Ligand effects in the copper catalyzed aerobic oxidative carbonylation of methanol to dimethyl carbonate (DMC)

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Abstract

The influence of the type and amount of added N-donor ligand, of the anion and the oxidation state on the copper catalyzed aerobic oxidative carbonylation of methanol to dimethyl carbonate (DMC) is systematically studied. A surprising increase in activity and selectivity compared to the plain copper halides CuX_n (X = Cl, Br, I; $n = 1, 2$) is found for catalyst complexes with three or four N-methylimidazole (NMI) ligands at $Cu^{+/2+}$, a ligand regime reminiscent of the oxygen activating copper enzymes in nature. However, a large excess of NMI inhibits the catalysis. The NMI complexes turned out to be more active and selective as redox catalysts and less active in the competing undesired hydrolytic cleavage of DMC into methanol and carbon dioxide by the unavoidable byproduct water. Furthermore, corrosion of stainless steel autoclaves is efficiently inhibited in the presence of ≥ 2 eq. of NMI per copper halide. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dimethyl carbonate synthesis; Oxidative carbonylation; Copper catalysts; N-ligands; Corrosion resistance
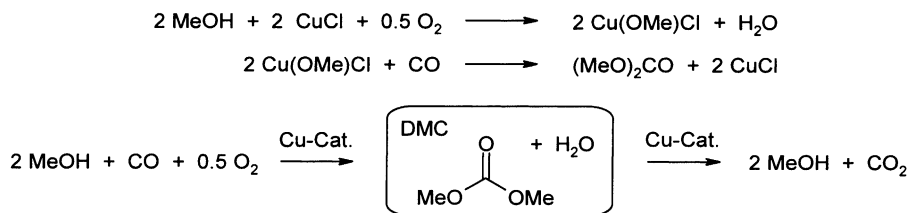
1. Introduction

Due to the increasing number of applications for organic carbonates their production on an industrial scale is of current interest ([1–3] and cited references). They are substances of low toxicity and good biodegradability which may in some cases replace toxic synthons such as phosgene in fine chemical and polymer syntheses [4,5]. They have a potential in the preparation of urethanes from aliphatic amines, which can in turn be cleaved to the corresponding isocyanates. The dimethyl carbonate (DMC) can also act as a non-toxic high-temperature methylating agent, as an alternative to dimethyl sulfate in the quaternization of reactive amines or in the methylation of phenol

and naphthols [6]. The DMC technology may contribute to "Green Chemistry" replacing toxic or high waste technology. Transesterification of DMC leads to diphenyl carbonate, an important component in condensation reactions yielding polycarbonates ([1] and cited references). Finally, DMC gained interest as dipolar aprotic solvent and as fuel additive improving the octane number and replacing more toxic or less biodegradable additives ([3] and cited references).

For many years, the reaction of methanol and phosgene — or chlorine and carbon monoxide — in the presence of bases such as pyridine has been applied for DMC production [7]. Alternative oxidants for carbon monoxide are alkyl nitrites in palladium and platinum catalyzed methanol carbonylations [8,9]. However, these processes have rather high E-factors [10] and will probably be replaced by catalytic low-waste "green" technologies using CO_2 as feedstock or using air as oxidant for CO. An example for

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$$2\ MeOH + 2\ CuCl + 0.5\ O_2 \longrightarrow 2\ Cu(OMe)Cl + H_2O$$

$$2\ Cu(OMe)Cl + CO \longrightarrow (MeO)_2CO + 2\ CuCl$$

$$2\ MeOH + CO + 0.5\ O_2 \xrightarrow{\text{Cu-Cat.}} \boxed{\begin{array}{c} \text{DMC} \\ \underset{MeO\quad\quad OMe}{\overset{O}{\|}}{C} + H_2O \end{array}} \xrightarrow{\text{Cu-Cat.}} 2\ MeOH + CO_2$$

Scheme 1. Redox reactions involved in the oxidative carbonylation of MeOH to DMC and net result.

the first strategy is the Lewis acid catalyzed two-step conversion of carbon dioxide and ethylene oxide into ethylene carbonate followed by its methanolysis to DMC and ethylene glycol [11,12]. The second strategy is laid out in numerous patents claiming the use of basic copper salts [13–17] in the oxidative carbonylation of methanol under various reaction conditions in batch reactors with catalyst slurries or molten salts [18]. The immobilization of copper salts on solid support [19–23] and the addition of bases as promoters such as hydroxides [24] and amines or pyridines [19,25,26] has been claimed, but the specific function of the nitrogen bases remained obscure. It has been proven by a number of carefully designed experiments that the stoichiometric comprehensible redox reactions [27,28] shown in Scheme 1 are most probably involved in the catalytic cycle [29].

There are a number of unresolved problems in the patent literature. Despite of the use of substoichiometric amounts of copper catalysts, only low conversions of up to 30% per batch were observed [13]. Further problems are low selectivities due to undesired byproducts [30] and the reactor corrosion [31–33]. In a recent paper by Sato et al., it was shown that copper chloride on polyvinyl pyridine loses much of its aggressive behavior in stainless steel corrosion [23]. However, there still remains an intrinsic problem in the oxidative carbonylation process: the same copper catalyst, that is performing the redox reaction to DMC and water as by-product appears to catalyze as a Lewis acid the hydrolysis of DMC to CO_2 and MeOH. The net result of this second undesired process is the oxidation of carbon monoxide to carbon dioxide by oxygen. In an attempt to overcome many of these drawbacks we followed a very simple concept of coordination chemistry: in complexes of a Lewis base L (e.g. N-donor) and a Lewis acid Cu^{2+} the acidity of the metal cation is reduced depending on the type and number of

coordinated ligands L of certain donor strength. Mixtures of such complexes of different Lewis acidity $[CuL]^{2+}$, $[CuL_2]^{2+}$, $[CuL_3]^{2+}$, $[CuL_4]^{2+}$ with coordinating (or non-coordinating) anions X^- may be regarded as a ligand buffered catalytic system, that may be more selective in redox reactions and less active in hydrolysis reactions. Therefore, the focus of the present study is a systematic investigation of the influence of the type of applied N-donor ligand, the equivalents of ligand employed per copper as well as the oxidation state and the counter anion of the copper salt on the performance of the oxidative carbonylation of methanol to DMC.

