(a–d)**. All the complexes were isolated and characterised by ^{1}H and ^{13}C NMR spectroscopy, HRMS and EA, which all supported formation of complexes of the type NHC–Cu-I.

Attempts to crystallise **2** failed due to decomposition in solution to reform **1** and unidentified insoluble copper salts (vide infra). On this basis, a study of the stability and decomposition rate of **2** was conducted and monitored after indicated time (Fig. 1). Complex **2a** was used as representative for the study. In the solid state, complex **2a** was found to be air-sensitive, transforming completely into a green insoluble solid within a few minutes. Under a N_2 atmosphere, no noticeable decomposition was observed, however, after 16 h in the same atmosphere, a degree of decomposition was recorded.

In solution, the decomposition of **2a** noticeably depends on the degree of solvent ($CDCl_3$) dryness and time in solution. A time-dependent study was set up, and the result is shown in Fig. 1. The progress of the decomposition was monitored by ^{1}H-NMR spectroscopy (by monitoring the signal of the triazolium C-2 proton, marked *d* in Fig. 1). The data obtained showed strong time dependence of the decomposition of **2a**, such that up to 2 h in solution there was not much decomposition, however, after 8 h, about 10% of **2a** was transformed back into **1a**, the starting triazolium salt. No signs of **2a** were observed after 24 h, suggesting

Fig. 1 Time-dependent ^{1}H NMR spectral changes of **2a** in $CDCl_3$



complete decomposition. This was also confirmed by ^{13}C-NMR (loss of the low field resonance at 168 ppm). The poor stability of complexes **2(a–d)** may be synthetically exploited as carbene transfer agents en route to the synthesis of NHC-transition metal complexes, similar to the well-established Ag_2O route.

Oxidation of cyclohexane

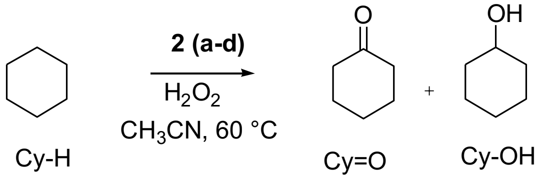
A preliminary attempt to isolate the NHC–Cu-I complexes and apply them as molecular catalysts for oxidation reactions was unsuccessful due to their decomposition, leading us to adopt in situ catalytic methods instead. Hence, the in situ-generated NHC–Cu-I complexes were evaluated as catalysts for oxidation catalysis. The first set of results were obtained on cyclohexane as a model substrate for the optimisation of reaction conditions, and the results are presented in Table 1. Entries 1 and 2 confirm the necessity for a transition metal in this catalytic study as no products were observed for a control experiment in the absence of Cu_2O (entry 1, Table 1). However, addition of the metal Cu_2O revealed vigorous oxidation products (entry 2) within 4 h of reaction, indicating its significance as the catalytic centre in the activation of cyclohexane. Furthermore, as revealed by entry 3, it takes a combination of both Cu_2O and **1a** to induce 27% cyclohexane conversion to the product mixture of cyclohexanone–cyclohexanol, so-called ketone–alcohol (K–A) oil. The K–A oil is an important feedstock for the industrial production of nylon. These results point to the direct influence of the Cu/triazolium ligand combination in the catalytic process.

The extent of substrate conversion was slightly improved when the reaction temperature was increased to 80 °C, suggesting the positive effect of temperature in this catalytic reaction (entry 4). The study was limited to 80 °C due to volatility of both the substrate and the solvent from the unpressurised reaction set-up. Increasing the amount of Cu_2O showed no positive effects on catalytic activity; however, a notable increase in ketone production was observed (entry 5), raising the K/A ratio.

On comparison of structure/activity relationships of the in situ-generated catalysts in this series, it is clear that due to steric reasons, the two complexes bearing bulky aromatic wingtip *N*-substituents **2(a–b)** showed lower catalytic activities (31 and 21% conversions, entries 5 and 10) than **2(c–d)** functionalised with aliphatic *N*-substituents (39 and 38% conversions, entries 11 and 12), respectively.

The addition of acids as promoters has been shown to improve substrate conversion in numerous oxidation reactions [12–14]. However, in this study, addition of acids (entries 7 and 8) rather retarded the oxidation reaction resulting in poor conversions, which is most likely due to catalyst decomposition in the harsh acidic environments.

