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Alkoxy-1,3,5-triazapentadien(e/ato) Copper(II) Complexes: Template Formation and Applications for the Preparation of Pyrimidines and as Catalysts for Oxidation of Alcohols to Carbonyl Products

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Abstract: Template combination of copper acetate ($Cu(AcO)_2{\cdot}H_2O$) with sodium dicyanamide ($NaN(C{\equiv}N)_2$, 2 equiv) or cyanoguanidine ($N{\equiv}CNHC(=NH)NH_2$, 2 equiv) and an alcohol ROH (used also as solvent) leads to the neutral copper(II)–(2,4-alkoxy-1,3,5-triazapentadienato) complexes [Cu{*N*H=C(OR)NC(OR)=*N*H}$_2$] (R = Me (**1**), Et (**2**), *n*Pr (**3**), *i*Pr (**4**), $CH_2CH_2OCH_3$ (**5**)) or cationic copper(II)–(2-alkoxy-4-amino-1,3,5-triazapentadiene) complexes [Cu{*N*H=C(OR)NHC(NH_2)=*N*H}$_2$]-$(AcO)_2$ (R = Me (**6**), Et (**7**), *n*Pr (**8**), *n*Bu (**9**), $CH_2CH_2OCH_3$ (**10**)), respectively. Several intermediates of this reaction were isolated and a pathway was proposed. The deprotonation of **6**–**10** with NaOH allows their transformation to the corresponding neutral triazapentadienates [Cu{*N*H=C(OR)NC(NH_2)=*N*H}$_2$] **11**–**15**. Reaction of **11**, **12** or **15** with acetyl acetone (MeC(=O)CH_2C(=O)Me) leads to liberation of the corresponding pyrimidines NC(Me)CHC(Me)NCNHC(=NH)OR, whereas the same treatment of the cationic complexes **6**, **7** or **10** allows the corresponding metal-free triazapentadiene salts {NH_2C(OR)=NC(NH_2)=NH_2}(OAc) to be isolated. The alkoxy-1,3,5-triazapentadiene/ato copper(II) complexes have been applied as efficient catalysts for the TEMPO radical-mediated mild aerobic oxidation of alcohols to the corresponding aldehydes (molar yields of aldehydes of up to 100% with >99% selectivity) and for the solvent-free microwave-assisted synthesis of ketones from secondary alcohols with *tert*-butylhydroperoxide as oxidant (yields of up to 97%, turnover numbers of up to 485 and turnover frequencies of up to 1170 h^{-1}).

Keywords: copper · heterocycles · oxidation · template synthesis · triazapentadiene

Introduction

Compounds containing the cyano (C≡N) moiety (e.g., nitriles, dicyanamide or cyanoguanidine) are well-recognised substrates for the synthesis of many nitrogen-containing products.[1] Usually the cyano group is rather inert and its activation is required upon coordination to a metal centre or introduction of a strong electron-withdrawing group.[1b–d] Triazapentadienes (tap), HN=C(R)-NH=C(R′)-NH_2, are important products of cyano-containing substrate transformations, which recently have been intensively studied and reviewed.[2–5] These compounds are of pharmaceutical significance[6] and are used as building blocks for further synthesis of, for example, triazines and oligonitriles.[2c]

The reported methods of preparation of tap by organic synthesis are usually based on the Ley and Muller procedure from amidine and *N*-imidoyl chloride,[2b,7a] amination of *N*-imidoylimidoates,[3c] desulfurising amination of *N*-thiobenzoylbenzamidines,[7b] amination of nitriles bearing strong electron-withdrawing groups[7c] or interaction of perfluoro-5-aza-4-nonene with primary amines.[3a,4,7d] Generally these organic syntheses are rather complicated, restricted to a few particular substrates, and the thus prepared free tap is frequently unstable and undergoes hydrolysis[8a] or cyclisation.[2b,8b]

Possible alternatives to the organic syntheses of tap are provided by metal-mediated reactions, and known routes include decomposition of 1,3,5-triazine,[9] oxidative addition of organonitriles and ammonia by means of solvothermal conditions[10] and condensation of protonated nucleophiles (e.g., methanol or pyrazole) with the dicyanamidate (dca) anion[11] or cyanoguanidine and its derivatives.[12] These template reactions are simple, and the formed tap ligands can

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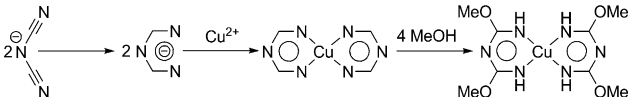
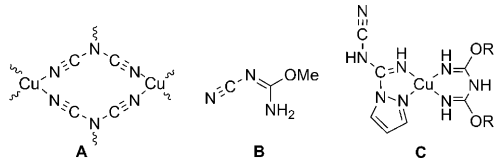
be stabilised by coordination, and are thus preserved and can be used for further synthesis.

Among the one-pot template syntheses,[11,12] those with dicyanamidate salts or cyanoguanidine, as cheap and available starting materials, are very attractive, but up to now the number of complexes (and corresponding ligands) synthesised in this way has been rather limited. Moreover, the earlier proposed[11b] pathway of this transformation (Scheme 1)



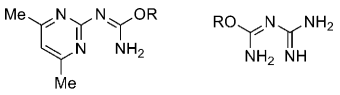
Scheme 1. Proposed mechanism of the template copper(II)–triazapentadienato complex formation.[11b]

looks rather questionable. The formation of the conjugated closed π system in the open dca anion and then its chelation to a Cu ion (Scheme 1) is not probable: the anion is significantly linear and without preliminary nucleophilic attack (with corresponding protonation) does not tend to form the metallacycle. Besides, other possible intermediates or by-products, including the rutile-related coordination polymer $[Cu(dca)_2]_n$ **A**,[13a] (methoxycarbimido)cyanoamine **B**[11f] and complex **C**[11f] (Scheme 2), were isolated and structurally characterised. Hence, the mechanism of the formation of the copper(II)–alkoxy–tap complexes looks to be more complicated and further detailed investigation would be desirable.



Scheme 2. Other reported possible intermediates or by-products.[11f,13a]

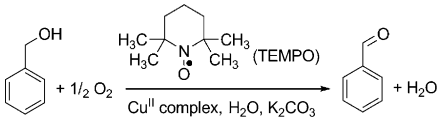
On a different note, a current interest of our group concerns the metal-mediated syntheses of valuable organic compounds and, for example, Δ^4-1,2,4-oxadiazolines,[14a] amidines,[14b,c] carboxamides,[14d] 1,2,4-oxadiazoles,[14e] oxazolines,[14c] heterodiazadienes,[14f] tap,[15] acetyl amides,[15a] tetrazoles,[14h] ketoimines[14i] and oxadiazolines[14j] were prepared from C≡N-containing starting materials. Another target in the search for new metal-mediated synthetic routes is pyrimidines, an important class of heterocycles that have been used as drugs of wide action.[16] Known routes to prepare pyrimidines usually involve condensation of 1,3-dicarbonyl compounds (and synthetic equivalents) with amines, amidines or amidinium salts.[16,17] However, examples of pyrimidines with alkoxy substituents of the type depicted in Scheme 3a are rather scant, and it seems there is only one known method for their preparation. Thus, 2-alkoxyamidino-4,6-dimethylpyrimidines were prepared by reaction of *N*-amidino-*O*-alkylisourea hydrochloride with acetylacetone in



Scheme 3. a) Pyrimidines and b) triazapentadienes discussed in this work.

the presence of sodium ethanolate. However, the reaction time is rather long (ca. 27–103 h) with low/modest yields (up to 14–55%).[18] As a result, the search for further preparative methods is worth exploring.

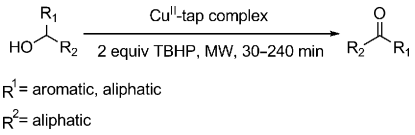
Copper complexes are known to be oxidation catalysts, for example, of alcohols into valuable carbonyl products.[19] Although a number of alcohol oxidation protocols is available, many of them involve stoichiometric heavy-metal oxidants or suffer from a low selectivity.[20] Furthermore, high catalyst loadings, the application of expensive catalysts and/or use of organic solvents or costly ionic liquids are frequently needed.[19,20] Recently some efficient systems involving both copper catalysts and a nitroxyl radical (e.g., 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO)) have been developed for the catalytic aerobic oxidation of primary alcohols to the corresponding aldehydes (Scheme 4).[21] However, the



Scheme 4. Selective oxidation of benzyl alcohol to benzaldehyde in water.

search for an efficient catalytic system under mild conditions in aqueous media still continues.[22] We have shown that Cu^{II} complexes of the related azoderivatives of β-diketones catalyze the aerobic oxidation of benzylic alcohols to the corresponding aldehydes in aqueous media.[22e] Moreover, it was also recently found that 2,4-methoxy(or ethoxy)–tap complexes effectively catalyze the microwave (MW)-assisted peroxidative oxidation of secondary alcohols to the corresponding ketones with *tert*-butylhydroperoxide (TBHP) as oxidant (Scheme 5).[12g] The extension of these studies to other tap–copper(II) complexes would also be desirable for comparative purposes and to show the generality of the systems.

Consequently, the main goals of the current work are 1) to expand the family of triazapentadiene(ato) complexes prepared by the template integration of alcohols with dicyanamide or cyanoguanidine, 2) to get insight into the path-



Scheme 5. MW-assisted oxidation of secondary alcohols to ketones catalyzed by copper(II)–triazopentadiene(ato) (tap) complexes.

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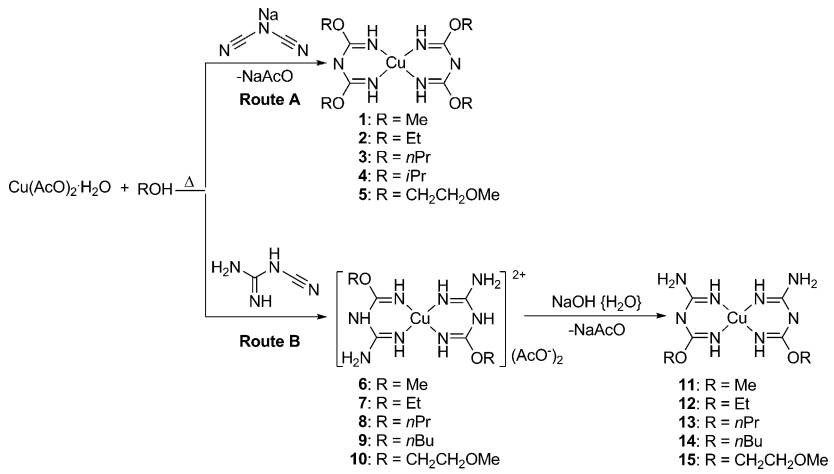
ways of this transformation, 3) to design copper(II)-mediated synthetic routes to pyrimidines and triazapentadienes, and 4) to study the catalytic potential of the synthesised complexes for the selective aerobic oxidation of primary and secondary alcohols to the corresponding carbonyl-containing products.

Results and Discussion

Synthesis of alkoxy-1,3,5-triazapentadienato–Cu^{II} complexes: For the preparation of (1,3,5-triazapentadienato)Cu^{II} complexes containing alkoxy substituents, a modified one-pot template synthesis, reported previously for the methanol(ethanol, pyrazole)–dicyanamidate[11] or methanol-(ethanol)–cyanoguanidine[12] integration at a Cu^{II} centre, was employed.

Cu^{II}-mediated coupling between alcohols and dicyanamidate: The previously reported syntheses of alkoxytriazapentadienate complexes involved copper(II) nitrates,[11a,b,d–g] perchlorates[11c,d,f] or tetrafluoroborates[11c] as starting materials. We found that the use of copper(II) acetate allows the procedure to be simplified and makes it more general. Thus, the reaction of $Cu(OAc)_2{\cdot}H_2O$ (1 equiv) with sodium dicyanamide (2 equiv) in neat ROH at reflux or with heating (temperature depending on the boiling point of the used alcohol) for approximately 12 h affords (91 to 72% yields) copper(II)–(2,4-alkoxy-1,3,5-triazapentadienato) complexes [Cu{*N*H=C(OR)NC(OR)=*N*H}$_2$] (R = Me (**1**), Et (**2**), *n*Pr (**3**), *i*Pr (**4**), $CH_2CH_2OCH_3$ (**5**)), which are soluble in the reaction mixture (partly soluble for R = Me), and a colourless precipitate of sodium acetate (Scheme 6, Route A). The contamination of the complexes with NaAcO (due to its partial solubility) can be easily removed by washing several times with water after solvent removal under vacuum. Further recrystallisation of the product (see the Experimental Section) allows the pure compounds **1**–**5** to be isolated.



Scheme 6. Syntheses of **1**–**15**.