2. Experimental

2.1. General

All reactions were carried out in a 100 ml V4A stainless steel autoclave, sealed with an EPDM O-ring and equipped with a teflon coated magnetic stirring bar, a 100 bar manometer and a Pt-100 thermoelement in the outer aluminum heating block as temperature control unit ($\pm 1^\circ$C).

The organic products were analyzed by quantitative gas chromatography on a HRGC 5300 (Carlo Erba Instruments) equipped with a fused silica guard column (5 m $\times$ 0.53 mm) and a Rtx®-200 analytical column (30 m $\times$ 0.53 mm $\times$ 0.50 μm; Restek); split injector (1:20); FID temperature 200°C, isothermic at 30°C, toluene as internal standard (IS). GC-MS analyses were carried out on a VG Masslab TRIO-2. Melting points were determined in capillary tubes on a Büchi MP B-540 apparatus and are uncorrected. The IR spectra were recorded on a Bruker IFS 88 FT and elemental analyses on a Heraeus CHN-Rapid analyzer.

2.2. Materials and apparatus

Methanol, toluene (IS), diethyl ketone as diluting solvent for GC samples and the ligands *N*-methylimidazole (NMI), 4-methylpyridine were freshly distilled prior to use. The following chemicals were prepared and purified by literature methods: *N*-methylpyrazole [34], CuCl [35], CuCl$_2$ and CuBr$_2$ [36], Cu(ClO$_4$)$_2$ [37], [Cu(C$_6$H$_6$)]$_{1/2}$OTf [38], Cu(OTf)$_2$ [39], [Cu(CH$_3$CN)$_4$]PF$_6$ [40]. Commercially available chemicals were used as received from Aldrich and Fluka: 4-dimethylaminopyridine (DMAP), CuI, CuBr, [Me$_4$N]OH × 5 H$_2$O; [Et$_4$N]$_2$CO$_3$ [Et$_4$N]CN; [Me$_4$N]F; [Et$_4$N]Cl; [Et$_4$N]Br; [Et$_4$N]I. The CO (3.5), O$_2$ (4.8), and synthetic air (20.5% O$_2$ in N$_2$) were obtained from Messer Griesheim.

2.3. Catalyst preparation

The following complexes were synthesized according to known literature methods and analyzed by IR spectroscopy and elemental analyses (L = *N*-methylimidazole, NMI): LCuCl$_2$, L$_4$CuCl$_2$, L$_4$CuBr$_2$, L$_4$CuI$_2$ [41]; L$_2$CuCl$_2$, L$_2$CuBr$_2$ [41,42]; L$_3$CuCl$_2$, LCuBr$_2$, L$_3$CuBr$_2$ [33].

2.3.1. [(NMI)$_4$Cu]PF$_6$, **1**

[Cu(CH$_3$CN)$_4$]PF$_6$ (1.86 g, 5 mmol) is dissolved in 35 ml dry MeOH and NMI (1.66 g, 1.61 ml, 20.25 mmol) is added to the vigorously stirred solution. After 24 h, the reaction mixture is evaporated to half of its volume. A thick colorless precipitate is filtered off, washed with dry ether and dried in vacuo to give [(NMI)$_4$Cu]PF$_6$ (2.63 g, 4.90 mmol) in 98% yield. Elemental analysis (%) calc. for C$_{16}$H$_{24}$N$_8$CuF$_6$P (536.99 g/mol): C, 35.79; H, 4.51; N, 20.87; Cu, 11.84; found: C, 36.13; H, 4.65; N, 20.58; Cu, 11.52, and mp: 113°C. IR (Nujol): $\tilde{\nu}$ = 3154 s, 3127 s, 1620 m, 1512 s, 1464 s, 1285 s, 1231 s, 1086 s, 1026 s, 932 s, 808 s, 760 s, 658 s, 557 s cm^{-1}.

2.3.2. (NMI)$_4$Cu(OTf)$_2$, **2**

Cu(OTf)$_2$ (723 mg, 2 mmol) is dissolved in 15 ml dry EtOH and NMI (723 mg, 8.8 mmol) is added to the vigorously stirred solution. After 24 h, 15 ml of dry ether is added. The precipitate is filtered, washed with dry ether and dried in vacuo to yield 1.325 g (1.92 mmol, 96%) (NMI)$_4$Cu(OTf)$_2$ as a purple powder. Elemental analysis (%) calc. for C$_{18}$H$_{24}$N$_8$O$_6$CuF$_6$S$_2$ (690.16 g/mol): C, 31.33; H, 3.51; N, 16.24; Cu, 9.21; found: C, 31.23; H, 3.64; N, 15.84; Cu, 9.76, and mp: 170°C (dec.). IR (Nujol): $\tilde{\nu}$ = 3136 w, 2967 w, 2851 vs, 1542 s, 1428 m, 1257 s, 1224 s, 1166 s, 1098 m, 1030 s, 952 m, 839 m, 757 m, 660 s, 638 s cm^{-1}.

2.4. Catalytic runs

The values for conversion and selectivity given in the charts and tables are based on an average of three experiments that have been reproduced within an experimental error of 2%.