Table 1 Oxidation of cyclohexane with in situ-generated **2**



Entry[a]	Catalyst NHC:Cu_2O	Temperature	Conversion (mol%)[b]	Selectivity (mol%)[c]	
				Cy=O	Cy–OH
1	1:0	50	–	–	–
2	0:1	50	12	85	15
3	1:1	50	27	39	61
4	1:1	80	31	32	68
5	1:2	80	33	48	52
6	2:1	80	31	28	72
7[d]	1:1.1	80	11	42	58
8[e]	1:1.1	80	14	39	61
9[f]	1:1.1	80	7	28	72
10[g]	1:1.1	80	21	47	53
11[h]	1:1.1	80	39	37	63
12[i]	1:1.1	80	38	39	61

[a] Reaction conditions (unless stated otherwise): Substrate (1.0 mol), **2(a)** (10 mmol, 1 mol% vs. substrate), H_2O_2 (10.0 mol), MeCN (5 mL), indicated temperature, 24 h

[b] Conversion = conc. products/initial conc. of cyclohexane × 100

[c] Selectivity = moles of CyO/(CyOH + CyO) × 100

[d] HCl added (1.0 mol)

[e] Acetic acid added (1.0 mol)

[f] TBHP used (instead of H_2O_2)

[g] **2(b)**

[h] **2(c)**

[i] **2(d)**

In an effort to relate the kinetics of the oxidation reaction with the lifespan of the generated catalyst, a time-dependent study was conducted, with the results presented in Fig. 2. It is clear that the catalytic conversion of cyclohexane to products is time-dependent with no induction period and the in situ-generated catalyst achieved a maximum production of 39% at 20 h reaction time. The initial rate tapered off after 4 h of reaction and then levelled off after a period of 16 h which matches the onset of gradual catalyst decomposition observed by time-dependent NMR study (Fig. 1).

It is also important to determine the active species in this catalytic study; hence, a stoichiometric amount of a radical scavenger (diphenylamine, Ph_2NH) was added to the cyclohexane oxidation catalysis set-up. Ph_2NH was observed to suppress the catalyst activity, indicating the

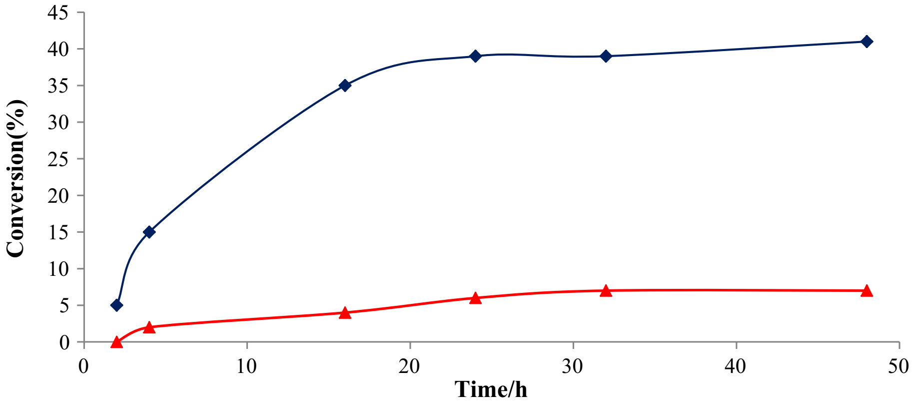


Fig. 2 Effect of reaction time on cyclohexane oxidation with in situ-generated **2a** [black diamond] conversion; [Red triangle] conversion (A) when Ph_2NH radical scavenger was added. Reaction conditions: same as in Table 1. (Color figure online)

Table 2 Comparative representation of oxidation of cyclohexane by a variety of Cu-based catalyst systems[a]

Entry	Catalytic system	Conversion (mol%)	References
1[b]	$[Cu^I(bpy)_2]$/pyridine	15	[14]
2	Cu powder/pyridine/Ac	5	[15]
3[c]	$([Cu_4(tea)–(BOH)_4(m–O)]^{2+})$	38	[16]
4[d]	Cu^I/TMPA	53	[17]
5[e]	Cu^I/(R,R)-BPBP	56	[18]
6	**2c**	39	This work

[a] All reactions were performed in MECN using H_2O_2 as an oxidant under mild reaction conditions

[b] *bpy* 2,2′-bipyridine

[c] *tea* trimethylamine

[d] *TMPA* (tris(2-pyridylmethyl)amine)

[e] *BPBP* ((2R,2′R)-1,1′-bis(2-pyridylmethyl)-2,2′-bipyrrolidine)

involvement of radical pathways in the oxidation reaction. Hence, we conclude that the in situ-generated catalytic systems based on a mixture of NHC/Cu_2O rely on $Cu^{+/2+}$ as the active species generated in solution from the gradual decomposition of **2(a–d)** which act as reservoirs of Cu^+ ions.

