Fluorous Biphasic Catalysis: Synthesis and Characterization of Copper(I) and Copper(II) Fluoroponytailed 1,4,7-R_f-TACN and 2,2′-R_f-Bipyridine Complexes—Their Catalytic Activity in the Oxidation of Hydrocarbons, Olefins, and Alcohols, Including Mechanistic Implications

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Abstract: In this contribution on fluorous biphasic catalysis (FBC), we present the synthesis and characterization of new copper complexes, and define their role, as precatalysts, in the FBC oxidation of hydrocarbons, olefins, and alcohols. Thus the previously reported, but poorly characterized, fluoroponytailed ligand, 2,2′-R_f-bipyridine ($R_f = -(CH_2)_3C_8F_{17}$) **2**, as well as the new Cu^{II} fluoroponytailed carboxylate synthon complex $[Cu(C_8F_{17}(CH_2)_2CO_2)_2]$ **3**, will be addressed. Moreover, the reaction of previously described ligands, 1,4,7-R_f-TACN **1**, or 2,2′-R_f-bipyridine **2** with **3** afforded new perfluoroheptane-soluble Cu^{II} complexes, $[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ **4** and $[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-bpy})]$ **5**, respectively. The reaction of **1** with $[Cu(CH_3CN)_4]PF_6$ or [CuCl] provided new Cu^I complexes, which could be isolated and fully characterized as $[Cu(R_f\text{-tacn})X']X$, in which $X = PF_6$ (**6**) or $X' = Cl$ (**7**) (soluble in perfluoroheptane). The Cu^{II} and Cu^I complexes, **4**–**7**, were characterized by elemental analysis, mass spectrometry, and IR, diffuse reflectance UV/Vis, and EPR spectroscopies; complex **7** was also characterized by ^1H and $^{19}F\{^1H\}$ NMR spectroscopy. Complexes **4** and **5**, as well as **6** and **7** generated in situ, were evaluated as precatalysts for hydrocarbon and olefin functionalization. The oxidation reactions of these substrates in the presence of the necessary oxidants, *tert*-butyl hydroperoxide (TBHP) and oxygen gas, proceeded under FBC conditions for **5**, **7**, and Cu^I salts with **2**. However, the complexes with ligand **2** could not be recycled, owing to significant ligand dissociation. The Cu^{II} complex **4**, with the ligand **1**, provide the oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde under single-phase FBC conditions at 90 °C with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) and O_2; the precatalyst **4**, can be utilized for an additional four catalytic cycles without loss of activity. Plausible mechanisms concerning these FBC oxidation reactions will be discussed.

Keywords: biphasic catalysis · copper · mechanisms · N ligands · oxidation

Introduction

The efficient, catalytic synthesis of alcohols, aldehydes, ketones, and epoxides from alkanes and alkenes is a cornerstone of global industrial research for the preparation of a variety of products for world-wide consumption.[1] Homogeneous catalytic oxidation is more selective toward the above-mentioned products and, in addition, the reactions are carried out at lower temperatures than those used in heterogeneous catalytic oxidation. Thus, the development of a homogeneous oxidation process for alkane and alkene functionalization has been an important goal in numerous industrial and academic laboratories.[1] In order for this process to be industrially practicable in view of economical and environmental concerns, new and innovative approaches for the separation of the homogeneous catalyst from the oxidation products are still needed. In recent years, Horváth and Rábai introduced the concept of fluorous biphasic catalysis (FBC),[2] and demonstrated that by using fluorocarbon solvents and modifying the homogeneous catalyst's ligand structure with long-chain perfluoroalkane derivatives (fluoroponytails) to make the precatalyst soluble in the fluorocarbon phase, the products of the catalytic reaction would be soluble in a separate solvent

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phase that is immiscible in the fluorocarbon phase; by removing this second phase, the products are easily separated from the precatalyst. It should also be noted that the miscibility of perfluoroalkanes and perfluoroethers with the products of alkane and alkene oxidation, such as alcohols, aldehydes, ketones, and epoxides, is extremely low or nonexistent.[3] This latter critical characteristic, and the fact that perfluoroalkanes and perfluoroethers are very interesting for their nonpolarity and extremely low intermolecular forces, makes them ideal solvents for homogeneous biphasic catalytic processes. The FBC concept has now been amply demonstrated with the conversion of many examples of classic organic catalytic reactions to the FBC paradigm,[4] amongst them oxidation reactions.[5–11] However, there is still an urgent need to synthesize and fully characterize new fluoroponytailed ligands and their metal complexes for unequivocal structural identification, and in order to understand the mechanisms of the oxidation chemistry under FBC reaction conditions.[7d]