Complexes **1**–**5** are highly soluble in organic solvents and insoluble in water. As expected, the solubility in unpolar solvents increases with the growth of R, for example, complexes containing *n*-propoxy moieties are soluble even in *n*-hexane. Compounds **1**[11a–c] and **2**[11g] were previously reported, and their authenticity was confirmed by IR spectroscopy, electrospray mass spectrometry (ESI-MS$^+$) and elemental analyses. The new complexes **3**–**5** were characterised by elemental analyses, ESI-MS$^+$ and IR spectroscopy, and complexes **4** and **5** additionally by single-crystal X-ray diffraction (see below). The ESI-MS$^+$ spectra of **1**–**5** display peaks from the $[M+H]^+$ ions. The IR spectra lack the ν(C≡N) stretches, and display strong ν(C=N) and δ(N–H) bands of the newly formed C=NH imine moiety in the respective ranges of 1576–1607 and 1528–1534 cm^{-1}, and ν(N–H) vibrations in the 3360–3225 cm^{-1} range, in agreement with the corresponding values of the known (1,3,5-triazapentadiene/ato)Cu^{II} complexes.[3d,4,10–12]

Cu^{II}-mediated coupling between alcohols and cyanoguanidine: A synthetic strategy similar to that utilised for the synthesis of compounds **1**–**5** but using cyanoguanidine instead of sodium dicyanamide was applied for the preparation of 2-alkoxy-4-amino-1,3,5-triazapentadiene complexes [Cu{*N*H=C(OR)NHC(NH$_2$)=*N*H}$_2$](AcO)$_2$ (R = Me (**6**), Et (**7**), *n*Pr (**8**), *n*Bu (**9**), $CH_2CH_2OCH_3$ (**10**)) (Scheme 6, Route B). As in the previous case, neat alcohol acts as both solvent and reactant, the temperature of the reaction (80 to 95 °C) depends on the boiling point of the alcohol and the typical reaction time is 24 h. Complexes **6**–**10** precipitate from the reaction mixture and are isolated by filtration (yields of 82–63%).

Their elemental analyses are consistent with the proposed formulations; the ESI$^+$-MS spectra contain $[M-2(AcO)-H]^+$ as the most intense peak with the characteristic isotopic distribution. In the IR spectra, ν(C≡N) of the starting cyanoguanidine has disappeared, while ν(N–H) for the newly formed C=NH imine moiety emerges in the 3435–3250 cm^{-1} range with the corresponding δ(N–H) at approximately 1556–1544 cm^{-1}. Two strong or very strong C=N vibrations appear in the 1627–1600 cm^{-1} range, with typical values for both symmetric [1662–1598 cm^{-1} ν(C=N)] and asymmetric [1665–1605 cm^{-1} ν(C=N)] (1,3,5-triazapentadiene)Cu^{II} complexes.[4,11,12] The medium intensity/weak stretches in the 2968–2827 cm^{-1} range are characteristic[23a] of ν_s(C–H) and ν_{as}(C–H).

Treatment of the aquasoluble compounds **6**–**10** with an excess amount (20 equiv) of sodium hydroxide in water led to the precipitation of the cor-

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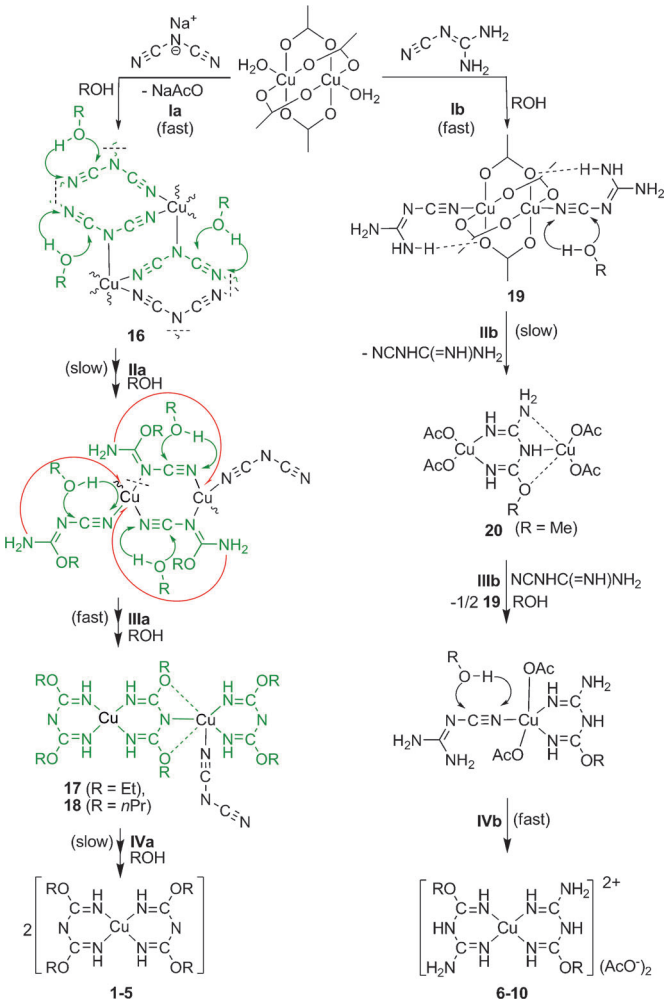
responding neutral triazapentadienate complexes [Cu{*N*H=C(OR)NC(NH$_2$)=*N*H}$_2$] (R = Me (**11**), Et (**12**), *n*Pr (**13**), *n*Bu (**14**), $CH_2CH_2OCH_3$ (**15**)) (Scheme 6, Route B), which were then separated by filtration, washed with a sodium hydroxide solution and with distilled water to eliminate the traces of sodium acetate contamination. The IR spectra of these complexes contain two strong or very strong C=N vibrations due to the C=NH imine groups in the 1622–1609 cm^{-1} range. The corresponding ν(N–H) are observed at 3476–3267 cm^{-1}, while δ(N–H) appear at approximately 1589–1536 cm^{-1}. Compounds **5**–**8**, **10**–**13** and **15** were also characterised by UV/Vis spectroscopy (Figure S1 in the Supporting Information). The crystal structure of **11** is described below.

Pathway studies

Reaction with dicyanamidate: Over the course of the synthesis of the 2,4-alkoxy-1,3,5-triazapentadienato complexes **1**–**5** (Scheme 6), a green precipitate was formed within the first 10–20 min. Its treatment with water and methanol allowed the removal of the coprecipitated sodium acetate and the overall formulation of the thus purified compound **16** was deduced from elemental analysis and IR spectroscopy as [Cu(dca)$_2$]. We believe that this green precipitate **16**, which is almost insoluble in all common solvents, is the known[13a] coordination polymer [Cu(dca)$_2$]$_n$ (**A**, Scheme 2; also see below).

After a certain time (1–8 h depending on the alcohol used; the longer the R substituent of the alcohol, the shorter this period is; see the Supporting Information) the precipitate dissolves fast and, in several minutes, the reaction mixture is converted into a violet homogeneous solution. If one evaporates the solvent at this stage, eliminates the sodium acetate by washing with water and then recrystallises the thus isolated compound from an acetone/water (10:1) mixture, the dinuclear copper(II) complexes [Cu{HN=C(OR)NC(OR)=NH}$_2${HN=C(OR)NC(OR)=NH}Cu{N≡C-N-C≡N}] (R = Et (**17**), *n*Pr (**18**)) (Scheme 7) can be isolated and characterised, also by X-ray diffraction (see below). They can be easily converted to the final products **2** and **3** by further heating with the corresponding alcohol. If the reaction mixture is not evaporated at the stage in which complexes **17** and **18** were isolated, but heated further, it gradually changes its colour to red (the shorter the substituent R, the faster this colour transition is; for details see the Supporting Information). The final complexes **1**–**5** (which are red with various gradations depending on R) are soluble in the reaction mixture (partly soluble for R = Me), while the colourless NaAcO precipitates.

Thus, based on our and other data,[11f,13] the following pathway of this template transformation (Scheme 7, path a) can be proposed. Firstly, dicyanamidate coordinates to copper(II) ions by the terminal and central nitrogen atoms, forming [Cu(dca)$_2$]$_n$ **16** (step Ia).[13a] In this way, the carbon atoms of dicyanamidate are "doubly activated" towards the nucleophilic addition. Then, nucleophilic attack of alcohol



Scheme 7. Proposed pathways for the template complex formation.

to the carbon atom occurs with further proton transfer to the nitrogen atom (Scheme 7, step IIa), leading to cleavage of some of the Cu–N bonds and thus to a partial decomposition of the polymeric **16** to oligomers and eventually dinuclear complexes. This proposal is supported by our results (compounds **17** and **18**) and those from others[13c] in which the dinuclear product of the copper(II)-mediated nucleophilic addition of water to dicyanamide was isolated and structurally characterised. Thus, the formed dinuclear species provide a higher activation of the remaining C≡N groups. The following nucleophilic attack of ROH to the carbon atoms of the CN triple bonds in the formed dicopper(II) complex (Scheme 7, step IIIa) proceeds readily and leads to intermediate **17**. Hence, every copper ion "helps" the other one to convert dicyanamidate to the triazapentadienate ligand with the corresponding metallacycle closure. This stepwise process proceeds further towards the final stable [Cu(2,4-alkoxy–tap)$_2$] complexes (Scheme 7, step IVa).

Reaction with cyanoguanidine: In the case of the template formation of the 2-alkoxy-4-amino-1,3,5-triazapentadiene

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complexes **6–10** from cyanoguanidine, the reaction also goes through a few observable stages (Scheme 7, path b). Firstly, an almost insoluble green precipitate $[Cu_2(AcO)_4\{HN{=}C(NH_2)NHCN\}_2]$ (**19**) was formed in the reaction mixture (Scheme 7, step Ib). This compound was removed by filtration, washed with water and methanol and recrystallised from an acetone/methanol (1:1) mixture. Its IR spectrum displays bands at 2211 and 2170 cm^{-1} that can be assigned to ν(C≡N). Elemental analysis supports the overall formulation, and single-crystal X-ray diffraction analysis reveals its dimeric character (see below).

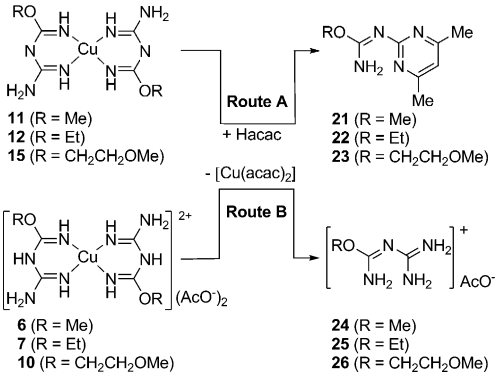
Continuation of the reaction for 1 h (if methanol was used as a nucleophile and solvent) results in dissolution of **19** with formation of a blue solution. Removal of the solvent leads to a mixture of **19** (traces), the copper(II)–tap compound **6** and a blue oil. However, isolation of **19** and subsequent heating at reflux in an acetone/methanol (5:1) mixture for several hours leads to the formation of a blue precipitate. Its IR spectrum has no ν(C≡N) signals and elemental and ESI-MS^+ analyses allow the overall formula $[Cu_2(AcO)_4\{HN{=}C(NH_2)NHC(OMe)NH\}]$ (**20**, Scheme 7, step IIb) to be proposed. All the attempts to get crystals of **20** suitable for single-crystal X-ray diffraction analysis failed.

Thus, the mechanism of the reaction with cyanoguaninde appears to be, in general, similar to that discussed above, but there are also some differences. For example, in this case (Scheme 7, pathway b) dinuclear copper(II) intermediate **19** with the copper(II)/cyanoguanidine ratio of 1:1 is formed at the first stage (Scheme 7, step Ib). Then a nucleophilic attack of alcohol on the carbon of the activated CN triple bond of the ligated cyanoguanidine (Scheme 7, step IIb) leads to the formation of the copper(II)–tap complex **20**. In the third step, coordination of another cyanoguanidine molecule occurs, followed by nucleophilic attack of alcohol to form the final product (Scheme 7, steps IIIb–IVb). Curiously, addition of a small quantity of the final complex (e.g., **6**) to the methanol-insoluble intermediate **19** leads to its fast dissolution and acceleration of the reaction rate, which supports an autocatalytic mechanism.

Metal-mediated synthesis of pyrimidines and triazapentadienes

Synthesis of pyrimidines: Reactions of the neutral 2-alkoxy-4-amino-1,3,5-triazapentadienato complexes **11**, **12** and **15** with an excess amount of 2,4-pentanedione (Hacac) in water under ambient conditions (Scheme 8, Route A) yielded (80–60%) the corresponding pyrimidines (soluble in the reaction mixture) and a blue precipitate of $[Cu(acac)_2]$. Separation of the products by filtration with subsequent solvent evaporation and further purification (see the Experimental Section) produced a white crystalline solid of the corresponding pyrimidine, which was fully characterised (in the case of **21**, also by X-ray diffraction; see below).