To put these results into context with closely related literature, comparative reports are summarised in Table 2. The group of Sawyer [14] reported good conversions of up to 15% with $[Cu^I(bpy)_2]$/pyridine catalyst mixture which followed the very low conversions (up to 5%) obtained by Barton et al. [15], using combined Cu powder/pyridine/acetic acid catalyst mixture. Having observed steric influence of ancillary ligands in the oxidation of cyclohexane, Pombeiro et al. [16] reported efficient conversions (up to 38%) for systems using a tetranuclear Cu cluster (entry 3). Recently, Siegler and Garcia-Bosch [17] reported a highly active and selective copper complex (entry 5) as a catalyst for the mild peroxidative activation and functionalisation of cyclohexane (conversions up to 56%) to the K–A oil product mixture.

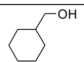
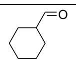
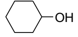
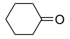
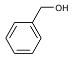
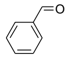
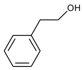
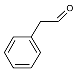
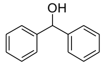
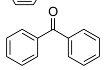
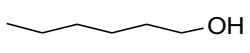
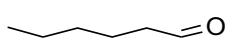
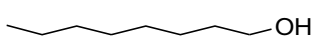
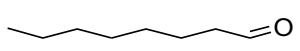
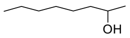
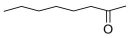
Oxidation of toluene

Toluene is an aromatic hydrocarbon commonly adopted as a safer and environmentally benign alternative to benzene and widely used as an organic solvent in laboratory and industrial applications. Hence, it is important to study its stability and tolerance of oxidising environments in the presence of transition metal salts with proven potential to activate the C–H bonds of hydrocarbon substrates. Also, the product of toluene oxidation, benzaldehyde is a desirable starting material due to its importance as a building block for the fine chemicals and pharmaceuticals industry. However, the oxidation of toluene is reported to suffer from low selectivity to the desired aldehyde due to the possibility of dual activation of both the methyl and/or aromatic C–H bonds depending on various reaction conditions (type of catalyst, solvent, oxidant, etc.). In this study with **2c** as catalyst, the oxidation of toluene resulted in a mixture of oxidation products (total conversion up to 11%) with benzaldehyde (PhCHO, 62%) and benzyl alcohol ($PhCH_2OH$, 29%) as the main products and o/m/p-cresols as minor products, which is inline with literature reports for similar studies [18–20].

Oxidation of *n*-octane

The results obtained with **2c** as the catalyst produced 22% total conversion of the substrate selectively to a mixture of C-8 oxidation products with 80% total selectivity to octanones. GC analysis of the product stream indicated no evidence of cracking or heavy products. Further analysis of the regioselectivity parameter showed that internal carbons [especially C(2)] are more reactive than terminal ones and only 8% terminal C(1) activation products were observed. Similarly, 2-octanone (ca. 38%) is the most abundant product in the stream. This is inline with observations that are numerously reported in the literature indicating 2-octanone as the more probable product of *n*-octane oxidation [21, 22].

Table 3 Oxidation of alcohols catalysed by **2c** with H_2O_2 as oxidant[a]

Entry	Substrate	Product	Conversion (%)
1			88
2			91
3			73
4			76
5			61
6			35
7			38
8			68

[a]Reaction conditions: same as in Table 1.

Oxidation of alcohols

Finally, complex **2c** was tested as a catalyst for the in situ homogeneous oxidation of alcohols to the corresponding carbonyl products using H_2O_2 under optimised reaction conditions. The results summarised in Table 3 revealed that phenolic and benzylic alcohols are more reactive than the aliphatic variants. This observation, which is attributed to activation of the C–OH bond in the cyclic hydrocarbons and aromatic systems, is consistent with related results reported in the literature. [23–27] Also, the oxidation of cyclohexanol (entry 2) with **2c** provided the highest conversion (91%).

Oxidation of linear alcohols resulted in lower conversions (entries 6, 7 and 8), whilst the primary alcohols are much less reactive than the secondary (2-octanol), which is consistent with reported observations suggesting that reactions at the secondary carbon positions of aliphatic hydrocarbons are more facile than terminal/primary carbons.