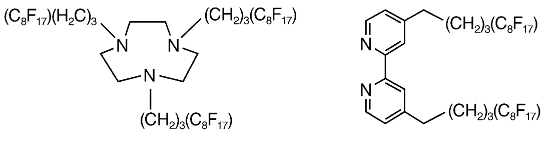
Abstract in Spanish: *En esta contribución en catálisis bifásica fluorada (FBC) presentamos la síntesis y caracterización de nuevos complejos de cobre y definimos su papel, como precatalizadores, en la oxidación FBC de hidrocarburos, olefinas y alcoholes. Así, se describe la preparación y caracterización del ligando fluorado 2,2'-R_f-bipiridina* ***2*** *(R_f = -$(CH_2)_3C_8F_{17}$), que había sido publicado anteriormente pero sin datos experimentales sobre síntesis o caracterización, y la preparación del compuesto sintón carboxilato [$Cu(C_8F_{17}(CH_2)_2CO_2)_2$],* ***3****. La reacción de los ligandos previamente descritos 1,4,7-R_f-TACN,* ***1****, o 2,2'-R_f-bipyridina,* ***2*** *con* ***3*** *permiten la formación de compuestos de Cu^{II} solubles en perfluoroheptano como [$Cu(C_8F_{17}(CH_2)_2CO_2)_2$($R_f$-tacn)],* ***4****, y [$Cu(C_8F_{17}(CH_2)_2CO_2)_2$($R_f$-bpy)],* ***5****, respectivamente. La reacción de 1,4,7-R_f-TACN,* ***1****, con [$Cu(CH_3CN)_4$]PF_6 o [CuCl] genera nuevos compuestos de Cu^I que pueden ser aislados y caracterizados completamente como [Cu(R_f-tacn)X']X, con X = PF_6,* ***6****, o X' = Cl,* ***7*** *(soluble en perfluoroheptano). Los compuestos de Cu^I y Cu^{II},* ***4–7****, se han caracterizado por análisis elemental, espectrometría de masas, IR, UV/Vis (reflectancia difusa) y espectroscopía de EPR. El derivado* ***7*** *ha sido caracterizado también por espectroscopía de RMN de ^1H y $^{19}F\{^1H\}$. Los compuestos* ***4*** *y* ***5****, asi como los derivados* ***6*** *y* ***7****, generados in situ, se evaluaron como precatalizadores en la funcionalización de hidrocarburos y olefinas. Las reacciones de oxidación de estos sustratos, en presencia de los oxidantes necesarios, hidroperóxido de tert-butilo (TBHP) y oxígeno gas, se consiguen en condiciones FBC para* ***5****,* ***7*** *y sales de Cu^I con el ligando* ***2****. No obstante, los compuestos con* ***2*** *no pudieron reciclarse debido a una gran disociación del ligando. El compuesto de Cu^{II},* ***4****, con el ligando R_f-TACN,* ***1****, permite la oxidación de alcoholes 4-nitro-bencílico a 4-nitro-benzaldehido en condiciones FBC, monofase a 90°C, con TEMPO (2,2,6,6-tetrametilpiperidina-N-oxilo) y O_2; el precatalizador,* ***4****, puede ser utilizado durante cuatro ciclos catalíticos adicionales, sin pérdida de actividad. Se discutirán mecanismos posibles para estas reacciones de oxidación en condiciones FBC.*

In this paper, we report on the synthesis and characterization of new Cu^I and Cu^{II} complexes with the previously described fluorocarbon-soluble 1,4,7-triazacyclononane (R_f-TACN)[7a] **1** and bipyridine (R_f-bpy)[10d] **2** ligands that contain the fluoroponytail, C_8F_{17}-$(CH_2)_3$-. We demonstrate their catalytic activity with hydrocarbons and olefins under FBC oxidation conditions, with *tert*-butyl hydroperoxide (TBHP) and the necessary oxygen gas, at room temperature. Furthermore, the oxidation of alcohols to aldehydes, under FBC conditions, has also been performed with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) and oxygen gas at 90°C, involving one phase during the reaction and two phases on cooling to room temperature. We also provide EPR results to ascertain the fate of the precatalyst, while presenting plausible mechanisms for all of these transformations under FBC conditions.