The ^1H and ^{13}C NMR spectra of the compounds show the expected signals. In the ^1H NMR spectrum of **21** the singlets



Scheme 8. Copper(II)-mediated synthesis of pyrimidines and triazapentadienes.

at $\delta = 2.26$ and 3.75 ppm can be assigned to the $-CH_3$ groups bonded to the pyrimidine ring and to the $-OCH_3$ group, respectively, whereas the resonance at $\delta = 6.75$ ppm is due to the −C*H* of the pyrimidine ring. The ^{13}C NMR spectrum shows signals of three nonequivalent carbon atoms of the pyrimidine ring at $\delta = 114.9$ (H*C*), 158.0 (N*C*=N) and 166.7 ppm (CH_3C). Other signals at $\delta = 22.7$, 54.2 and 163.9 ppm were assigned to the CH_3C, CH_3O and N*C*=NH groups, respectively. The elemental analysis data and ESI-MS^+ spectra of the compounds are in agreement with the proposed formulations. The IR spectra show typical ν(NH) stretches at approximately 3400–3200 cm^{-1} with δ(N−H) at 1561–1544 cm^{-1}, and strong ν(C=N) bands at approximately 1670–1620 cm^{-1}.

It is worthwhile to mention that the reaction does not proceed in the absence of water. It is known that the addition of water decreases the concentration of the enol form relative to the keto form of Hacac,[23b] which suggests that the reaction can proceed through the nucleophilic attack of the nitrogen atom of the amine group of the tap ligand to the carbonyl carbon of the β-diketone.

Synthesis of triazapentadiene salts: In contrast to the neutral compounds **11**, **12** and **15**, the reaction of the cationic 2-alkoxy-4-amino-1,3,5-triazapentadiene complexes $[Cu\{NH{=}C(OR)NHC(NH_2){=}NH\}_2](AcO)_2$ with an excess amount of Hacac in water, under the same conditions as described in the section above, yields not pyrimidines, but the corresponding triazapentadiene salts **24–26** and a blue solid of $[Cu(acac)_2]$ (Scheme 8, Route B). The procedures for the $[Cu(acac)_2]$ separation and for the purification of the final compounds **24–26** are similar to those discussed above. Hence, when the tap ligands are protonated, as in the cationic complexes **6–10**, they do not exhibit nucleophilic ability and the heterocyclisation does not proceed.

Compounds **24–26** were characterised by elemental analysis; ^1H NMR, ^{13}C NMR and IR spectroscopies; ESI-MS^+ and, in the case of **24**, also by single-crystal X-ray diffraction (see below). Thus, the IR spectra of the compounds contain typical ν(NH) stretches at 3375–3180 cm^{-1} with corresponding δ(N−H) at approximately 1562–1550 cm^{-1}, and ν(C=N)

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at 1656–1630 cm^{-1}. The ESI-MS^+ spectra show, as a main signal, a peak at m/z $[M-AcO]^+$, and the ESI-MS^- spectra contain the signal of acetate ($[AcO]^-$). The ^1H NMR spectrum of **24** reveals signals of two types of protons assigned to the CH_3COO and CH_3O groups (at $\delta=1.90$ and 3.78 ppm, respectively). The ^{13}C NMR spectra show typical signals for the imine ($\delta=161.1$ and 164.8 ppm), CH_3COO ($\delta=24.3$ and 180.6 ppm) and methoxy ($\delta=55.5$ ppm) groups. The ^1H NMR spectra of **25** and **26** (see the Experimental Section) also contain similar typical signals of the substituents and acetate ion, whereas the resonances of the imine and acetate carbon atoms are observed by ^{13}C NMR spectroscopy.

X-ray diffraction analyses

General description of the copper complexes: X-ray-quality crystals were obtained upon slow evaporation of solutions of the compounds in methanol/chloroform (**4** and **5**), acetone (**11**), acetone/water (10:1) (**17** and **18**), acetone/methanol (1:1) (**19**) or water/methanol (**21** and **24**) in air at approximately 20–25 °C. The crystallographic data and processing parameters are summarised in Table 1, representative plots are displayed in Figures 1–8 below, and a comparison of selected dimensions is presented in Table 2.

In compounds **4**, **5** and **11** (Scheme 6), the central Cu atoms are in square-planar coordination environments with two monoanionic 1,3,5-triazapentadienato species acting as N,N-chelators and forming two six-membered Cu metallacycles; the N-Cu-N and the Cu–N bond lengths are close to those in relevant bis-1,3,5-triazapentadienato-Cu^{II} complexes[3d,4,9b,10–12] (Table 2 and Table S1 in the Supporting Information). The alternating double and single CN bonds[24] support the formation of delocalised π-bonding systems within the metallacycles.

There are three singly negatively charged 1,3,5-triazapentadienato ligands in the structures of the dinuclear complexes **17** and **18** (Scheme 7), two of them behaving as the previously described N,N-chelators, one for each copper, and the third as a N_2,N-chelator bridging between the two metal centres. Both copper ions are in square-planar N_4-coordination environments similar to the ones previously described. However, due to the orientation of the substituents of the bridging chelating ligand, some strong Cu···O contact interactions occur and the geometry around one of the copper ions can be envisaged as a highly distorted square-based bipyramid with oxygen atoms in the axial sites and the four N atoms in the equatorial positions, one of which from a pendent dicyanamidate ligand. Thus, this latter copper ion is in the corner of one six-membered and two four-membered rings.

The molecule of **19** (Scheme 7) consists of dinuclear copper(II) acetate paddle-wheel units with two cyanoguanidine molecules linked to the metal centre. The presence of the amine groups leads to extensive hydrogen bonds that extend the structure to the three dimensions.

Table 1. Crystal data and structure refinement details for compounds **4**, **5**, **11**, **17–19**, **21** and **24**.

	4	**5**	**11**	**17**	**18**	**19**	**21**	**24**
formula	$C_{16}H_{32}CuN_6O_4$	$C_{16}H_{32}CuN_6O_8$	$C_6H_{14}CuN_8O_2$	$C_{20}H_{36}Cu_2N_{12}O_6$	$C_{26}H_{42}Cu_2N_{12}O_6$	$C_{12}H_{20}Cu_2N_8O_8$	$C_6H_{12}N_4O$	$2(C_3H_5N_4O)$, $2(C_2H_3O_2)$
M_r	436.02	500.02	293.79	667.69	751.84	531.44	180.22	370.39
T [K]	150(2)	150(2)	293	150	295(2)	150(2)	150(2)	150(2)
crystal system	triclinic	monoclinic	tetragonal	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P41212$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$I2/a$	$Pbcn$
a [Å]	8.0599(2)	8.3916(10)	7.889(2)	10.0124(8)	10.9893(14)	8.3858(11)	11.8484(15)	8.7586(8)
b [Å]	10.3711(2)	10.3722(11)	7.889	10.2015(8)	12.3886(15)	15.361(2)	11.4039(15)	11.9146(11)
c [Å]	13.5271(3)	13.6481(14)	19.361(5)	15.7629(15)	13.6198(17)	8.6634(10)	13.7785(19)	17.4733(14)
α [°]	82.621(2)	90	90	76.487(4)	87.657(8)	90	90	90
β [°]	75.066(1)	95.228(7)	90	88.148(3)	87.503(4)	110.259(7)	105.167(8)	90
γ [°]	83.456(1)	90	90	72.438(2)	85.391(3)	90	90	90
V [$Å^3$]	1079.61(4)	1183.0(2)	1205.0(4)	1491.2(2)	1845.2(4)	1046.9(2)	1796.9(4)	1823.4(3)
Z	2	2	4	2	2	2	8	4
ρ_{calcd} [$Mg\,m^{-3}$]	1.341	1.404	1.619	1.487	1.353	1.686	1.332	1.349
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.043	0.974	1.819	1.481	1.205	2.088	0.094	0.113
total reflns	10878	9486	2646	20805	16967	9778	8642	9779
obsd reflns	4105	2389	826	4081	2234	1839	1290	1340
R_{int}	0.0204	0.0451	0.2344	0.0445	0.1025	0.0462	0.0432	0.0762
$R1$[a] ($I\geq 2\sigma$)	0.0254	0.0304	0.0856	0.0349	0.0640	0.0322	0.0409	0.0567
$wR2$[b] ($I\geq 2\sigma$)	0.0707	0.0831	0.1870	0.0795	0.1290	0.0732	0.1041	0.1071
GOF	1.507	1.040	1.055	1.018	0.890	1.066	1.042	1.043

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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Table 2. Selected distances [Å] and angles [°] for the copper compounds **4**, **5**, **11** and **17**–**19**.

		4	5	11	17	18	19
				general			
Cu–N							
	shortest	1.9339(13)	1.9142(13)	1.930(7)	1.908(3)	1.882(6)	2.134(2)
	longest	1.9399(13)	1.9499(14)	1.966(7)	2.020(3)	2.015(5)	–
Cu–O							
	shortest	–	–	–	2.757(2)	2.669	1.9614(19)
	longest	–	–	–	2.817(2)	2.910(6)	1.9852(17)
Cu–Cu		–	–	–	–	–	2.6203(6)
Cu···Cu[a]		5.186	8.392	6.351	5.0308(6)	3.571(1)	7.537(1)
∢O-Cu-N							
	shortest	–	–	–	50.69(8)	48.8(3)	93.37(8)
	longest	–	–	–	52.06(8)	52.9(2)	97.91(8)
				six-membered metallacycles			
C–N							
	shortest	1.2982(19)	1.295(2)	1.296(11)	1.285(4)	1.281(10	–
	longest	1.3337(19)	1.328(2)	1.349(9)	1.352(4)	1.354(10)	–
∢N-Cu-N							
	shortest	87.30(6)	87.95(6)	87.3(3)	87.40(11)	89.2(3)	–
	longest	87.75(5)	–	–	88.79(11)	90.1(3)	–
∢N-C-N							
	shortest	128.14(15)	129.04(15)	127.3(8)	125.9(9)	128.0(7)	–
	longest	128.83(13)	129.20(15)	130.5(8)	129.7(9)	129.5(9)	–
∢C-N-C							
	shortest	119.48(13)	119.06(14)	118.8(7)	118.2(3)	118.2(8)	–
	longest	119.77(13)	–	–	122.1(2)	121.2(7)	–

[a] The shortest intermolecular interaction is indicated.

Detailed description: In the structure of **4** (Scheme 6, Figure 1) two half molecules are found in the asymmetric unit, with both copper ions at inversion centres. The molecules are displayed in such a way that the planes defined by their own coordinated nitrogen atoms make an angle of 85.02°. The six-membered Cu metallacycles are co-planar in both molecules of **4** with the alkoxy arms slightly bent out of each plane, as indicated by the CuNCO torsion angles of 170.3 and 175.6° for the Cu1 molecule, or 176.5 and 179.4° for the Cu2 one. Moreover, the molecules are held together by means of medium-strong H···π interactions between the N21 and the N22 hydrogen atoms in the Cu2 molecule (Figure 2) with one of the Cu1 metallacycles, and one of the hydrogen atoms of the C14 and C17 methyl groups and the Cu2 metallacycles, thus giving rise to the formation of 1D polymeric chains that spread along the crystallographic *b* axis (Figure S4 in the Supporting Information). The minimum intrachain Cu···Cu distance in **4** is 5.186 Å, half the crystallographic *b* dimension, whereas the minimum interchain Cu···Cu distance is 8.06 Å, half the crystallographic *a* dimension.

Only half of a molecule could also be found in the asymmetric unit of **5** (Scheme 6); their molecules are also displayed in two different relative orientations (Figure 3) linked by medium-intensity hydrogen-bond interactions involving the C=NH imine groups and the methoxyethanolate O4 oxygen atoms, as well as medium-strong H···π interactions involving one of the hydrogen atoms of the C7 methyl group of a vicinal metallacycle. Such interactions also orient the structure in a 1D polymeric chain along the crystallographic *a* axis (Figure S5 in the Supporting Information). In contrast with what was found in **4**, the planes of the molecules, defined by the coordinated N atoms, make angles of only 44.59°. Probably resulting from the bulkiness of the methoxyethanolate moieties, the molecules in **5** are further apart than those in **4** with minimum intrachain Cu···Cu distances of 8.392 Å, half the crystallographic *a* dimension, and minimum interchain Cu···Cu distances of 9.266 Å.