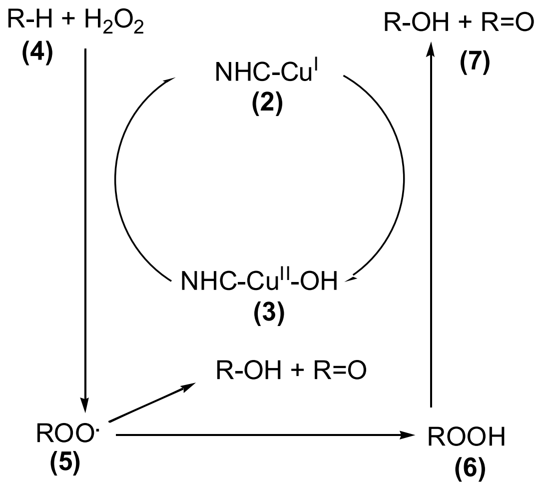
Mechanistic considerations

On the basis of all the experimental data presented herein, it is proposed that these alkane oxidation reactions progress via the formation of alkyl hydroperoxide (ROOH) as the major product. As was shown in this study, the addition of a radical scavenger (Ph_2NH) inhibited the oxidation of cyclohexane (Fig. 2), affirming a radical pathway for the oxidation process. The full understanding of the mechanistic steps involved in this pathway has been the main subject of many research publications [17, 28–31]. Although researchers are still debating some of the mechanistic steps, a radical mechanism is now well established for these oxidation reactions. In this study, we present a simplified mechanism (Scheme 2) that accounts for the ketone and alcohol products we observed. The proposed mechanism involves the interaction of catalytically active Cu(I) species with H_2O_2 to generate a hydroxyl radical ($HO^{\cdot}$) which then activates the substrate alkane (R-H, **4**) via proton abstraction, leading to a highly activated alkyl radical ($R^{\cdot}$) which further reacts with molecular oxygen (O_2) present in the reaction medium to form an alkyl peroxyl radical ($ROO^{\cdot}$, **5**) [17]. We believe, this is the rate-determining step that is curtailed by a radical scavenger such as Ph_2NH. The alkyl peroxyl radical may undergo dismutation to yield the alcohol and ketone products or undergo reduction into the major product, alkyl hydroperoxide (ROOH, **6**).

The ROOH decomposes to the corresponding alcohol (R-OH) and ketone (R = O, **7**) products depending on reaction conditions, and it is also often reduced to R-OH and R=O by the addition of suitable reducing agents such as PPh_3, in a method developed by Shulpin et al. [29].

Conclusion

The chemistry of a series of easily prepared NHC–Cu-I complexes was presented. These complexes are unstable both in the solid state and in solution, decomposing within a 24 h period. We believe that their stability may be improved by the utilisation of bulky and electron-donating wingtip substituents such as mesitylenyl or adamantyl instead of simple methyl and phenyl groups. As in situ-generated copper catalysts, all the complexes were effective for the homogeneous oxidation of alkanes and alcohols under mild reaction conditions and at low concentrations. A reaction pathway involving alkyl peroxyl radicals was proposed because of the



Scheme 2 Simplified reaction mechanism for the oxidation of an alkane by the NHC–Cu^I catalysts

negative effects of a radical scavenger and the product selectivity of the systems. Given the promising catalytic results obtained with these new NHC–Cu-I systems, further work will be devoted to the development of multidentate NHC ligands (with potential auxiliary donor atoms) also aimed at achieving bench-top stability and furthering the range of applications for the complexes.

Experimental section

General

All the reagents were purchased from Sigma-Aldrich and used as received. All the solvents (acetonitrile, tetrahydrofuran, diethyl ether and hexanes) were purchased from Merck and purified using a commercially available MBraun MB-SP Series solvent purification system equipped with activated alumina columns. Unless otherwise stated, all syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. Triazoles and their corresponding salts were synthesised as described in published literature and characterisation data are consistent with reported literature values [32, 33]. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operated at ambient temperature with δ values reported in ppm referenced to Me_4Si as the internal standard for both ^1H and ^{13}C NMR data. Elemental analysis (CHN) was performed on a LECO CHNS elemental analyser, and the mass spectrometric data were collected on a Bruker Daltonics (micro TOF) instrument.