Results and Discussion

Synthesis and characterization of R_f-Cu^I and R_f-Cu^{II} complexes: In the field of FBC, several Cu^I derivatives with fluoroponytailed amine ligands have been previously synthesized. These complexes were prepared in situ from either CuCl or $CuBr \cdot SMe_2$ and the corresponding ligands, R_f-macrocycles[7b] or R_f-bipyridine,[10d] and were evaluated in the oxidation of alkanes and alkenes,[7b] or the oxidation of alcohols,[8] respectively. Several other Cu^I complexes containing tri- or tetradentate amine ligands have been prepared in situ in a similar manner, and have been used as precatalysts for the cyclization of unsaturated esters[12] or living radical polymerizations[13] under FBC conditions. However, these complexes, usually generated in situ, were not isolated or characterized properly. The synthesis consisted of the addition of an excess of the Cu^I salt to a perfluorocarbon solution of the fluoroponytailed amine ligand, and the new fluorocarbon-soluble compound was characterized in some cases[7b] by the UV/Vis spectrum of the resulting green solution. We believe that not only the green color of the perfluorocarbon solutions, but also the UV/Vis data, tentatively demonstrated that the oxidation of the fluoroponytailed Cu^I complexes to Cu^{II} derivatives was occurring. Thus, we wanted to synthesize and isolate not only the Cu^I, but also Cu^{II} fluoroponytailed complexes, as both Cu^I and Cu^{II} salts and complexes have previously displayed catalytic activity in the homogeneous oxidation of hydrocarbons, olefins, and alcohols.[14]

The fluoroponytailed ligands employed in this study were the previously described fluorocarbon soluble 1,4,7-triazacyclononane (R_f-TACN),[7a] **1** and bipyridine (R_f-bpy),[10d] **2** ligands (Figure 1) that contained the C_8F_{17}-$(CH_2)_3$- group. The convenient three carbon spacer in the fluoroponytail was necessary, not only to insulate the amine from the powerful electron-withdrawing effect of the perfluoroalkyl group, but also to avoid a facile elimination reaction of HI when synthesizing fluoroponytailed amine ligands by alkylation reactions with $C_8F_{17}(CH_2)_3I$. The latter compound, along with ligand **1**, have been previously reported by Fish et al.[7a,d] Although ligand **2** has been prepared before, its synthesis was not completely described, and its characterization was not

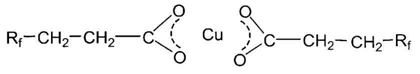


R_f-TACN, **1** R_f-bpy, **2**

Figure 1. Perfluoroponytailed amine ligands **1** and **2**.

provided. Thus, we have also described the synthesis and characterization of **2**.

In order to insure the fluorocarbon solubility of the Cu^{II} complexes of ligands **1** and **2**, we appended fluoroponytailed groups to the metal complex we were going to utilize as a synthon, as previously discovered by Fish et al., since metal complexes with multiple charges and counter anions, such as ClO_4^-, PF_6^-, or even Cl^- would be very difficult to solubilize in perfluorocarbons.[7a,d] Thus, the new Cu^{II} complex $[Cu(C_8F_{17}(CH_2)_2CO_2)_2]$ **3**, was synthesized by reaction of $CuSO_4 \cdot 5H_2O$ in acetone with two equivalents of the triethylammonium salt of the 3-R_f-alkylpropionic acid $C_8F_{17}(CH_2)_2CO_2H$; elemental analysis of **3** revealed a metal/carboxylate ratio of 1:2. Complex **3** was found not to be soluble in perfluorocarbons, soluble in trifluorotoluene, and only partly soluble in CH_2Cl_2. It further appears that the carboxylate group is chelating rather than being in a monodentate coordination mode, as suggested by the small difference ($\nu = 153\ cm^{-1}$) observed between the asymmetric and symmetric C–O stretches ($\nu = 1573$ and $1420\ cm^{-1}$, respectively) in its IR spectrum.[15] Its lack of solubility prevented us from obtaining its UV/Vis spectrum in perfluoroheptane or CH_2Cl_2 solutions. However, we were able to record the UV/Vis spectrum in the solid state by using diffuse reflectance measurements. The intense absorption band displayed by **3** (tentative structure given in Figure 2, $R_f = C_8F_{17}$-$(CH_2)_3$-) at 666 nm was in accordance with values found for other Cu^{II} complexes.[16]