2.4.1. Typical experimental procedure with isolated catalyst

The copper complex (0.3 mmol, 1 mol% relative to MeOH) is placed into the autoclave and methanol (30 mmol, 961 mg, l215 μl) is added via a syringe. In order to avoid the risk of working within the explosion area of the mixture CO/O$_2$ [43], the autoclave is filled at 20°C first with 2.65 bar oxygen (12.5 or 23 bar synthetic air, respectively, see Table 2), then with additional 50 bar carbon monoxide. After disconnecting the autoclave from the gas supply it is inserted into an aluminum heating block preheated to 150°C. Within 5 min, the autoclave reaches the reaction temperature of 120°C that is held constant. After a reaction time of 4 h, the autoclave is depressurized over a period of 10 min via a liquid nitrogen trap and finally all volatiles at 150°C/10^{-2} mbar are collected in that trap as well. To the condensate 5 mmol (461 mg) of toluene as internal standard (IS) is added. After diluting the condensate with 10 ml of diethyl ketone the homogenous mixture was analyzed via quantitative capillary gas chromatography. Products were identified and quantified by comparison of retention times and calibrated integrals with authentic samples.

2.4.2. Typical experimental procedure with catalyst prepared in situ

The copper salt (0.3 mmol, 1 mol% relative to MeOH or EtOH), N-ligand (molar quantities with respect to the desired equivalents, e.g. NMI, 99 mg, 96 μl, 1.2 mmol, 4 eq.) and methanol (30 mmol, 961 mg, 1215 μl) are placed into the autoclave and the procedure described above is followed.

The same procedure is followed with 1.5 mmol (5 mol%) and 3 mmol (10 mol%) copper salt relative to MeOH and the corresponding equivalents of ligand (see Section 3.4.2).

2.4.3. Added ammonium salts to Cu(I)

About 161 mg (0.3 mmol, 1 mol% relative to MeOH) of copper complex $[(NMI)_4Cu]PF_6$ (**1**), 961 mg (30 mmol, 1215 μl) MeOH, and equimolar amounts of tetraalkyl ammonium salts (see Section 3.4.1) containing the desired anion are placed together into the autoclave and the procedure described above is followed.

2.4.4. Hydrolysis experiments

About 15 mmol DMC (1351 mg, 1263 μl) and 15 mmol H_2O (271 mg, 271 μl) are placed together into the autoclave and then pressurized with 2.15 bar O_2 and 40 bar CO (the consumption of reaction gases under catalytic conditions is taken into account). After a reaction time of 1 h, (30 min at 20–120°C followed by 30 min at 120°C) the content of the autoclave is analyzed in the same way as described before.

2.4.5. Catalysis in the presence of molecular sieves 3 Å

The experiments were carried out by applying exactly the procedure described above for catalyst preparation in situ (Section 2.4.2), however, 2.7 g 3 Å molecular sieves as beads (Fluka, Ø ∼ 2 mm) were added together with the catalyst and substrate.

3. Results and discussion

3.1. Influence of the type of N-ligand

As already mentioned, some patents are claiming the addition of bases such as hydroxides, amines or pyridines as promoters for the formation of basic copper catalysts in the presence of water and as corrosion inhibitors. In our first experiments, we tested the performance of isolated complexes L_4CuCl_2 (L = N-methylimidazole (NMI) and 4-methylpyridine) versus the blank sample of anhydrous $CuCl_2$ under identical conditions in DMC production: 1 mol% Cu catalyst in MeOH, 2.5 bar O_2, 50 bar CO, 120°C, 4 h. We observed that conversion of MeOH and selectivity in DMC synthesis did not deviate within the limits of experimental error (±2%) from those experiments obtained from in situ prepared complexes (Scheme 1). There is even a tendency, that injection of the 4 eq. of the corresponding ligand to a methanol solution of $CuCl_2$ gave slightly better results (+1–2%) than the use of isolated and analytically characterized complexes L_4CuCl_2. Therefore, whenever possible we preferred the in situ generation of the catalytically active complexes.

Fig. 1 demonstrates that under the given conditions of our batch experiment the blank sample of $CuCl_2$ leads to a MeOH conversion of 15% and a DMC selectivity of 46%; this corresponds to a theoretical yield of 7% DMC. A number of added N-donor ligands including pyrazole, N-methylpyrazole and 4-methylpyridine
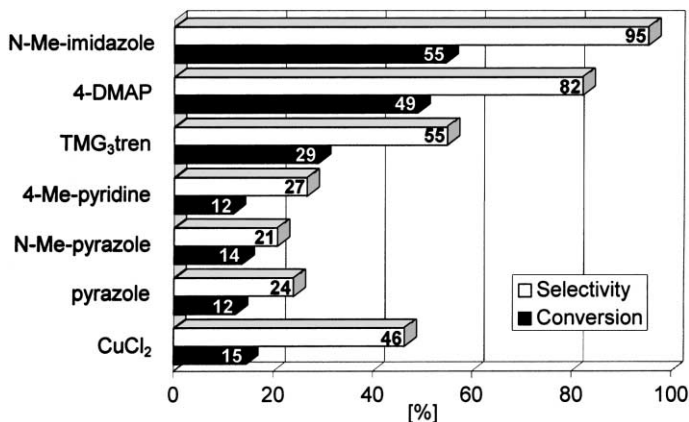

Fig. 1. $CuCl_2$ catalyst with added 4 eq. of various N-ligands. Reaction conditions: 1 mol% catalyst, 2.5 bar O_2, 50 bar CO, 120°C, 4 h.
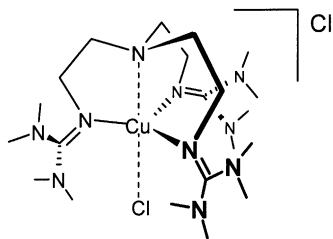
Fig. 2. Complex of TMG$_3$tren and Cu^{II}Cl$_2$.

did not increase the conversion whereas the selectivity drops to 20–30%. With respect to the DMC yields, it is clearly unfavorable to add 4 eq. of such ligands. However, we were surprised to find that addition of very basic N-donors such as TMG$_3$tren, 1,1,1-tris[2-(N^2-(1,1,3,3-tetramethylguanidino))ethyl] amine (see Fig. 2) [44,45], a superbasic peralkyl-guanidine derivative of tren (1 eq. of tetradentate ligand added), DMAP (4-dimethylaminopyridine) and NMI did significantly increase both, conversion and selectivity. It is noteworthy that the typical byproducts of the oxidative carbonylation of MeOH such as dimethoxy methane CH$_2$(OCH$_3$)$_2$ (DMM) and methyl formate HCOOCH$_3$ (MF) [22] could not be detected by means of GC-MS and by comparison with authentic samples.