In the crystal structure of **11** (Scheme 6, Figure 4), the two six-membered metallacycles are not co-planar as indicated by the angle between their planes (11.80°), with the consequent absence of a delocalised π-bonding system over the entire ring. However, the range of CN bond lengths (Table 2) agrees with those found in previous cases. Extensive medium-intensity hydrogen interactions expand the structure in three dimensions. The minimum Cu···Cu distance is 6.351 Å.

There are some interesting differences between the structures of **17** and **18** (Scheme 7, Figure 5), the most striking one being, for the latter complex, the co-planarity of the six-membered Cu1-containing metallacycle and all the atoms of the dicyanamidate ligand. Moreover, the angles involving this ligand, the Cu1-N10-C10 and C10-N20-C20, are also quite different (135.2(3) and 120.8(3)° in **17**; 175.0(8) and 126.0(9)° in **18**, respectively). The planes of the two six-membered metallacycles linking Cu2 make an angle of 7.41° in the structure of **17** but in **18** that angle is 14.37°, even higher than the one measured in **11** (see above). The planes defined by the coordinated nitrogen atoms around each copper ion are almost perpendicular in **17** (87.07°) while in **18** they make an angle of only 79.55°. The Cu···O bond lengths in both structures, in the 2.669–2.910 Å range, are well within the sum of the van der Waals radii of copper and oxygen, although quite above the values found in a diversity of Cu-containing compounds.[24] In both complexes, stacking interactions are observed and involve vicinal Cu2-containing metallacycles (see Figure S6 in the Supporting Information for **17**). The centroid–centroid distance of the adjacent rings is considerably lower in **17** than in **18** (3.491 and 3.850 Å, respectively) indicating a normal to weak π–π interaction. Several intermolecular hydrogen interactions were also detected in which the donor atoms are N1, N3, N4, N6

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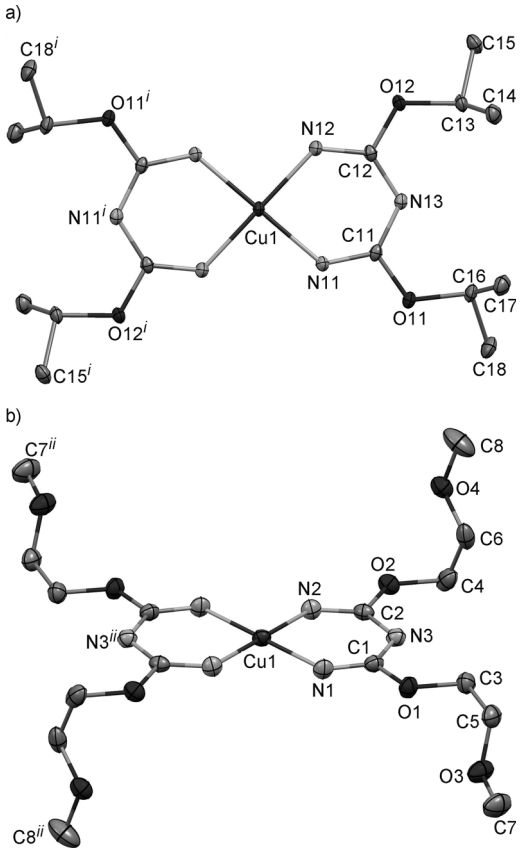

Figure 1. Crystal structure fragment of complexes a) **4** and b) **5** with atomic numbering scheme (ellipsoid probability level of 30%). The hydrogen atoms have been omitted for clarity. In **4**, only one of the molecules is shown. Symmetry operations to generate equivalent atoms: *i*) $1-x, 1-y, -z$; *ii*) $-x, -y, -z$.

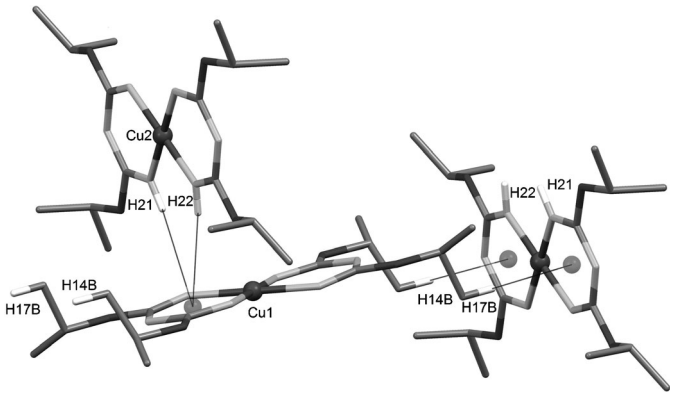

Figure 2. Structural representation of **4** showing the relative orientation of Cu1- and Cu2-containing molecules, the metallacycle centroids (as semitransparent balls) and the respective intermolecular H···centroid interactions (as dotted lines). The H atoms, apart from those involved in the interactions, have been omitted for clarity. *d*(H14B···centroid) 2.61 Å, ∢(C14-H14B···centroid) 171°; *d*(H17B···centroid) 2.67 Å, ∢(C17-H17B···centroid) 179°; *d*(H21···centroid) 3.00 Å, ∢(N21-H21···centroid) 168°; *d*(H22···centroid) 2.88 Å, ∢(N22-H22···centroid) 173°.

and N9 whereas the acceptor atoms are the cyanoguanidate N10 and N30 as well as, but only in **17**, the alkoxy O2

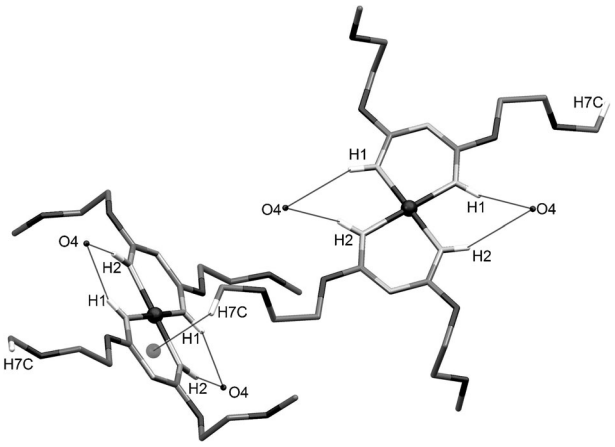

Figure 3. Structural representation of **5** showing the relative orientation of the molecules, the metallacycle centroids (as semitransparent balls) and the respective intermolecular hydrogen-bond and H···centroid interactions (as dotted lines). The H atoms, apart from those involved in the interactions, have been omitted for clarity. Intermolecular hydrogen bonds (as dotted lines), *d*(D···A) and angles ∢(D-H···A): N1-H1···O4 2.14 Å, 156°; N2-H2···O4 2.56 Å, 155°; H7C···centroid 2.87 Å; C7-H7C···centroid 118°.

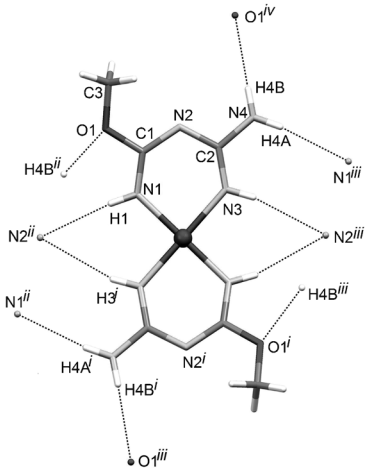

Figure 4. Crystal structure fragment of complex **11** with atomic numbering scheme. Symmetry operations to generate equivalent atoms: *i*) $x, y, -z$; *ii*) $-1/2+y, 1/2+x, -1/4+z$; *iii*) $1/2+x, 1/2-y, -1/4-z$; $1/2-y, 1/2+x, 1/4-z$. Intermolecular hydrogen bonds (as dotted lines), *d*(D···A) and angles ∢(D-H···A): N1-H1···N2 2.53 Å, 147°; N3-H3···N2 2.55 Å, 161°; N4-H4A···N1 2.32 Å, 172°; N4-H4B···O1 2.39 Å, 162°.

atoms. Specifically in **18**, intramolecular hydrogen bonds were found involving the propanoxy C21 and C53 as donor atoms, and the vicinal N2 and O5, respectively, as acceptors.

In the structure of **19** (Scheme 7, Figure 6), each copper can be considered as being in an octahedral O_4NCu coordination environment with the oxygen atoms in the equatorial positions and the N and the other metal in the axial sites. A packing diagram of **19** is drawn in Figure S7 in the Supporting Information to show that the molecular packing is typical of a monoclinic system with the molecules lying in reversed orientations. The overlap of the amine and the coordinated carboxylate groups of the molecules produces inter-

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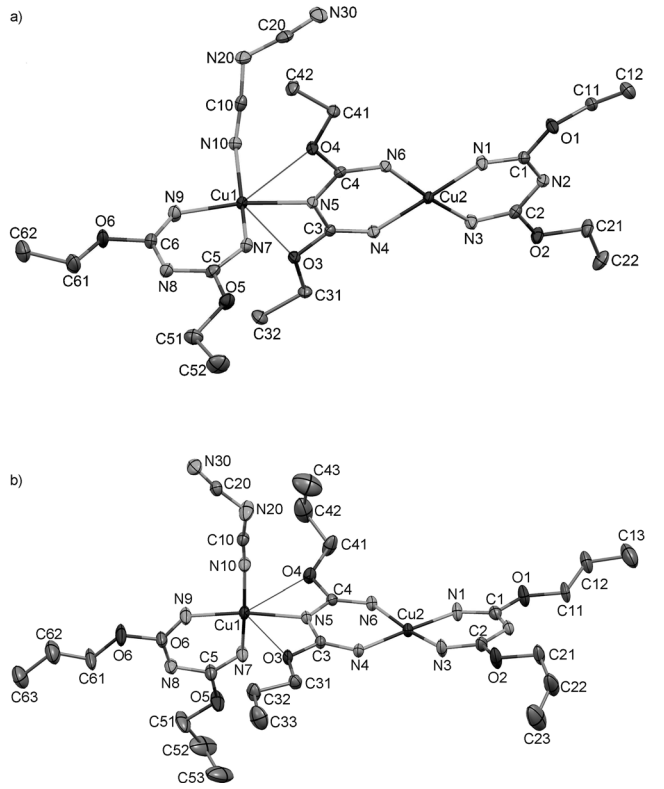

Figure 5. Crystal structures of complexes a) **17** and b) **18** with atomic numbering scheme (ellipsoid probability level of 30% for **17** and, due to a lesser quality of the data (see Table 1), 10% for **18**). The hydrogen atoms have been omitted for clarity.

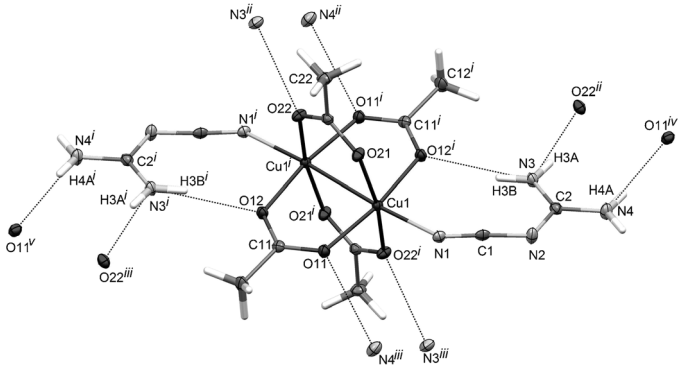

Figure 6. Crystal structure of complex **19** with atomic numbering scheme (ellipsoid probability level of 30%). Intra- and intermolecular hydrogen bonds (as dotted lines), *d*(D···A) and angles ∢(D-H···A): N3-H3B···O12 3.028(3) Å, 167°; N3-H3A···O22 2.943(3) Å, 164°; N4-H4A···O11 3.013(3) Å, 163°; N4-H4B···O21 3.189(3) Å, 162°. Symmetry operations to generate equivalent atoms: *i*) $2-x, -y, 1-z$; *ii*) $1.5-x, 0.5+y, 0.5-z$; *iii*) $0.5+x, 0.5-y, 0.5+z$; *iv*) $-0.5+x, 0.5-y, -0.5-z$; *v*) $2.5-x, -0.5+y, 1.5-z$.

molecular interactions of the type N−H···O leading to an infinite three-dimensional framework (Figure S8 in the Supporting Information).

The structure of compound **21** (Scheme 8) confirmed the aromaticity of the pyrimidine ring (Figure 7),[24] with the C−N and C−C bonds in the 1.3444(19)–1.391(2) Å range.