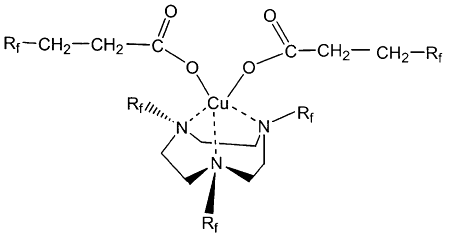


3

Figure 2. Tentative structure of complex **3**.

The addition of ligands **1** or **2** to perfluoroheptane suspensions of **3** allowed the total (for **1**) or partial (for **2**) solubilization of the Cu^{II} complex at room temperature, giving deep green solutions. In order to isolate these compounds, we added ligands **1** and **2** to blue solutions of **3** in CH_2Cl_2, which almost immediately produced green solids that could be isolated and characterized as $[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ **4** and $[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-bpy})]$ **5**. Unfortunately, none of the Cu complexes reported gave single crystals suitable for X-ray analysis.

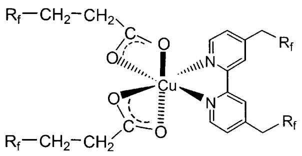
Complex **4** was found to be totally soluble in perfluoroheptane, while its UV/Vis spectrum in this solvent had only one absorption band at 272 nm, which could be assigned to the fluorous ligand. However, its diffuse reflectance spectrum (solid state) showed two bands at 1013 and 700 nm that could be directly attributed to a Cu^{II} complex.[16] The stoichiometry of **4** was confirmed by elemental analysis and its LSIS-MS spectrum displayed a signal at m/z 2063 (75 %), which could be assigned to the $[M - \{C_8F_{17}(CH_2)_2CO_2\}]^+$ ion. The IR spectrum had bands corresponding to the carboxylate group, in addition to those that can be assigned to the R_f-TACN ligand. It appears that the carboxylate group in **4** (tentative structure in which $R_f = C_8F_{17}$-$(CH_2)_3$- in Figure 3) was in a monodentate rather a chelating or bridging coordination mode, resulting in the bigger difference ($\nu = 229\ cm^{-1}$) observed between the asymmetric and symmetric C–O stretches ($\nu = 1632$ and $1403\ cm^{-1}$, respectively) in its IR spectrum.



4

Figure 3. Tentative structure of compound **4**.

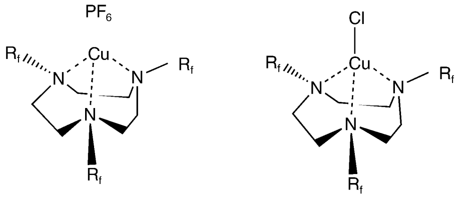
Compound **5** was not soluble in cold perfluoroheptane, but it could be solubilized in hot perfluoroheptane (above 40 °C). Again, elemental analysis and LSIMS-MS confirmed the composition of the compound. The UV/Vis spectrum, recorded in perfluoroheptane, showed one absorption band at $\lambda = 246$ nm, which can be assigned to the fluorous ligand, but its diffuse reflectance spectrum (solid state) showed one intense absorption band at 680 nm in accordance with values obtained for Cu^{II} compounds.[16] In contrast to compound **4**, it appears that the carboxylate group in **5** is in a bidentate rather than a monodentate coordination mode, as evidenced by the smaller difference ($\nu = 173\ cm^{-1}$) observed between the asymmetric and symmetric C–O stretches ($\nu = 1569$ and $1394\ cm^{-1}$, respectively) in its IR spectrum. This is in accordance with the bidentate coordination mode of the R_f-bpy, which would allow the R_f-carboxylate groups to bind in a chelating mode to the Cu^{II} center in **5** (Figure 4), while in **4** the three N-donor atoms of the R_f-TACN appear to limit the carboxylate coordination to the Cu^{II} to a monodentate mode.



5

Figure 4. Tentative structure of compound **5**.