The best performance (55% conversion and 95% selectivity) is achieved by addition of 4 eq. of NMI. For technical reasons, the consumption of oxygen has not been monitored. However, the initial partial pressure of oxygen (2.5 bar O$_2$ in a 100 ml reactor) has been chosen to assure theoretically a full conversion of methanol even in the presence of the large excess of carbon monoxide (CO:O$_2$ = 91:9 mol%) being employed in order to stay outside the upper explosion area. It is expected that conversion and selectivity will become even better, if the technical requirements of the reactor would allow us to hold the oxygen concentration constant and to monitor the undesired CO oxidation to CO$_2$. It is important to note that corrosion of the stainless steel autoclave is most striking with the blank CuCl$_2$ sample, however, the corrosion is perfectly inhibited in each experiment with 4 eq. of added N-ligand.

3.2. Influence of the number of equivalents NMI at CuCl$_2$ and CuBr$_2$

The question arose how many equivalents of added NMI would give the best performance. Fig. 3 presents the results of a series of experiments with 1, 2, 3, 4, and 10 eq. NMI added. We observe a continuous increase in MeOH conversion with a peak of 55% at 4 eq. If more than one ligand NMI is added to the catalytic reaction the selectivity is increasing significantly, at the same time the corrosion is efficiently inhibited. It is interesting to note that a large excess of 10 eq. added NMI tends to inhibit the catalytic cycle.

A similar but not identical trend is observed for the corresponding CuBr$_2$ complexes (Fig. 4). They

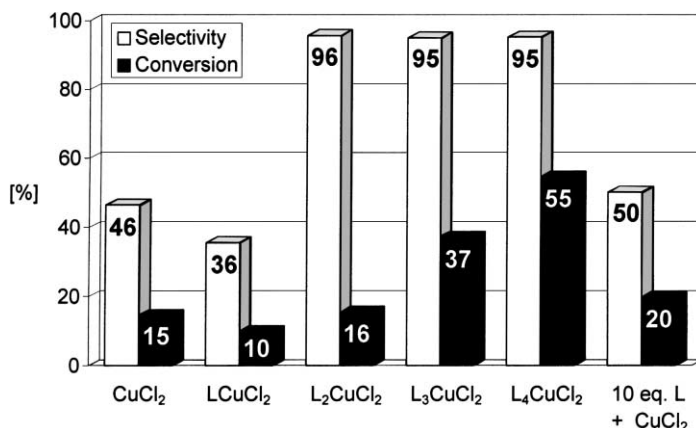Fig. 3. CuCl$_2$ catalyst with various added equivalents of *N*-methylimidazole (L). Reaction conditions: 1 mol% catalyst, 2.5 bar O$_2$, 50 bar CO, 120°C, 4 h.
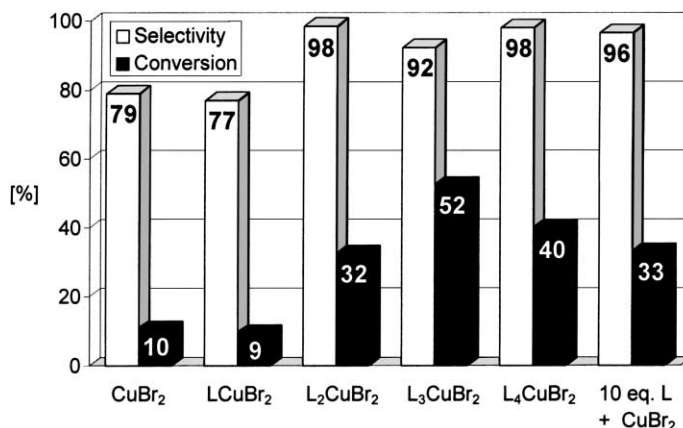
Fig. 4. CuBr$_2$ catalyst with various added equivalents of N-methylimidazole (L). Reaction conditions: 1 mol% catalyst, 2.5 bar O$_2$, 50 bar CO, 120 °C, 4 h.

tend to be slightly more selective than their chloro counterparts and interestingly the peak of performance is found for the complex (NMI)$_3$CuBr$_2$. We observe the trend, that more than three added ligands NMI tend to inhibit the catalysis.

Inhibition of catalysis by an excess of NMI may be taken as an indication that an important step of the catalytic cycle might involve the dissociation of a [(NMI)$_4$Cu]$^{n+}$ complex into a [(NMI)$_3$Cu]$^{n+}$ species. Even though, nature does not know the problem of DMC synthesis from CO, we were very surprised to learn, that our best results were obtained with a copper center coordinated by three or four imidazole ligands.

The [(NMI)$_3$Cu]$^{n+}$ core is reminiscent of the coordination site of the oxygen activating non-blue copper proteins in nature and the oxygen carrier hemocyanine. In the latter, copper is coordinated by three histidine ligands (Fig. 5). It is occurring in molluscs and arthropods in order to make oxygen available for their metabolism [46,47].