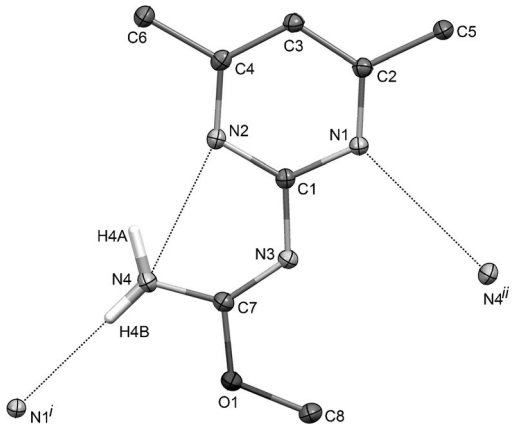

Figure 7. Crystal structure of **21** with atom numbering scheme (ellipsoid probability level of 30%). Selected bond lengths [Å] and angles [°]: C1−N2 1.3444(19), C1−N1 1.3521(19), C2−C3 1.391(2), C3−C4 1.374(2), C7−N3 1.302(2), C7−N4 1.322(2); N2-C1-N1 125.06(13), N3-C7-N4 130.82(15). Intra- and intermolecular hydrogen bonds (as dotted lines), *d*-(D···A) and angles ∢(D-H···A): N4-H4A···N2 [2.701(2); 124], N4-H4B···N1 [3.0664(19); 177]. Symmetry operations to generate equivalent atoms: *i*) $1-x, -0.5+y, 0.5-z$; *ii*) $1-x, 0.5+y, 0.5-z$.

Moreover, there are weak π···π interactions (Figure S9 in the Supporting Information) with distances between the adjacent pyridine-ring centroids of 3.474 and 3.679 Å. This compound is an example of the recognised tendency of aromatic nitrogen heterocycles to π···π stack.[26] Such values are within the range of centroid–centroid distances between two pyridine-containing metal molecules,[26a] and is shorter than those for connecting benzene rings of symmetry-related complex molecules.[26b] The NH_2 protons are involved in medium-intensity hydrogen bonding to the pyrimidine N atoms of neighbouring molecules (footnote of Figure 7), thereby enabling the building of 1D chains along the crystallographic *b* axis.

The guanidine derivative **24** (Scheme 8) crystallised with an acetate moiety as counterion as well as with a water molecule (Figure 8). As evidenced by the N−C bond lengths (footnote of Figure 8) the cation includes a π-delocalised system that imparts a torsion centred in the N2 atom. As a result, the N2-N3-C3-N4 guanidine group makes an angle of 54.38° with the remaining set. The availability of hydrogen-donor and -acceptor atoms in this structure enabled the building up of extensive intermolecular hydrogen bonds that expand to an infinite three-dimensional framework.

Catalytic studies

Aerobic oxidation of benzyl alcohols to aldehydes: Several of the synthesised copper(II) complexes with triazapentadienate ligands (**1–3**, **5–7** and **11–13**) were used to evaluate their activity in TEMPO-mediated alcohol-oxidation reactions (Scheme 4). Benzyl alcohol was selected as a model substrate for the catalyst screening. Reactions were carried out in an aqueous medium, free from any organic solvent and under atmospheric pressure of air (or O_2). As shown previously,[21,22] the use of basic additives, which plausibly fa-

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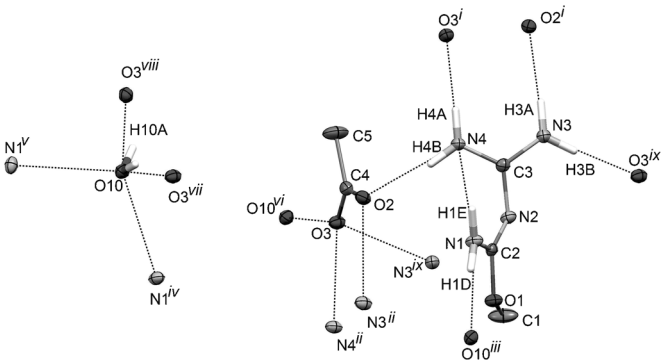

Figure 8. Crystal structure of **24** with atom numbering scheme (ellipsoid probability level of 50%). Selected bond lengths [Å] and angles [°]: C2–N2 1.295(2), C2–N1 1.327(3), C2–O1 1.337(2), C3–N3 1.313(2), C3–N4 1.322(2), C3–N2 1.362(2); N3-C3-N4 120.12(16), N3-C3-N2 117.79(17), C2-N2-C3 121.11(16), N2-C2-N1 129.73(17). Intra- and intermolecular hydrogen bonds (as dotted lines), d(D···A) and angles ∢(D-H···A): N1-H1D···O10 2.911(2) Å, 172(2)°; N3-H3A···O2 2.870(2) Å, 175(2)°; N3-H3B···O3 2.980(2) Å, 164(2)°; N4-H4A···O3 2.831(2) Å, 168°; N4-H4B···O2 2.890(2) Å, 148°; O10-H10A···O3 2.7751(15) Å, 157°. Symmetry operations to generate equivalent atoms: *i*) 1.5−x, −0.5+y, z; *ii*) 1.5−x, −0.5+y, z; *iii*) 0.5+x, 1.5−y, 1−z; *iv*) −0.5+x, 1.5−y, 1−z; *v*) 0.5−x, 1.5−y, −0.5+z; *vi*) 1+x, y, z; *vii*) −1+x, y, z; *viii*) 1−x, y, 0.5−z; *ix*) 2−x, 2−y, 1−z.

cilitate deprotonation of the alcohol, increases the efficiency of the system. In this respect we have used basic (K_2CO_3) aqueous solutions as the reaction medium. The results of the oxidation of benzyl alcohol with dioxygen, catalyzed by different copper complexes are summarised in Table S2 in the Supporting Information. Benzyl alcohol can be almost quantitatively converted into benzaldehyde (96%) in 6 h (Table S2 in the Supporting Information, run 1). To compare the activities of the studied complexes, the reaction time was shortened to 2 h, and moderate yields (29–57%) were achieved (Table S2 in the Supporting Information).

Complex **1**, one of the most efficient and simplest catalyst precursor in the series, was selected for further studies of the oxidation of primary and secondary alcohols by air (an ideal oxidant[20] in economic and environmental terms) (Table 3). The system has proved its efficiency towards benzyl alcohol oxidation by providing a benzaldehyde yield of 83% in 6 h (Table 3, run 1) that is comparable to those used with O_2 (Table S2 in the Supporting Information) and significantly higher than that in the presence of copper nitrate (20%, Table 3, run 2). Substituted benzylic alcohols, such as 4-MeO- and 4-Me-benzyl alcohols, were also converted efficiently into the corresponding benzaldehydes. However, a longer reaction time was needed (Table 3, runs 6 and 7). The typical secondary benzylic alcohol, 1-phenylethanol, was oxidised to acetophenone with a moderate yield (Table 3, run 8), probably due to steric effects.[21] Allylic benzylic alcohol (cinnamyl alcohol) provided the corresponding unsaturated aldehyde with a high yield without affecting the double bond (Table 3, run 9). Unfortunately, aliphatic alcohols (both primary and secondary) were barely reactive under the applied conditions (Table 3, runs 10–12). The importance of TEMPO and the basic additive (K_2CO_3) is reflected by the dramatic yield drops for the corresponding blank experiments (Table 3, runs 3–5).

We presume the present catalysts may function according to the previously proposed[21,27,28] galactose oxidase-type mechanisms for other Cu/TEMPO/O_2 systems. These mechanisms involve coordination of both benzyl alcohol and TEMPO to a Cu centre followed by metal-centred dehydrogenation and oxidation of the alcohol through hydrogen abstraction or one-electron oxidation processes.

Oxidation of secondary alcohols to ketones: Earlier we reported[11g] that symmetrical copper(II) triazapentadienate complexes with methoxy or ethoxy substituents are efficient catalysts for the microwave (MW)-assisted oxidation of secondary alcohols to the corresponding ketones, using *tert*-butylhydroperoxide (TBHP) as an oxidant (Scheme 5). In continuation of that work, we have studied the activities of the newly synthesised copper complexes **3**, **5**, **6**, **8**, **11**, **13** and **18**. Moreover, here we also compare the MW-assisted process (method A) with the reaction in a sealed tube (method B) and under conventional heating with a condenser (method C).

1-Phenylethanol was chosen as a model substrate to optimise conditions and for comparative purposes (Table 4). The symmetrical complexes **3** and **5** with considerably long substituents are less active (30 and 41%, respectively; Table 4, runs 3 and 4) in the MW-assisted process than those (above 90%) with the shorter methoxy and ethoxy substituents.[11g] However, the unsymmetrical ionic complexes **6** and **8**, containing either methoxy or *n*-propoxy substituents, or their neutral analogues **11** and **13**, provide higher acetophenone yields, that is, 81 and 72% (Table 4, runs 13, 19) or 90 and 95% (Table 4, runs 6 and 16), respectively. In the case of **11**, the yield increases from 39 to 97% with increase of the reaction time from 10 to 60 min (Table 4, runs 5–7). Hampering of the reaction by a radical trap (diphenylamine,

Table 3. Oxidation of selected alcohols using **1** as catalyst and air as oxidant.[a]

Run	Time [h]	Substrate	Product	TON	Yield [%][b]
1	6	benzyl alcohol	benzaldehyde	83	83
2[c]	6	benzyl alcohol	benzaldehyde	20	20
3[d]	6	benzyl alcohol	benzaldehyde	1	1
4[e]	6	benzyl alcohol	benzaldehyde	–	9
5[f]	6	benzyl alcohol	benzaldehyde	26	26
6	20	4-MeO-benzyl alcohol	4-MeO-benzaldehyde	83	83
7	20	4-Me-benzyl alcohol	4-Me-benzaldehyde	100	100
8	24	1-phenylethanol	acetophenone	34	34
9	24	cinnamyl alcohol	cinnamyl aldehyde	96	96
10	24	1-hexanol	1-hexanone	6	6
11	24	2-hexanol	none	0	0
12	24	cyclohexanol	none	0	0

[a] Conditions, unless stated otherwise: 3 mmol substrate, 1 mol% catalyst, 5 mol% TEMPO, in 0.1 M K_2CO_3 aqueous solution, at 50 °C. [b] Based on GC, selectivity of all products >99%. [c] Reaction using $Cu(NO_3)_2{\cdot}2.5H_2O$ as catalyst. [d] Reaction without TEMPO. [e] Without any Cu catalyst. [f] In the absence of K_2CO_3.

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Table 4. Oxidation of 1-phenylethanol.[a]

Run	Catalyst	Method	Time [min]	TON (TOF [h^{-1}])	Yield [%][b]
1[c]	none	A	30	–	9
2[d]	$Cu(NO_3)_2$	A	30	185 (370)	37
3	**3**	A	30	150 (300)	30
4	**5**	A	30	205 (410)	41
5	**11**	A	10	195 (1170)	39
6	**11**	A	30	450 (900)	90
7	**11**	A	60	485 (485)	97
8[e]	**11**	A	30	20 (40)	4
9[f]	**11**	A	30	10 (20)	2
10[g]	**18**	A	30	450 (900)	90
11	**11**	B	30	360 (720)	72
12	**11**	C	30	335 (670)	67
13	**6**	A	30	405 (810)	81
14	**6**	B	30	275 (550)	55
15	**6**	C	30	195 (390)	39
16	**13**	A	30	475 (950)	95
17	**13**	B	30	390 (780)	78
18	**13**	C	30	285 (570)	57
19	**8**	A	30	360 (720)	72

[a] Conditions, unless stated otherwise: 5 mmol substrate, 0.01 mmol catalyst (0.2 mol% vs. substrate), 10 mmol TBHP (2 equiv), at 50°C. Methods: A: microwave; B: sealed tube, in oil bath; C: conventional (flask + condenser, oil bath). [b] GC yield; acetophenone was detected as the only product. [c] Blank experiment. [d] For comparative purposes. [e] Reaction in the presence of 5 mmol diphenylamine (radical trap). [f] Hydrogen peroxide (10 mmol, 2 equiv) used instead of TBHP, at 60°C. [g] 0.005 mmol catalyst (0.1 mol% vs. substrate) was used due to the dinuclear nature of **18**.

run 8) suggests a radical pathway.[24] The use of hydrogen peroxide instead of TBHP results in a lower yield (2%, Table 4, run 9), probably reflecting extensive decomposition of the oxidant under the reaction conditions. It is interesting that complex **18**, being an intermediate in the synthesis of **3**, is a more efficient catalyst precursor than **3** and **5**, providing 90% yield (Table 4, run 10).

With regard to the comparison of the different methods, the MW-assisted reaction (method A; Table 4, runs 6, 13 and 16) is the most efficient one, providing approximately 18–27% higher yields than those obtained for the sealed tube (method B; Table 4, runs 11, 14 and 17) and approximately 23–42% higher than those for conventional heating (method C; Table 4, runs 12, 15 and 18). The turnover number (TON) and turnover frequency (TOF) values for the MW-assisted oxidation are quite high, that is, for **11** up to 450 and 900 h^{-1}, respectively. It is worth noting that the catalyst can be recycled, although this leads to gradually decreasing yields (ca. 15% yield drop per cycle, see Figure S21 in Supporting Information), thus the total TON values might be significantly higher.