After synthesizing these paramagnetic Cu^{II} fluorous compounds, we attempted the preparation of Cu^I complexes with the more fluorocarbon soluble ligand **1**, at room temperature. In this case, we did not use R_f-carboxylate synthon **3**, as it had been previously shown that the in situ synthesis of Cu^{I}-fluorous amine derivatives could be achieved by using the Cu^{I} salt and the corresponding fluoroponytailed ligands. The addition of **1** to [Cu(CH$_3$CN)$_4$]PF$_6$ or CuCl afforded an off-white ([Cu(R$_f$-tacn)]PF$_6$ **6**) and a white ([Cu(R$_f$-tacn)Cl] **7**) solid in moderate (36 %), and high (78 %) yields, respectively (Figure 5). Satisfactory elemental analyses were obtained for both compounds, and their LSIMS-MS spectra had signals that corresponded to the monocationic complexes, [Cu(R$_f$-tacn)]$^+$, at *m*/*z* 1573 for **6** (60 %) and **7** (88 %). Complex **6** was only soluble in trifluorotoluene; however, compound **7** was totally soluble in cold perfluoroheptane and partly soluble in CHCl$_3$, allowing for its characterization by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy in CDCl$_3$. UV/Vis data for **7** were also obtained in perfluoroheptane, revealing two absorption bands at 212 and 260 nm. However, its solubility in CH$_2$Cl$_2$, or even in CHCl$_3$, was not enough to perform a cyclic voltammetric study. In addition, the EPR spectra of **6** and **7** were silent, as expected for Cu^{I} diamagnetic complexes. We also found that **6** and **7** were light sensitive, and that they could be easily oxidized to Cu^{II} species (especially **6**) after several hours at room temperature. However, they could also be kept for longer periods of time at $-20\,^{\circ}$C under argon, while being protected from direct light exposure.



6

7

Figure 5. Tentative structures of **6** and **7**.

We mentioned in the introduction that the combination of CuBr•SMe$_2$ and **2** had produced a deep green solution in perfluoroheptane,[8] but the characterization of this putative Cu^{I} complex had not been reported thus far. When we attempted the reaction between CuCl and **2** in trifluorotoluene in order to synthesize the compound analogous to **7**, we immediately obtained a deep green solution, from which a deep green solid was isolated. Although its LSIMS-MS spectrum displayed a prominent signal at *m*/*z* 1167 (100 %), which can be assigned to the species [*M* – Cl]$^+$, its elemental analysis did not fit with a stoichiometry of a complex like [Cu(R$_f$-bpy)Cl]. This complex was partly soluble in trifluorotoluene and in cold perfluoroheptane (it was soluble in hot perfluoroheptane) and thus we were not able to obtain its NMR or UV/Vis spectra in perfluoroheptane solution. However, its green color, as well as its EPR spectrum, indicated that a partial oxidation to a Cu^{II} complex had occurred.

The EPR spectra of solid, powdered samples of compounds **3**, **4**, **5**, and **7**, as well as the solid from the reaction of CuCl and **2**, were measured at room temperature. Figure 6 shows the EPR spectra of all the samples studied (spectra a–e). In all cases except for the Cu^{I} compound **7** (spectrum d), the EPR spectra had signals from several Cu^{II} complexes. In the cases of the Cu^{II} complexes, **3** (spectrum a), **4** (spectrum b), and **5** (spectrum c), as well as the putative Cu^{I} complex from CuCl and **2** (spectrum e), there were strong indications of intermolecular exchange reactions.[17] This was particularly evident in the EPR spectrum of compound **3** (spectrum a), and the spectrum recorded with the solid from the reaction of CuCl and **2** (spectrum e). In these EPR spectra, similar features appeared at $g_1 = 2$, $g_2 = 2.06$ (spectrum a), and $g_1 = 2.15$, $g_2 = 2.06$ (spectrum e), suggesting a mixture of Cu^{II} complexes. In accordance with the nature of **7**, a Cu^{I} complex, no indication of a Cu^{II} complex was detected in its silent EPR spectrum (spectrum d).