3.3. Anion influence on Cu(II) and Cu(I)

Stimulated by the slightly different results of CuCl$_2$ versus CuBr$_2$ and by the fact that copper proteins in nature are using the Cu(I) oxidation state in their

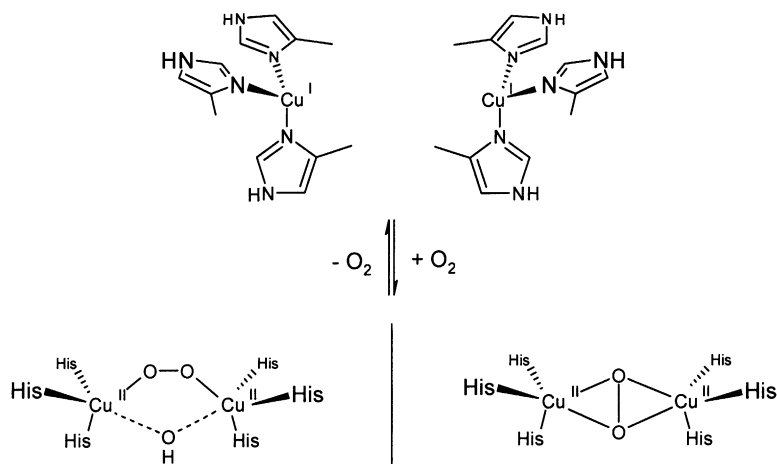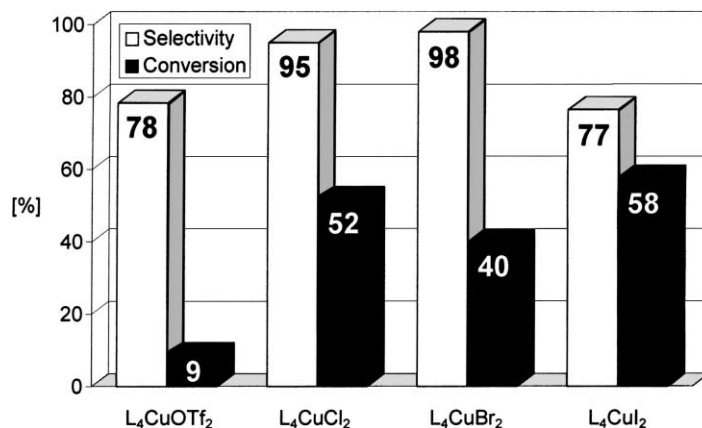Fig. 5. Binding and transport of dioxygen in hemocyanine.

Fig. 6. Influence of various anions X^- (=OTf^-, Cl^-, Br^-, I^-) on the performance of isolated *N*-methylimidazole (L) complexes of Cu(II) L_4CuX_2. Reaction conditions: 1 mol% catalyst, 2.5 bar O_2, 50 bar CO, 120°C, 4 h.

desoxy form we prepared a series of known and comparable Cu(I) and -(II) complexes $(NMI)_4CuX_n$ (n = 1, 2; X = Cl, Br, I, OTf) in order to investigate the anion effect on the catalysis more thoroughly. This series includes iodide as anion which is not oxidized by Cu(II) within the ligand regime of $[(NMI)_4Cu]^{2+}$ and triflate as a weakly or non-coordinating anion. The results with Cu(II) are shown in Fig. 6. The triflate is not competitive with respect to conversion and selectivity. The best conversion (58%) is achieved with the iodo complex, however, at the expense of selectivity (77%), thus, the theoretical yield of DMC is not exceeding 44%. The top performance with respect to

the DMC yield (49%) is shown by the chloro complex (52% conversion and 95% selectivity) and the top performance with respect to selectivity by the bromo complex (98% selectivity at a conversion of 40% corresponding to 39% yield).

The results under identical catalytic conditions but with Cu(I) as the coordination center are shown in Fig. 7. Again the triflate shows the lowest conversion and selectivity. Most interestingly, the Cu(I) halide complexes follow the same trend in activity (conversion $Cl^- > Br^- \ll I^-$) as the corresponding Cu(II) halide complexes. There is a tendency that Cu(II) complexes are slightly more active and selective than the
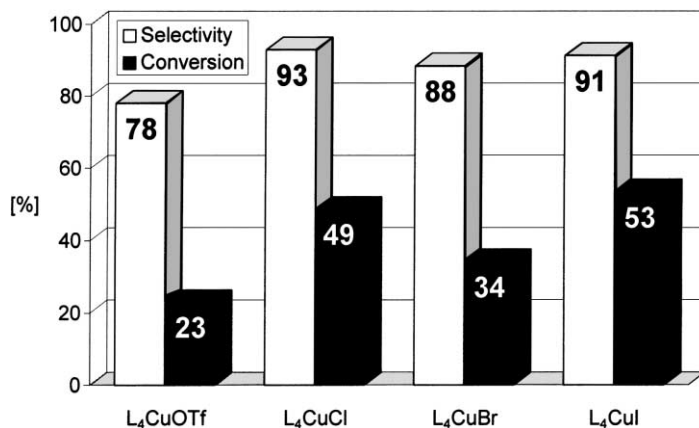

Fig. 7. Influence of various anions X^- (=OTf^-, Cl^-, Br^-, I^-) on the performance of isolated *N*-methylimidazole (L) complexes of Cu(I) L_4CuX. Reaction conditions: 1 mol% catalyst, 2.5 bar O_2, 50 bar CO, 120°C, 4 h.

corresponding Cu(I) complexes. The same order of magnitude and the same trend with respect to their catalytic performance is in accord with the assumption that the same catalytic species is formed by both catalyst precursors. If both, Cu(I) and Cu(II) centers, are involved in the catalytic cycle, it seems not to be relevant, whether we start with one or the other, but obviously it appears to be much more relevant, how many equivalents of a strong N-donor are present per copper atom.