General procedure for synthesis of the complexes (2a–d)

Procedure for the synthesis of NHC–Cu complexes [11]: triazolium salt (0.3 mmol) and Cu_2O (0.4 mmol) in 4 mL of dioxane were heated at 60 °C for 8 h. The reaction mixture was then cooled to room temperature, and the unreacted Cu_2O was removed by filtration. The remaining solvent was evaporated to yield precipitates of the complex. Characterisation data are:

(2a) White solid product (0.41 g, 71%). ^1H-NMR ($CDCl_3$, 400 MHz): δ 7.1–7.6 (*bm*, 10H, Ar), 4.7 (*s*, 3H, N-CH_3), $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.6 MHz): δ 168.4, 148.5, 129.9, 129.7, 129.1, 128.7, 128.3, 126.8, 125.0, 121.0, 120.5, 117.6, 37.9. TOF MS$^+$ (ESI) *m/z* for $C_{15}H_{13}CuN_3$ [M$^+$-I]: calculated: 298.0, found: 298.0. Anal. (%) calc. for ($C_{15}H_{13}CuIN_3$, 425.7): C, 42.3; H, 30.0; N, 9.8; found: C, 42.3; H, 3.0; N, 9.8.

(2b) Greenish solid product (0.38 g, 68%). ^1H-NMR ($CDCl_3$, 400 MHz): δ 7.5–7.7 (*m*, 5H, Ar), 6.0 (*s*, 2H, Ar), 4.3(*s*, 3H, N–CH_3), 2.0(*bs*, 9H, 3CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.6 MHz): δ 166.5, 142.7, 131.9, 131.5, 130.5, 129.8, 129.6, 129.6, 129.3, 128.0, 121.9, 38.0, 22.3. TOF MS$^+$ (ESI) *m/z* for $C_{18}H_{19}CuN_3$ [M$^+$-I]: calculated: 340.0, found: 340.0. Anal. (%) calc. for ($C_{18}H_{19}CuIN_3$, 466.9): C, 46.2; H, 4.0; N, 8.9; found: C, 46.2; H, 4.1; N, 9.0.

(2c) Greenish solid product (0.53 g, 73%). ^1H-NMR ($CDCl_3$ 400 MHz): δ 7.2–7.4 (*m*, 5H, Ar), 4.7 (*m*, 2H, CH_2), 4.2 (*s*, 3H, N–CH_3), 1.9 (*m*, 2H, CH_2), 0.9 (*t*, 3H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.6 MHz): δ 165.0, 143.3, 131.9, 130.9, 129.7, 129.6, 129.4, 121.8, 38.7, 27.4, 13.9. TOF MS$^+$ (ESI) *m/z* for $C_{12}H_{15}CuN_3$ [M$^+$-I]: calculated: 264.0, found: 264.1. Anal. (%) calc. for ($C_{12}H_{15}CuIN_3$, 390.9): C, 36.8; H, 3.9; N, 10.7; found: C, 36.8; H, 3.9; N, 10.7.

(2d) Greenish solid product (0.86 g, 75%). ^1H-NMR ($CDCl_3$ 400 MHz): δ 7.6–7.8 (*m*, 5H, Ar), 4.7 (*m*, 2H, CH_2), 4.3 (*s*, 3H, N–CH_3), 2.1 (*m*, 2H, CH_2) 1.4–1.5 (*m*, 6H, 3CH_2), 0.9 (*t*, 3H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.6 MHz): δ 166.8, 144.5, 132.90, 130.8, 130., 130.02, 124.0, 55.3, 39.7, 32.3, 30.35, 27.0, 23.5, 14.4. TOF MS$^+$ (ESI) *m/z* for $C_{15}H_{21}CuN_3$ [(M$^+$-I) + 2Li]: calculated: 320.1, found: 320.2. Anal. (%) calc. for ($C_{15}H_{21}CuIN_3 + 2CH_3CN$, 515.1): C, 44.2; H, 5.3; N, 13.6; found: C, 44.2; H, 5.3; N, 11.5.

General procedure for catalytic reactions

The oxidants H_2O_2 (30%) and TBHP (70%) were, respectively, purchased from Aldrich and DLD Scientific and used as supplied. A typical oxidation reaction was carried out in a 2-neck round-bottom flask fitted with an efficient reflux condenser operating in air as follows: an appropriate amount of the precursor salt **1(a–d)** was treated with a stoichiometric amount of Cu_2O in CH_3CN (5 mL) for the indicated temperature and time. The substrate and oxidant were then added, and the mixture was heated at the indicated temperature for the required time. The product was analysed after the required time period, an aliquot of sample was removed using a Pasteur pipette and filtered through a cotton wool plug, after which 0.5 µL of the aliquot was injected into the GC for analysis and quantification. 2,4,6-Trichlorobenzene was used as the internal standard, and all experiments were conducted with an Agilent Technology 6820 GC System equipped with a flame ionisation detector (FID), and an Agilent DB-Wax column with a length of 30 metres, inner diameter of 0.25 mm and a thickness of 0.25 mm.

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