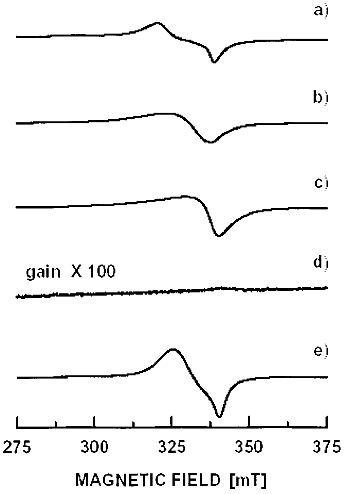
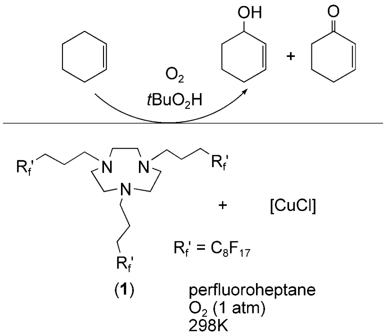


Figure 6. X-band EPR spectra of powdered samples: a) complex **3**; b) complex **4**; c) complex **5**; d) compound **7**; e) isolated complex from **2** and [CuCl].

Functionalization of alkenes, alkanes, and alcohols using copper(II) complexes and in-situ-generated [Cu(R$_f$-ligand)]$^+$ derivatives as precatalysts

Oxidation of alkenes and alkanes: The FBC oxidation results for substrates cyclohexene, cyclohexane, and toluene in the presence of fluoroponytailed copper complexes are presented in Table 1. All of the experiments were carried out under biphasic conditions in perfluoroheptane; the upper phase was the substrate itself (Scheme 1). Cu^{II} complexes **4** and **5** were dissolved in perfluoroheptane; however, we found it more



Scheme 1. Cyclohexene FBC oxidation with complex **7** as precatalyst.

convenient to generate the Cu^I derivatives **6** and **7** in situ for catalytic experiments by the addition of excess (2:1) $[Cu(CH_3CN)_4]PF_6$ or CuCl to the perfluoroheptane solutions of **1**, with subsequent filtration through celite to remove any undesired excess of Cu^I salts. The molar ratio between the substrate, the oxidant, and the catalyst was S/O/C = 5000:62.5:1 in all experiments.[7b]

The oxidation of alkenes and alkanes always provided a mixture of alcohols and ketones. As previously described,[7a,b,d] Table 1 demonstrates that the olefin with allylic hydrogens, cyclohexene, provides the highest yield of oxidation products with TBHP/O_2. In the absence of O_2 or TBHP, only negligible amounts of cyclohexenol and cyclohexenone were detected, which is fully indicative of an autoxidation reaction, that is, both were necessary for oxidation to proceed (Table 1, entries 4 and 5).[7a,d]

All of the complexes derived from the ligand **1**, showed catalytic activity (Table 1, entries 1–3, 7–9), but only **7** (prepared in situ from CuCl and R_f-TACN) afforded yields or TON that could be compared with those previously reported for CuCl and the fluoroponytailed macrocyclic ligands derived from tetraazacyclotetradecane (R_f-CYCLAM)[7b] or $[M(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ (M = Mn, Co).[7a,d] The first system afforded yields of 514 % and TON of 320 for the oxidation of cyclohexene to cyclohexenol and cyclohexenone after eight hours.[7b] The latter complexes gave yields of 650 % and TON of 131 (M = Mn) after three hours or 750 %, TON = 156 (M = Co^{II}) after 20 hours.[7a,d] We found that for the same substrate, yields of 136 % (with a TON of 85) were obtained after eight hours (entry 3) for **7**, while after 24 hours (same conditions, entry 7) the yields and TON were increased to 425 % and 276, respectively. More importantly, we were able to recover the fluorous phase and recycle it for a second (entry 8) or a third (entry 9) catalytic experiment. The overall yield was then 938 % and the TON = 609, with the catalytic activity decreasing to around 75 % in the second run and to half of the initial value in the third experiment. With the Cu/R_f-CYCLAM system, the catalytic activity in a second run decreased to half of its initial value (yield 248 %, TON 155), and the authors mentioned that the hydrocarbon layer turned increasingly blue.[7b] Moreover, in a second run $[Mn(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ afforded a yield of 400 % (vs 650 % in the first run).[7a,d]