3.4. Influence of other parameters

3.4.1. Added ammonium salts to [Cu(NMI)$_4$]PF$_6$

Because of the strong impact of the anion on this catalysis, we were interested to evaluate a much greater number of anions in their effect on the catalytic performance of [(NMI)$_4$Cu]$^{n+}$ centers. It was found that a combination of equimolar amounts of [Cu(NMI)$_4$]PF$_6$ with a non-coordinating anion and a quaternary ammonium salt of coordinating anions Cl$^-$, Br$^-$, and I$^-$ gave nearly the same results (Fig. 8) as the use of the isolated complexes of these anions (Fig. 7). Therefore, we set out to test carbonate, hydroxide, fluoride, cyanide and other anions which were added as ammonium salts. We learned, that activity and selectivity is increasing dramatically if chloride, bromide, and iodide is added to the standard catalyst with PF$_6^-$ counter anion (same trend PF$_6^-$ ≪

Cl$^-$ > Br$^-$ < I$^-$). However, activity and selectivity is decreasing with a trend PF$_6^-$ > F$^-$ > CN$^-$ > CO$_3^{2-}$ > OH$^-$ if these anions were added as corresponding ammonium salts. In patent literature, basic copper halides are made responsible for catalytic activity. Therefore, it is surprising, that added hydroxide shows one of the lowest conversions and the lowest selectivity. However, it has to be noted that in our experiment added ammonium salt [Me$_4$N]OH × 5H$_2$O was added as hydrate. Now it becomes evident that water obviously inhibits an important step of the catalytic cycle, furthermore, it seems to lower the selectivity, e.g. by hydrolysis and formation of carbon dioxide.

3.4.2. Concentration of catalyst

In many patents, substoichiometric (or even stoichiometric) amounts of copper catalysts were employed. This led us to the question whether our well-defined complexes may show even higher yields of DMC if the catalyst concentration is increased. We had to learn, that higher catalyst concentrations result only in moderate increases of conversion but at the expense of selectivity (Table 1). Consequently, the yields are not increasing very much.

3.4.3. Oxygen versus synthetic air as oxidant

With respect to industrial applications in DMC synthesis the use of synthetic air instead of pure oxygen was tested. In a comparative study, the best catalyst
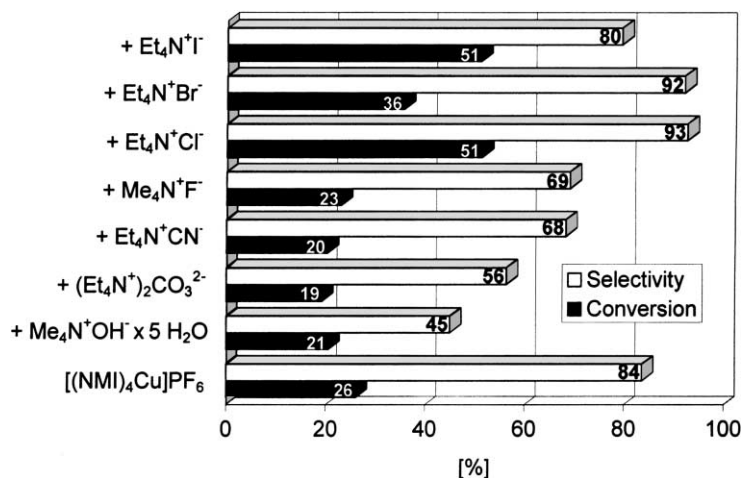

Fig. 8. Added ammonium salts equimolar to [(NMI)$_4$Cu]PF$_6$. Reaction conditions: 1 mol% (NMI)$_4$CuPF$_6$ (+1 mol% X$^-$; +0.5 mol% X^{2-}), 2.5 bar O$_2$, 50 bar CO, 120°C, 4 h.

Table 1
Variation of catalyst concentration[a]

Catalyst (mol%)	1	5	10
Conversion	55	61	67
Selectivity	95	90	87
DMC yield	52	55	58

[a] Catalyst $(NMI)_4CuCl_2$, 2.5 bar O_2, 50 bar CO, 120°C, 4 h.

Table 2
Comparison oxygen vs. synthetic air[a]

Partial press (bar)	Synthetic air 12.5	Synthetic air 23	O_2 2.5
Conversion	43	40	55
Selectivity	76	88	95
DMC yield	33	35	52

[a] 1 mol% $(NMI)_4CuCl_2$, 50 bar CO, 120 °C, 4 h.

$(NMI)_4CuCl_2$ and 12.5 bar synthetic air representing an equivalent partial pressure of 2.5 bar pure oxygen was investigated. However, the conversion and particularly the selectivity is significantly lower, even if the effect of diluting oxygen by nitrogen was in part compensated with an even higher pressure (23 bar) of synthetic air (Table 2).

3.4.4. Reaction time

A rough kinetic profile of the catalysis is given in Fig. 9. After a reaction time of 4 h, a maximum of conversion and selectivity is achieved. Longer reaction times result in a formal decrease of conversion

and selectivity as more and more methanol is produced by hydrolysis of DMC by the unavoidable byproduct water. With decreasing conversion and selectivity, the yields of DMC are going down from the maximum of 52% (after 4 h) via 42% (after 8 h) to 41% (after 16 h). At longer reaction times, the system appears to approach an equilibrium state between DMC production and DMC hydrolysis.

3.4.5. Ethanol as substrate

In order to evaluate whether our catalyst system is applicable to other substrates we carried out experiments using EtOH producing diethylcarbonate (DEC). Under the previously established optimized conditions (1 mol% $(NMI)_4CuCl_2$; 2.5 bar O_2; 50 bar CO; 4 h; 120°C) DEC was formed with a conversion of 35% EtOH and in 79% selectivity. Apparently, the steric requirement and pKs of the alcohol are responsible for the lower yield of 28% DEC. Our current interest is focused on the direct catalytic synthesis of diphenylcarbonate (DPC) without major loss of phenol as polyphenyleneoxide (PPO).