The unsymmetrical complexes **6**, **8**, **11** and **13** were further tested as catalyst precursors for the oxidation of primary and secondary aliphatic alcohols (Table 5). Aliphatic alcohols, as expected, were less reactive than the benzylic ones, and a longer reaction time was needed. Thus, MW-assisted oxidation of 2-hexanol with **11** yields 73% of 2-hexanone in 240 min (Table 5, run 1), which is significantly better than in the cases of the sealed tube and conventional methods (60 and 62%, respectively; Table 5, runs 2 and 3). Reactions in the presence of complexes **6**, **8** and **13** gave comparable results (Table 5, runs 4–9). MW-assisted oxidations of other secondary hexanols, that is, 3-hexanol and cyclohexanol, result in good yields of the corresponding ketones (up to 68%, Table 5, runs 10–14). Interestingly, the oxidation of 1-hexanol leads to the formation of hexanoic acid as the main product in moderate yields, practically without any formation of hexanal (Table 5, runs 15–18).

Conclusion

The main general conclusions of this work can be summarised as follows. Firstly, dicyanamidates of alkali metals and cyanoguanidine can be used as convenient starting materials for the preparation of a diversity of copper(II)–triazapentadiene(ate) (Cu^{II}–tap) complexes by an easy one-pot procedure. Several previously unknown intermediates of

Table 5. Oxidation of selected aliphatic alcohols.[a]

Run	Catalyst	Substrate	Method	Product	TON (TOF [h^{-1}])	Yield [%]
1	**11**	2-hexanol	A	2-hexanone	365 (91)	73
2	**11**	2-hexanol	B	2-hexanone	300 (75)	60
3	**11**	2-hexanol	C	2-hexanone	310 (77)	62
4	**6**	2-hexanol	A	2-hexanone	385 (96)	77
5	**6**	2-hexanol	B	2-hexanone	315 (79)	63
6	**13**	2-hexanol	A	2-hexanone	380 (95)	76
7	**13**	2-hexanol	B	2-hexanone	340 (85)	68
8	**8**	2-hexanol	A	2-hexanone	340 (85)	68
9	**8**	2-hexanol	B	2-hexanone	275 (69)	55
10	**11**	3-hexanol	A	3-hexanone	290 (72)	58
11	**6**	3-hexanol	A	3-hexanone	205 (51)	41
12	**13**	3-hexanol	A	3-hexanone	320 (80)	64
13	**8**	3-hexanol	A	3-hexanone	310 (77)	62
14	**11**	cyclohexanol	A	cyclohexanone	340 (85)	68
15	**11**	1-hexanol	A	hexanal (hexanoic acid)	115 (29)[c]	0 (23)[d]
16[b]	**11**	1-hexanol	A	hexanal (hexanoic acid)	215 (54)[c]	1 (43)[d]
17	**6**	1-hexanol	A	hexanal (hexanoic acid)	130 (32)[c]	1 (26)[d]
18	**13**	1-hexanol	A	hexanal (hexanoic acid)	135 (34)[c]	0 (27)[d]

[a] Conditions, unless stated otherwise: 5 mmol substrate, 0.01 mmol catalyst (0.2 mol% vs. substrate), 10 mmol TBHP (2 equiv), MW at 80°C, 240 min, otherwise see Table 1. Yields based on GC analyses. [b] Reaction with 4 equivalents of TBHP. [c] TON and TOF values concern hexanoic acid. [d] The yields of hexanoic acid are given in parentheses; the other values concern hexanal.

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the template copper(II)-mediated synthesis of tap were isolated and fully characterised, which allowed us to get an insight into the pathway of this important transformation and to generalise this type of reaction.

Secondly, an easy and convenient copper-assisted synthesis of pyrimidine and triazapentadiene derivatives from cheap and commercially available cyanoguanidine was achieved.

Thirdly, the synthesised Cu^{II}–tap complexes were shown to be active catalysts for the oxidative conversions of the C–OH moiety (in alcohols) to carbonyl (in aldehydes and ketones products), in high yields and selectivities, under mild conditions, transformations that are of industrial significance.

Based on the obtained results, a range of other Cu^{II}–tap complexes (e.g., with pyrazole instead of alkoxy substituents) can be prepared, used for the synthesis of different pyrimidines and applied as effective catalysts for oxidations of alcohols. This is work that deserves further exploration and is underway in our laboratory.

Experimental Section

Materials and instrumentation: Solvents, most of the alcohols and aldehydes for the study of oxidation, $Cu(NO_3)_2{\cdot}2.5\,H_2O$, $Cu(OAc)_2{\cdot}H_2O$ and all organonitriles were obtained from commercial sources (Aldrich) and used as received. 4-MeO-benzyl alcohol and 4-Me-benzyl alcohol were prepared according to a reported procedure from the corresponding aldehydes.[29] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^1H and ^{13}C NMR spectra (in $CDCl_3$, $CDCl_3/CD_3OD$ or $[D_6]DMSO$) were measured on Bruker Avance II 300 and 400 MHz (UltraShield Magnet) spectrometers at ambient temperature. ^1H and ^{13}C chemical shifts (δ) are expressed in ppm relative to $Si(Me)_4$. J values are in Hz. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument as KBr pellets. $ESI^{+/-}$ mass spectra were obtained in methanol, acetone or water on a VARIAN 500-MS LC ion-trap mass spectrometer equipped with an electrospray ion source. For electrospray ionisation, the drying gas and flow rate were optimised for each sample with 35 psi nebuliser pressure. Scanning was performed from m/z 50 to 1000. The compounds were observed in the positive and negative modes (capillary voltage 80–105 V). Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software.

X-ray structure determinations: X-ray-quality single crystals of **4**, **5**, **11**, **17**–**19**, **21** and **24** were obtained as indicated in the section below. They were mounted in inert oil within the cold N_2 stream of the diffractometer. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Data were collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structures were solved by direct methods by using the SHELXS-97 package[30] and refined with SHELXL-97[31] with the WinGX graphical user interface.[32] All hydrogen atoms were inserted in calculated positions. The crystallographic details are summarised in Table 1; CCDC-827519, -827520, -827521, -827522, -827523, -827524, -827525, and -827526 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

UV/Vis spectra measurements: Solutions of Cu^{II}–tap complexes (5×10^{-4} M in propanol) and solutions of reaction mixtures (see the Supporting Information) were analyzed by a Perkin–Elmer Lambda 35 UV/Vis spectrometer (Helma, 111QS, 10 mm/Helma 114F-QS 10 mm).

Preparation of copper(II) 2,4-alkoxy-1,3,5-triazapentadienates: Copper acetate ($Cu(AcO)_2{\cdot}H_2O$, 199.0 mg, 1 mmol) and sodium dicyanamidate ($NaN(CN)_2$, 2 mmol) were added to a flask with neat ROH (5 mL), and the blue suspension was heated at reflux (R = Me, Et, *n*Pr, *i*Pr) or 100 °C ($R=CH_2CH_2OMe$) with stirring. After about 5 min a green precipitate (insoluble in all common solvents) was formed. With continuous heating at the same temperature the reaction mixture apparently does not change over 1–4 h depending on R (the shorter R, the longer the period). Then, rapidly, over 1–5 min, the reaction mixture homogenises and its colour changes to violet. If the reaction is stopped at this moment, the reaction mixture taken to dryness and the residue washed with water and recrystallised from an acetone/water mixture, the intermediate complexes **19** and **20** described below can be isolated. But if the reaction is left to continue, the mixture becomes dark red (the longer R, the more slowly this conversion occurs) accompanied by a release of a colourless precipitate (IR, NMR spectroscopy and elemental analysis proved that it is NaAcO). The reactions were stopped 12 h after their beginning, then the reaction mixtures were filtered from sodium acetate, dried in vacuo at room temperature, washed with water (3×10 mL) and recrystallised from acetone/water (ca. 10:1). Crystals of **4** and **5** suitable for X-ray analysis were prepared by slow evaporation of their solutions in methanol/chloroform (1:1).

*[Cu{NH=C(OMe)NC(OMe)=NH}$_2$] (**1**)*: Yield 91 %; IR (KBr, selected bands): $\tilde{\nu}=3359$ (s), 3342 (s) ν(N–H); 2992 (m–w), 2954 (m–w) ν(C–H); 1609 (s) ν(C=N); 1563 cm^{-1} (s) δ(N–H); ESI^+-MS: (in acetone): m/z: 324 $[M+H]^+$; elemental analysis calcd (%) for $C_8H_{16}CuN_6O_4$: C 29.67, H 4.98, N 25.95; found: C 30.06, H 4.92, N 26.11.

*[Cu{NH=C(OEt)NC(OEt)=NH}$_2$] (**2**)*: Yield 89 %; IR (KBr, selected bands): $\tilde{\nu}=3336$ (s), 3306 (s) ν(N–H); 2981 (s), 2928 (m–w) ν(C–H); 1608 (s) ν(C=N); 1536 cm^{-1} (s) δ(N–H); ESI^+-MS: (in acetone): m/z: 380 $[M+H]^+$; elemental analysis calcd (%) for $C_{12}H_{24}CuN_6O_4$: C 37.94, H 6.37, N 22.12; found: C 38.12, H 6.46, N 22.00.

*[Cu{NH=C(OnPr)NC(OnPr)=NH}$_2$] (**3**)*: Yield 81 %; IR (KBr, selected bands): $\tilde{\nu}=3338$ (s), 3312 (m–w) ν(N–H); 2964 (s), 2933 (s), 2875 (m–w) ν(C–H); 1599 (s) ν(C=N); 1531 cm^{-1} (s) δ(N–H); ESI^+-MS: (in acetone): m/z: 437 $[M+2H]^+$; elemental analysis calcd (%) for $C_{16}H_{32}CuN_6O_4$: C 44.08, H 7.40, N 19.28; found: C 44.50, H 7.33, N 19.09.

*[Cu{NH=C(OiPr)NC(OiPr)=NH}$_2$] (**4**)*: Yield 85 %; IR (KBr, selected bands): $\tilde{\nu}=3360$ (m–w), 3325 (s) ν(N–H); 2978 (s), 2934 (m–w), 2872 (m–w) ν(C–H); 1597 (s), 1576 (s) ν(C=N); 1534 cm^{-1} (s) δ(N–H); ESI^+-MS: (in acetone): m/z: 436 $[M+H]^+$; elemental analysis calcd (%) for $C_{16}H_{32}CuN_6O_4$: C 44.08, H 7.40, N 19.27; found: C 43.50, H 7.58, N 19.04.

*[Cu{NH=C(OCH$_2$CH$_2$OCH$_3$)NC(OCH$_2$CH$_2$OCH$_3$)=NH}$_2$] (**5**)*: Yield 72 %; IR (KBr, selected bands): $\tilde{\nu}=3330$ (s), 3229 (s) ν(N–H); 2974 (s), 2953 (s), 2893 (s), 2835 (m–w), 2812 (m–w) ν(C–H); 1607 (s) ν(C=N); 1528 cm^{-1} (s) δ(N–H); ESI^+-MS: (in acetone): m/z: 500 $[M+H]^+$; elemental analysis calcd (%) for $C_{16}H_{32}CuN_6O_8$: C 38.44, H 6.45, N 16.81; found: C 38.66, H 6.70, N 16.53.

Preparation of copper(II) 2-amino-4-alkoxy-1,3,5-triazapentadien(e/ate)s

Synthesis of cationic complexes: $Cu(AcO)_2{\cdot}H_2O$ (100 mg, 0.5 mmol) and cyanoguanidine (84 mg, 1 mmol) were added to a flask with ROH (10 mL for R = Me, Et, *n*Pr; 5 mL for R = *n*Bu, CH_2CH_2OMe), equipped with a magnetic stirrer, and the resulting mixture was heated at reflux (R = Me, Et) or at 95 °C (R = *n*Pr, *n*Bu, CH_2CH_2OMe) for 24 h. Over approximately 30 min a green precipitate was formed, then with further heating, in 1–4 h, the precipitate dissolved, the colour of the mixture became blue and finally in a few hours a violet or pink precipitate formed. Then the reaction mixture was filtered off, the eluate was evaporated under vacuum and the pink residue was washed with acetone and then recrystallised from methanol. Yields of the complexes (based on copper(II) acetate) were 82–63 %.

*[Cu{NH=C(OMe)NHC(NH$_2$)=NH}$_2$](AcO)$_2$·2H$_2$O (**6**)*: Yield 82 %: IR (KBr, selected bands): $\tilde{\nu}=3327$ (s), 3159 (s) ν(N–H); 2823 (m–w) ν(C–

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H); 1646 (s) ν(C=O); 1611 (s) ν(C=N); 1556 cm^{-1} (s) δ(N−H); ESI^+-MS (in methanol): *m/z* (%): 294 (100) $[M-2(AcO)-H]^+$, 296 (43), 295 (10), 297 (4); elemental analysis calcd (%) for $C_{10}H_{22}CuN_8O_6\cdot(2H_2O)$: C 26.70, H 5.82, N 24.91; found: C 27.07, H 5.73, N 25.20.

[Cu{NH=C(OEt)NHC(NH$_2$)=NH}$_2$](AcO)$_2$·3H$_2$O (**7**): Yield 78%; IR (KBr, selected bands): $\tilde{\nu}=3435$ (s), 3325 (s) ν(N−H); 2923 (m–w) ν(C−H), 1666 (s) ν(C=O), 1627 (s) ν(C=N), 1535 cm^{-1} (s) δ(N−H); ESI^+-MS (in methanol): *m/z* (%): 322 (100) $[M-2(AcO)-H]^+$, 324 (46), 323 (12), 325 (2); elemental analysis calcd (%) for $C_{12}H_{26}CuN_8O_6\cdot(3H_2O)$: C 29.06, H 6.50, N 22.59; found: C 29.00, H 6.14, N 22.64.

*[Cu{NH=C(O*n*Pr)NHC(NH$_2$)=NH}$_2$](AcO)$_2$·2H$_2$O* (**8**): Yield 80%; IR (KBr, selected bands): $\tilde{\nu}=3406$ (s), 3277 (s) ν(N−H); 2968 (m–w), 2930 (m–w), ν(C−H); 1671 (s) ν(C=O); 1572 (s) ν(C=N); 1554 cm^{-1} δ(N−H); ESI^+-MS (in methanol): *m/z* (%): 350 (100) $[M-2(AcO)-H]^+$, 352 (43), 351 (15), 353 (4); elemental analysis calcd (%) for $C_{14}H_{30}CuN_8O_6\cdot(2H_2O)$: C 33.23, H 6.77, N 22.14; found: C 33.27, H 6.97, N 22.14.

*[Cu{NH=C(O*n*Bu)NHC(NH$_2$)=NH}$_2$](AcO)$_2$* (**9**): Yield 75%; IR (KBr, selected bands): $\tilde{\nu}=3276$ (s) ν(N−H); 2930 (m–w), ν(C−H); 1667 (s) ν(C=O); 1603 (s) ν(C=N); 1544 cm^{-1} δ(N−H); ESI^+-MS (in methanol): *m/z* (%): 379 (100) $[M-2(AcO)-H]^+$, 381 (46), 380 (12); elemental analysis calcd (%) for $C_{16}H_{34}CuN_8O_6$: C 38.59, H 6.88, N 22.50; found: C 38.52, H 6.22, N 22.45.

[Cu{NH=C(OCH$_2$CH$_2$OCH$_3$)NHC(NH$_2$)=NH}$_2$](AcO)$_2$ (**10**): Yield 63%; IR (KBr, selected bands): $\tilde{\nu}=3294$ (s), 3154 (m–w) ν(N−H); 2940 (m–w), 2907 (m–w) ν(C−H); 1673 (s) ν(C=O); 1563(s) ν(C=N); 1530 cm^{-1} (s) δ(N−H); ESI^+-MS (in methanol): *m/z* (%): 382 (100) $[M-2(AcO)-H]^+$, 384 (44), 383 (15), 385 (2); elemental analysis calcd (%) for $C_{14}H_{30}CuN_8O_8$: C 33.50, H 6.02, N 22.32; found: C 33.46, H 6.10, N 22.28.

Synthesis of neutral complexes: The dissolution of the cationic complexes **6**–**10** (1 mmol) in distilled water (15 mL) followed by addition of an excess amount (20 equiv) of solid sodium hydroxide led to the formation of reddish precipitates. The precipitates were removed by filtration and washed on the filter with an aqueous solution of sodium hydroxide (1 M) and then by distilled water to remove traces of the formed sodium acetate. The thus obtained complexes **11**–**15** are not soluble in water, but are highly soluble in acetone and moderately in methanol. Recrystallisation of **11**–**15** from acetone leads to the formation of dark red crystals. Yields of the neutral complexes lay in the range 81–68%.

[Cu{NH=C(OMe)NC(NH$_2$)=NH}$_2$] (**11**): Yield 76%; IR (KBr, selected bands): $\tilde{\nu}=3358$ (s), 3342 (s) ν(N−H); 2991 (m–w), 2954 (m–w), 2852 (w) ν(C−H); 1609 (s) ν(C=N); 1561 cm^{-1} δ(N−H); ESI^+-MS (in acetone): *m/z* (%): 294 (100) $[M+H]^+$, 296 (42), 295 (12), 297 (3); elemental analysis calcd (%) for $C_6H_{14}CuN_8O_2$: C 24.53, H 4.80, N 38.14; found: C 24.53, H 4.84, N 37.90.

[Cu{NH=C(OEt)NC(NH$_2$)=NH}$_2$] (**12**): Yield 72%; IR (KBr, selected bands): $\tilde{\nu}=3444$ (s), 3355 (m–w) ν(N−H); 2982 (m–w), 2927 (m–w) ν(C−H); 1620 (s) ν(C=N); 1589 cm^{-1} (s) δ(N−H); ESI^+-MS (in acetone): *m/z* (%): 322 (100) $[M+H]^+$, 324 (47), 321 (16), 323 (11), 325 (5); elemental analysis calcd (%) for $C_8H_{18}CuN_8O_2$: C 29.86, H 5.64, N 34.82; found: C 29.96, H 5.64, N 34.77.

*[Cu{NH=C(O*n*Pr)NC(NH$_2$)=NH}$_2$]* (**13**): Yield 81%; IR (KBr, selected bands): $\tilde{\nu}=3410$ (s), 3306 (m–w) ν(N−H); 2965 (m–w), 2944 (m–w), 2877 (w) ν(C−H), 1622(s) ν(C=N); 1536 cm^{-1} δ(N−H); ESI^+-MS (in acetone): *m/z* (%): 350 (100) $[M+H]^+$, 352 (44), 351 (11), 353 (7); elemental analysis calcd (%) for $C_{10}H_{22}CuN_8O_2$: C 34.33, H 6.34, N 32.03; found: C 34.27, H 6.57, N 32.11.

*[Cu{NH=C(O*n*Bu)NC(NH$_2$)=NH}$_2$]* (**14**): Yield 78%; IR (KBr, selected bands): $\tilde{\nu}=3321$, 3282 (s) ν(NH); 2938, 2921 (m–w) ν(C−H); 1622 (s) ν(C=N); 1549 cm^{-1} (s) δ(N−H); ESI^+-MS (in acetone): *m/z* (%): 379 (100) $[M+H]^+$, 381 (43), 380 (14), 382 (5); elemental analysis calcd (%) for $C_{12}H_{26}CuN_8O_2$: C 38.14, H 6.93, N 29.65; found: C 38.08, H 6.71, N 29.61.

[Cu{NH=C(OCH$_2$CH$_2$OCH$_3$)NC(NH$_2$)=NH}$_2$] (**15**): Yield 68%; IR (KBr, selected bands): $\tilde{\nu}=3476$, 3375, 3332, 3267 (m) ν(N−H); 2980, 2926, 2890, 2813 (w) ν(C−H); 1617 ν(C=N); 1579 (s) δ(N−H); 1479, 1445 (m), 1264 (s) ν(C−O); 1081 cm^{-1} (s); ESI^+-MS (in acetone): *m/z* (%): 382 (100) $[M+H]^+$, 384 (41), 383 (15), 385 (3); elemental analysis calcd (%) for $C_{10}H_{22}CuN_8O_4$: C 31.45, H 5.81, N 29.34; found: C 31.61, H 5.75, N 29.33.

Pathway mechanistic studies

Reaction with dicyanamide: Compound **16** was isolated after 30 min from the preparative reaction of **2**. Thus, green precipitate **16** was removed by filtration, washed on the filter with 5 portions (20 mL) of water to eliminate sodium acetate, then with 3 portions (10 mL) of MeOH and dried in air. Compounds **17** and **18** were isolated from the preparative reactions of **2** and **3** (after 3 and 4 h), respectively, by evaporation of the solvents and washing the residues with water to remove the sodium acetate. Crystals of **17** and **18** suitable for single-crystal X-ray diffraction analysis were obtained upon recrystallisation of the compounds from an acetone/water (10:1) mixture.

[Cu(N≡C-N-C≡N)$_2$]$_n$ (**16**): Yield 94%; IR (KBr, selected bands): $\tilde{\nu}=$ 2287 (s), 2177 cm^{-1} (s) ν(C≡N); elemental analysis calcd (%) for C_4CuN_6: C 24.56, N 42.96; found C 24.63, N 43.35.

[Cu{HN=C(OEt)NC(OEt)=NH}$_2$[HN=C(OEt)NC(OEt)=NH}Cu{N≡C-N-C≡N}] (**17**): Yield 85%; IR (KBr, selected bands): $\tilde{\nu}=3340$ (m–w), 3300 (m–w) ν(NH); 2974 (s), 2933 (s), 2877 (m–w) ν(CH); 2280 (m–w), 2180 (s) ν(C≡N); 1599 (s) ν(C=N); 1521 cm^{-1} (s) δ(NH); ESI^+-MS (in acetone): *m/z* (%): 668 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{20}H_{36}Cu_2N_{12}O_6$: C 35.98, H 5.43, N 25.17; found C 34.05, H 5.33, N 25.09.

*[Cu{HN=C(O*n*Pr)NC(O*n*Pr)=NH}$_2$[HN=C(O*n*Pr)NC(O*n*Pr)=NH}Cu{N≡C-N-C≡N}]* (**18**): Yield 81%; IR (KBr, selected bands): $\tilde{\nu}=$ 3347 (m–w), 3306 (m–w) ν(NH); 2967 (s), 2938 (m–w), 2878 (m–w) ν(CH); 2284 (m–w), 2170 (s) ν(C≡N); 1601 (s) ν(C=N); 1520 cm^{-1} (s) δ(N−H); ESI^+-MS (in acetone): *m/z* (%): 684 (100) $[M-dca]^+$; elemental analysis calcd (%) for $C_{26}H_{48}Cu_2N_{12}O_6$: C 41.54, H 6.44, N 22.36; found C 41.46, H 6.48, N 22.91.

Reaction with cyanoguanidine: 20 min after the start of the preparative reaction of **6**, the formed green precipitate **19** was removed by filtration, washed with water and methanol and recrystallised from an acetone/methanol (1:1) mixture. Compound **19** (its identity was confirmed by IR and elemental analyses) was also formed in the first stage of the reaction of the preparation of **7**–**10** (the time of its formation depends on the alcohol used). Heating of **19** for 4 h in an acetone/methanol (5:1) mixture led to the formation of blue precipitate **20**, which was then removed by filtration and washed with acetone.

[Cu$_2$(AcO)$_4$[HN=C(NH$_2$)NHCN}$_2$] (**19**): Yield 89%; IR (KBr, selected bands): $\tilde{\nu}=3440$, 3375, 3230 (s) ν(N−H); 2937 (w) ν(C−H); 2211, 2170 (s) ν(C≡N); 1675, 1646 (s) ν(C=O); 1606 ν(C=N); 1557 (s) δ(N−H); 1440 (s), 1264 (s), 1081 (s), 689 cm^{-1} (s); elemental analysis calcd (%) for $C_{12}H_{24}Cu_2N_8O_8$: C 26.92, H 4.52, N 20.93; found: C 27.23, H 3.80, N 20.63.

[Cu$_2$(AcO)$_4$[HN=C(NH$_2$)NHC(OMe)NH}] (**20**): IR (KBr, selected bands): $\tilde{\nu}=3424$, 3367, 3294 (s) ν(NH); 2931, 2830 (w) ν(C−H); 1678 (s) ν(C=O); 1625 ν(C=N); 1559 (s) δ(N−H); 1433 (s), 1217 (m), 1049 (w), 684 cm^{-1} (m); ESI^+-MS (in MeOH): *m/z* (%): 238 (100) $[M-Cu(CH_3COO)_3]^+$; elemental analysis calcd (%) for $C_{11}H_{24}Cu_2N_4O_9$: C 27.56, H 4.20, N 11.69; found C 27.38, H 4.27, N 12.10.