3.5. Hydrolysis of DMC

With the aim to compare the redox versus hydrolytic activity of our catalyst complex $(NMI)_4CuCl_2$ with anhydrous $CuCl_2$ an experiment was designed where the starting point of the observation of hydrolytic activity is set at theoretical 100% conversion of MeOH and 100% selectivity to yield DMC and
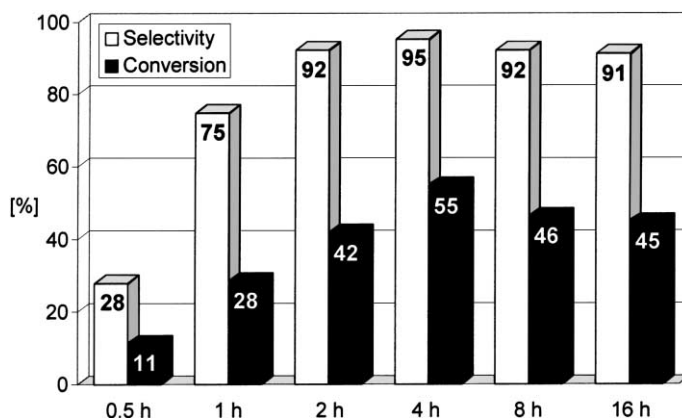

Fig. 9. Variation of reaction times. 1 mol% $(NMI)_4CuCl_2$, 2.5 bar O_2, 50 bar CO, 120°C.

Table 3
Ratio DMC/MeOH as a consequence of hydrolysis[a]

Catalyst	DMC/MeOH (%)	
	$t = 0$ h	$t = 1$ h
$CuCl_2$	100/0	73/27
$(NMI)_4CuCl_2$	100/0	91/9

[a] DMC: H_2O (1:1), 1 mol% catalyst, 2.15 bar O_2, 40 bar CO, $t = 30$ min at 20–120°C followed by 30 min at 120°C.

H_2O. An equimolar mixture of DMC and water is exposed to the same conditions as in the catalytic runs. After a reaction time, of 60 min (30 min at 20–120°C followed by 30 min at 120°C) the content of the autoclave is analyzed. Indeed, $CuCl_2$ buffered by 4 eq. of NMI leads to only 10% hydrolysis of DMC compared to 27% for $CuCl_2$ without any N-donor ligands (Table 3). This fact clearly emphasizes that a catalyst system containing N-donor ligands such as NMI is not only superior in catalyzing the redox reaction with oxygen but also in retarding the DMC hydrolysis back to MeOH. It is plausible that for example intermediate species with a $[Cu(\mu\text{-OH})Cu]^{n+}$ core are stronger protic acids and stronger Lewis acids when the copper centers are not coordinated by a set of three–four strong N-donor ligands. With respect to the better redox activity we already noted that imidazole coordination mimics histidine coordination of the oxygen activating copper redox enzymes of nature.

Finally, experiments employing 3 Å molecular sieves as water withdrawing agent in order to reduce the risk of hydrolysis were carried out and the conversion as well as selectivity was compared with the blank experiment without added molecular sieves and the catalyst $(NMI)_4CuCl_2$.

In the presence of molecular sieves, the conversion is rising from 55 to 87% whereas the selectivity is decreasing from 95 to 75%. Nevertheless, the DMC yield of 65% (compared to 52%) is the highest achieved in our experiments. Our current investigations are aimed at the extraction of water by different strategies.

3.6. Mechanistic aspects

The mechanism of the copper catalyzed oxidative carbonylation of methanol to DMC has been the focus of some detailed studies. First insight was published

by Saegusa et al. [27,28]. More detailed studies have been performed by Romano et al. including an investigation on the effect of water on DMC formation [29]. Extensive FTIR studies were performed by King gaining further evidence for certain intermediates such as $Cu^I(CO)$, $Cu^{II}(OMe)$ and a copper methoxycarbonyl intermediate [48]. In order to exclude a mechanism via radical coupling of Cl (from $CuCl_2$) and CO to phosgene and its methanolysis to DMC, we have investigated the reaction of anhydrous $CuCl_2$ with carbon monoxide in chlorobenzene as solvent. After 4 h/120°C at a pressure of 50 bar CO a first fraction of volatiles (ca. 10 ml condensate) was collected in a liquid nitrogen trap. We were not able to detect any phosgene in that condensate. As a most sensitive test for phosgene we used the trapping reaction with an equimolar mixture of methanol/pyridine, but could not detect any DMC via GC.

Based on the previous mechanistic proposals and taking our own observation into account that it is not critical whether to start with Cu(I) or Cu(II) salts, we propose a slightly modified mechanism involving a path of reductive oxygen activation, a path of carbon monoxide activation, an equilibrium of competing methanolysis versus hydrolysis of a copper oxo complex, and finally, two consecutive C–O-bond forming steps, the first performed in a mixed valence Cu(I, II) cluster, the second in a Cu(II) cluster. A proposed catalytic cycle is shown in Scheme 2.