Preparation of pyrimidines: The reaction of the neutral copper(II)–triazopentadiene complexes **11**, **12** and **14** with an excess amount (20 equiv) of 2,4-pentanedione (Hacac) in water at 25°C yields the pyrimidine derivatives **21**–**23** that are soluble in the reaction mixture, and a blue solid characterised as $[Cu(acac)_2]$. The latter complex was separated by filtration, and its residual traces were extracted from the reaction mixture by chloroform. The evaporation of the aqueous phase gives an oil, which is further washed with acetone, to give a white solid of the respective pyrimidine **21**–**23** (81–72%).

NC(Me)CHC(Me)NCNHC(=NH)OMe (**21**): Yield 81%; ^1H NMR (D_2O): $\delta=2.26$ (s, 6H; CH_3C=N), 3.75 (s, 3H; CH_3O), 6.75 ppm (s, 1H; *CH*); $^{13}C\{^1H\}$ NMR (D_2O): $\delta=22.7$ (CH_3), 54.2 (CH_3O), 114.9 (*C*H), 158.0 (N*C*=N), 163.9 (NH*C*=NH), 166.7 ppm (CH_3C=N); IR (KBr, selected bands): $\tilde{\nu}=3308$, 3155 (m) ν(NH); 2840, 2777 (w) ν(C−H); 1646, 1624 (s) ν(C=N); 1590, 1545 (s) δ(N−H); 1410 (m), 1383 (s), 1107 (s), 733 (m), 644 (m), 621 cm^{-1} (m); ESI^+-MS (in H_2O): *m/z* (%): 181 (100)

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$[M+H]^+$, 182 (8); elemental analysis calcd (%) for $C_8H_{12}N_4O$: C 53.32, H 6.71, N 31.09 found: C 53.36, H 6.53, N 31.73.

NC(Me)CHC(Me)NCNHC(=NH)OEt (**22**): Yield 72%; ^{1}H NMR (D_2O): $\delta = 1.20$ (t, J(H,H) = 6.9 Hz, 3H; CH_3CH$_2$), 2.29 (s, 6H; CH_3C=N), 4.07 (q, J(H,H) = 6.9 Hz, 2H; CH$_3$CH_2), 6.80 ppm (s, 1H; CH); ^{13}C{^{1}H} NMR (D_2O): $\delta = 13.3$ (*C*H$_3$CH$_2$), 22.5 (*C*H$_3$), 63.6 (CH$_3$*C*H$_2$), 114.7 (*C*H), 157.9 (N*C*=N), 161.6 (NH*C*=NH), 167.5 ppm (CH$_3$*C*=N); IR (KBr, selected bands): $\tilde{\nu} = 3330$ (sh), 3195 (br) ν(N−H); 2988, 2960 (w) ν(C−H); 1643, 1616, (s) ν(C=N); 1587 (s) ν(C=C); 1542, 1524 (s) δ(N−H); 1437 (m), 1384 (s), 1105 (s), 809 (m), 875 (m), 598 cm^{-1} (m); ESI$^+$-MS (in H_2O): m/z (%): 195 (100) $[M+H]^+$, 196 (13); elemental analysis calcd (%) for $C_9H_{14}N_4O$: C 55.65, H 7.27, N 28.85; found: C 55.12, H 6.94, N 28.34.

NC(Me)CHC(Me)NCNHC(=NH)OCH$_2$CH$_2$OMe (**23**): Yield 80%; ^{1}H NMR (D_2O): $\delta = 2.31$ (s, 6H; CH_3C=N), 3.32 (s, 3H; CH_3O), 3.65 (t, J(H,H) = 4.2 Hz, 2H; CH_2), 4.22 (t, J(H,H) = 4.2 Hz, 2H; CH_2), 6.81 ppm (s, 1H; CH); ^{13}C{^{1}H} NMR (D_2O): $\delta = 22.5$ (*C*H$_3$), 58.0 (*C*H$_3$O), 65.6 (*C*H$_2$), 69.8 (*C*H$_2$), 114.8 (*C*H), 160.1 (N*C*=N), 162.2 (NH*C*=NH), 169.0 ppm (CH$_3$*C*=N); IR (KBr, selected bands): $\tilde{\nu} = 3362$, 3188 (br) ν(NH); 2898, 2860 (w) ν(C−H); 1664(s), 1584 (s) ν(C=N); 1544 (s) δ(N−H); 1408 (m), 1125 (s), 803 (s), 652 (m), 618 (m), 562 cm^{-1} (m); ESI$^+$-MS (in H_2O): m/z (%): 225 (100) $[M+H]^+$, 226 (12); elemental analysis calcd (%) for $C_{10}H_{16}N_4O_2$: C 53.56, H 7.19, N 24.98; found: C 52.97, H 7.02, N 25.00.

Preparation of triazapentadiene salts: The reaction of the cationic copper(II)–triazopentadiene complexes **6**, **7** and **9** with an excess amount (20 equiv) of 2,4-pentanedione (Hacac) in water at 25°C in a few minutes yields the triazopentadiene salts **24**–**26** and a blue solid characterised as [Cu(acac)$_2$]. The procedure for the [Cu(acac)$_2$] separation is similar to that discussed above. Further evaporation of the reaction mixture gave an oil. Washing the mixture with acetone allowed products **24**–**26** to be separated as white solids.

[NH=C(OMe)NC(NH$_2$)=NH](AcO) (**24**): Yield 92%; ^{1}H NMR (CD_3OD): $\delta = 1.90$ (s, 3H; CH_3COO), 3.78 ppm (s, 3H; CH_3O); ^{13}C{^{1}H} NMR (CD_3OD): $\delta = 24.3$ (*C*H$_3$COO), 55.5 (*C*H$_3$O), 161.1 (CH$_3$O*C*=NH), 164.8 (NH*C*=NH), 180.6 ppm (CH$_3$*C*OO); IR (KBr, selected bands): $\tilde{\nu} = 3136$ (m) ν(N−H); 2753 (w) ν(C−H); 1673 (s) ν(C=O); 1623 (s) ν(C=N); 1561, 1543 δ(N−H); 1399 (s), 1181 (m), 999 (m), 879 (w), 832 (m), 804 (m), 709 cm^{-1} (m); ESI$^+$-MS (in MeOH): m/z (%): 117 (100) $[M-AcO]^+$, 118 (5); elemental analysis calcd (%) for $C_5H_{12}N_4O_3$: C 34.09, H 6.87, N 31.80; found: C 33.75, H 7.24, N 31.47.

[NH=C(OEt)NC(NH$_2$)=NH](AcO) (**25**): Yield 88%; ^{1}H NMR (D_2O): $\delta = 1.18$ (t, J(H,H) = 6.5 Hz, 3H; CH_3CH$_2$), 1.78 (s, 3H; CH_3COO), 4.10 ppm (q, J(H,H) = 6.5 Hz, 2H; CH$_3$CH_2); ^{13}C{^{1}H} NMR (D_2O): $\delta =$ 13.3 (*C*H$_3$CH$_2$), 23.2 (*C*H$_3$COO), 65.3 (CH$_3$*C*H$_2$), 160.3 (CH$_3$CH$_2$O*C*=NH), 162.3 (NH*C*=NH), 181.5 ppm (CH$_3$*C*OO); IR (KBr, selected bands): $\tilde{\nu} = 3400$, 3125 (br) ν(NH); 2992, 2891 (w) ν(C−H); 1655 ν(C=O); 1648 ν(C=N); 1559 (s) δ(N−H); 1420 (m), 1384 (s), 1096 (m), 1018 (m), 818 (m), 654 cm^{-1} (s); ESI$^+$-MS (in H_2O): m/z (%): 131 (100) $[M-AcO]^+$, 132 (7); elemental analysis calcd (%) for $C_6H_{14}N_4O_3$: C 37.89, H 7.42, N 29.46; found: C 38.03, H 7.77, N 29.39.

[HN=C(NH$_3$)-NH-C(OCH$_2$CH$_2$OCH$_3$)=NH](AcO) (**26**): Yield 87%; ^{1}H NMR (D_2O): $\delta = 1.79$ (s, 3H; CH_3COO), 3.29 (s, 3H; CH_3O), 3.62 (t, J(H,H) = 4.4 Hz, 2H; CH_2), 4.21 ppm (t, J(H,H) = 4.4 Hz, 2H; CH_2); ^{13}C{^{1}H} NMR (D_2O): $\delta = 23.2$ (*C*H$_3$COO), 58.1 (*C*H$_3$O), 67.0 (*C*H$_2$), 69.8 (*C*H$_2$), 159.6 (CH$_2$O*C*=NH), 162.5 (NH*C*=NH), 181.4 ppm (CH$_3$*C*OO); IR (KBr, selected bands): $\tilde{\nu} = 3328$, 3170 (br) ν(NH); 2988, 2945 (w) ν(C−H); 1630 (m) ν(C=O); 1617 (s) ν(C=N); 1587 (s) δ(N−H); 1437 (s), 1410 (s), 1384 (s), 1105 (m), 809 (m), 655 (m), 595 cm^{-1} (m); ESI$^+$-MS (in H_2O): m/z (%): 161 (100) $[M-AcO]^+$, 162 (7); ESI$^-$-MS (in H_2O): m/z (%): 59 (100) $[AcO]^-$; elemental analysis calcd (%) for $C_7H_{16}N_4O_4$: C 38.18, H 7.32, N 25.44; found: C 38.30, H 7.60, N 25.41.

Catalytic studies

Aerobic oxidation: Oxidation reactions under atmospheric pressure were typically carried out in 100 mL two-necked round-bottomed flasks equipped with a condenser and connected to a balloon filled with O_2. Before the experiment, the apparatus was vacuumed and flushed with O_2 (three times). The experiments with air as oxidant were performed in a similar way, but with the atmospheric air being taken up through the upper part of the reflux condenser. Under typical conditions, the reaction mixtures were prepared as follows: benzyl alcohol (3.06 mmol, 320 μL), catalyst (1 mol%), TEMPO (5 mol%) and K_2CO_3 (1.00 mmol, 33 mol%; as a base) were added to water (10 mL). All the above mol% are versus the substrate. For the reactions under elevated pressure, a stainless steel reactor (13.0 mL) was used. In this case, the reactor was loaded with reagents and solvent (5.0 mL of water) and then pressurised with O_2 (10 bar) from a dioxygen cylinder. The reaction solutions in all cases were vigorously stirred using magnetic stirrers. The desired reaction temperature (in the 25–80°C range) was achieved using an oil bath. The reaction mixtures after the oxidations were neutralised by appropriate amounts (typically ca. 1.0 mL) of 1M HCl, and then ethyl acetate (10.0 mL) was added for the extraction. The organic phase was analyzed by gas chromatography in the presence of acetophenone (150 μL) as an internal standard. Blank tests were performed under typical reaction conditions in the absence of the Cu catalyst and showed the formation of only small amounts (<10%) of benzaldehyde.

Peroxidative oxidation of alcohols with TBHP: Three methods were used for this type of oxidation: a MW-assisted process (method A), a reaction in a sealed tube (method B) and conventional heating with a condenser (method C).

Method A: The alcohol substrate (5 mmol), TBHP (10 mmol) and the copper(II)–triazapentadienato complex (usually 0.01 mmol) were added to a cylindrical Pyrex tube that was then closed and placed in the focused microwave reactor. The system was left under stirring and irradiation for 10–240 min at 50–80°C. After the reaction, the mixture was allowed to cool down, and MeCN (5 mL) was added. Small aliquots (ca. 0.2 mL) were then removed, mixed with Et_2O (ca. 1:5 v/v), centrifuged and subjected to GC analysis. A power of 10 W was selected for all experiments, since we have found that 5 W is not sufficient to maintain the desired reaction temperature, and a higher power (e.g., 20 W) does not significantly affect the product yield.

Method B: The substrate (5 mmol), TBHP (10 mmol) and the copper(II)–triazapentadienato complex (0.01 mmol) were added to a cylindrical Pyrex tube that was then closed and placed in the heating (50°C) oil bath. The system was left under stirring by a magnetic stirrer for a certain time. After the reaction, the mixtures were treated like those described in method A.

Method C: The substrate (5 mmol), TBHP (10 mmol) and the copper(II)–triazapentadienato complex (0.01 mmol) were added to a round-bottomed flask equipped with a condenser and placed in a heating oil bath. The system was left under stirring by a magnetic stirrer for a certain time. After the reaction, the mixtures were treated like those described in method A

Recyclisation of catalyst 1: Conditions: 1-phenylethanol (5 mmol), **1** (0.1 mmol), MW, 30 min, 80°C.

Method A: The aqueous phase from the post-reaction mixture, after removing the organic phase (containing the substrate, product and oxidant) was used for the next run (with new loadings of substrate and oxidant). This procedure was repeated six times.

Method B: The aqueous phase of the post-reaction mixture, after removing the organic phase (containing the substrate, product and oxidant) was evaporated until dryness with air flow and then the solid residue was used for the next run (with new loadings of substrate and oxidant). This procedure was repeated six times.

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