In Scheme 2, neither the anion — preferably chloride — nor the neutral N-donor ligand — preferably NMI — is taken into account. We learned from our experiments, that both ligands play an important part. It is assumed that chloride is providing the ideal three-electron donor ligand (μ-Cl) for the formation of mixed valent Cu(I, II)-chloro- and -methoxo-bridged clusters that may be involved in the cycle. Furthermore, imidazole is providing a perfect ligand regime for the activation of molecular oxygen [49,50] in a dinuclear or even higher-nuclear Cu(I) complex environment. If we assume that Cu(III) species are not involved in the O_2 reduction process, which is plausible at high concentrations of Cu(I), triplet oxygen will be reduced by 4 eq. of Cu(I) via a peroxo intermediate to give either 2 eq. of $[Cu(\mu\text{-OH})_2Cu]^{2+}$ (in the presence of water) or 2 eq. of $[Cu(\mu\text{-OMe})_2Cu]^{2+}$ (in the presence of excess methanol). Both structural units may be in equilibrium via competing methanolysis/hydrolysis
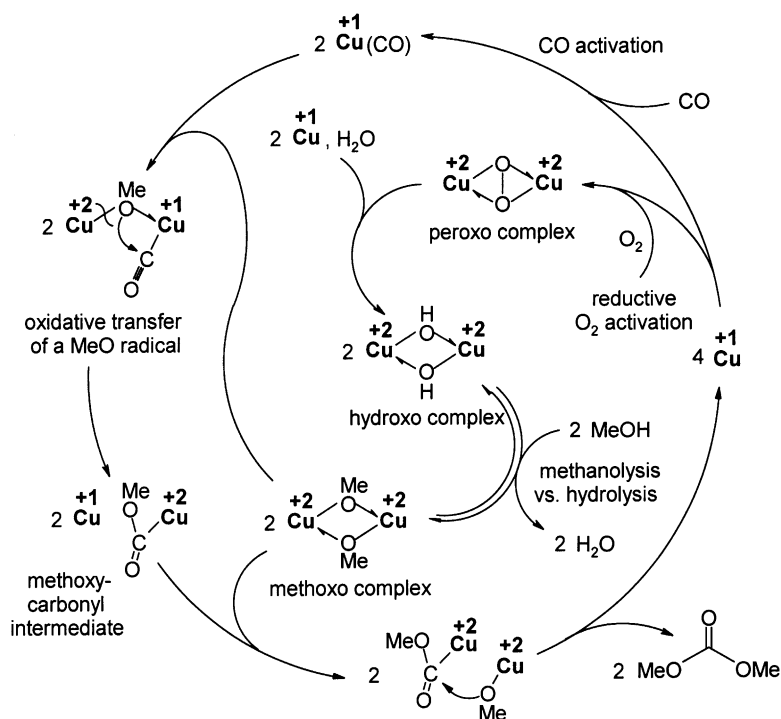
Scheme 2. Proposed catalytic reaction cycle for the oxidative carbonylation of methanol to DMC.

processes, respectively. Hydrolysis may be even the preferred process, if the water content of the mixture becomes significant. Structural evidence for the existence of μ-peroxo, -hydroxo, and -oxo complexes stabilized by chelating N-donor ligands has been provided by Karlin [51,52], Kitajima [53,54], Tolman [55] and other authors ([56] and cited references). A structurally characterized example for a dinuclear μ-methoxo complex is [Cu(C₅H₅N)(OCH₃)Cl]₂ [57]. The second reaction path of Scheme 2 illustrates the CO activation at a Cu(I) site. It is known that strong N-donor ligands render Cu(I) more electron rich and more capable for CO coordination [58]. We propose that a Cu(I) site for CO coordination and a Cu(II)-methoxo/-chloro species may form a mixed valent cluster via bridging ligands. In such clusters a latent methoxy radical may be formally transferred from Cu(II) to a CO ligand coordinated at an adjoining Cu(I) center. As a result, a new Cu(I) and a new Cu(II) methoxycarbonyl species would be generated. Equally, the nucleophilic attack of a methoxide

anion at CO activated at Cu(I) followed by an electron transfer from Cu(I) to Cu(II) may be discussed. Coupling of a methoxycarbonyl radical and a methoxy radical should occur at a multinuclear Cu(II) cluster as there is no conceivable pathway which would allow the reductive elimination of both radicals [MeO] and [C(O)OMe] at a mononuclear Cu(II) site.

While it is known that a certain amount of water is required in the catalytic cycle [59], it is evident that larger amounts of water lead to unselective oxidation of CO to CO_2. The water sensitive spot in our mechanistic proposal is the equilibrium between the copper methoxo and hydroxo complex. Transfer of an OH radical would generate a carbonic acid monoester, which would decompose to carbon dioxide [60] and MeOH. On the other hand, hydrolysis of the methoxycarbonyl intermediate would generate a carbonic acid monoester and formally a copper hydrido species, methanolysis of the methoxycarbonyl species would generate the carbonic acid diester and a copper hydrido species. As long as

there are no model reactions available it can only be speculated that there might be even more or other mechanistic pathways involved in this DMC synthesis, e.g. involving reoxidation of such copper hydrido species by either oxygen or Cu(II)-peroxo/-oxo species. We are currently working on these model reactions.

4. Conclusion

The present paper describes a systematic study of ligand effects of anions and neutral N-donors on the oxidative carbonylation of dimethyl carbonate to dimethylcarbonate. Whereas in a qualitative manner the preference for copper halides has been reported before, a most surprising impact of NMI coordination to copper has been discovered here. The activity in methanol conversion and selectivity in DMC production is drastically increased if three or four strong N-donor ligands of the pentaalkylguanidine type, 4-dimethylaminopyridine (DMAP), and preferably NMI are coordinated at the catalytically active copper center. The imidazole coordination mimics the histidine coordination in oxygen activating copper enzymes of nature. Surprisingly, the number and type of coordinated N-ligands has a much higher impact on the catalytic performance, than the oxidation state of the copper complex and its counter anion — as long as it belongs to the group of heavier halides (chloride, bromide and iodide). All other anions including fluoride, hydroxide, carbonate, and cyanide (cyanate) give only poor results. The three top catalyst complexes $(NMI)_4CuCl_2$, $(NMI)_3CuBr_2$, and $(NMI)_4CuI$ show selectivities exceeding 90% in DMC production at methanol conversions exceeding 50% under our standard batch reaction conditions (1 mol% catalyst, 2.5 bar O_2, 50 bar CO, 120°C, 4 h). The great advantage of these complexes is their higher activity and selectivity in oxygen activation and redox catalysis combined with their lower hydrolytic activity in the undesired DMC hydrolysis by the unavoidable byproduct water. Catalytic runs with such complexes require only low catalyst concentrations of 1 mol% compared to substoichiometric or even higher amounts of copper halides without N-ligand support. Finally, corrosion of the stainless steel reactors is efficiently inhibited if ≥ 2 eq. of N-donor ligand are present.

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