We believed that **6** (formed in situ from $[Cu(CH_3CN)_4]PF_6$ and **1**) was not an efficient catalyst (entry 2) under FBC conditions, owing to its lack of solubility in perfluoroheptane, as shown with the isolated compound. The reaction of cyclohexene with **7** (formed in situ) in the presence of oxidants (H_2O_2/O_2) was also studied (entry 6) but no oxidation products were formed. Although complexes of Cu^{II} and Cu^I with the R_f-bpy ligand **2** (entries 7–11) did catalyze the oxidation of cyclohexene (TBHP/O_2), they could not be recycled (see complex **5**, entries 10 and 11; CuCl and ligand **2** (entries 13 and 14). We found that after the reaction had taken place, the fluorous phase turned colorless, while the organic layer became blue, indicating that Cu^{II} ions were present in this upper layer. We believe that the different behavior between the compounds with R_f-TACN and R_f-bpy ligands might be due to the different coordination modes of these ligands to the Cu^I and Cu^{II} centers, which may be related to the steric and electronic properties of the catalytic active sites, as well as their stability constants. In all oxidation experiments, it was observed that the TBHP employed as a free radical initiator was converted to *tert*-butyl alcohol and acetone, indicative of *tert*-butyloxy radical formation.[7a,d] We also attempted the oxidation of cyclohexane and toluene with the best catalytic system, **7**, generated in situ, and, as described for the $[M(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ {M = Mn^{II}, Co^{II}} systems,[7a,d] the yields of oxidation products were much lower than for cyclohexene (entries 15 and 16, Table 1).

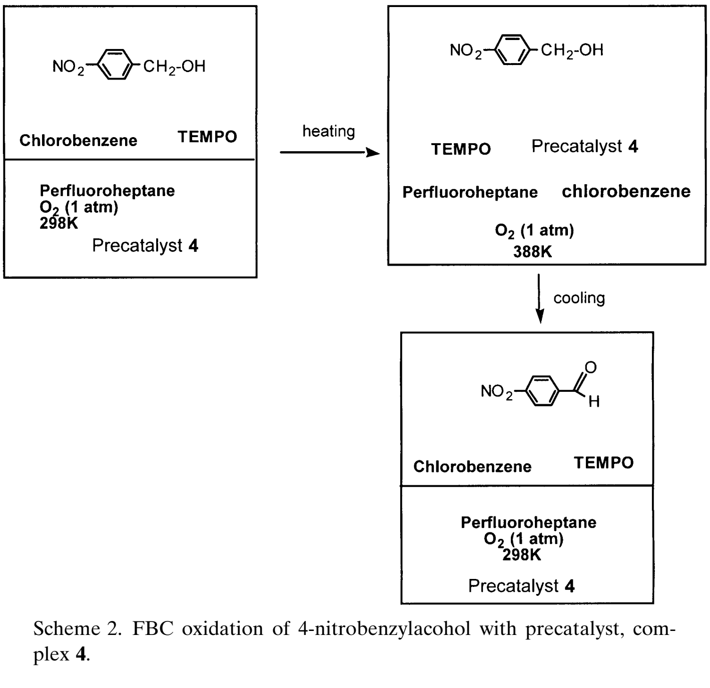
Table 1. Alkene and alkane functionalization with fluorous Cu^{II} and Cu^I complexes under FBC conditions.[a]

Entry	Substrate	Oxidant	Precatalyst	t [h]	Substrate converted[b] [μmol]	Selectivity alcohol [%][c]	Ketone/ aldehyde [%]	Total yield [%][d]	TON[e]
1	cyclohexene	TBHP/O_2	**4**	8	175	3.2	96.8	35	22
2	cyclohexene	TBHP/O_2	$[Cu(CH_3CN)_4]PF_6$ + R_f-TACN (**6**)	8	86	1.3	98.7	17	11
3	cyclohexene	TBHP/O_2	CuCl + R_f-TACN (**7**)	8	678	27	73	136	85
4	cyclohexene	O_2	**7**	8	12	–	100	2.2	1.5
5	cyclohexene	TBHP	**7**	8	13	–	100	3	1.6
6	cyclohexene	H_2O_2	**7**	8	8	–	100	1.5	0.9
7	cyclohexene	TBHP/O_2	**7**	24	2210	21.8	78.2	425	276
8	cyclohexene	TBHP/O_2	fluorous recovered phase from entry 7	24	1601	29.3	70.7	308	200
9	cyclohexene	TBHP/O_2	fluorous recovered phase from entry 8	24	1068	18.6	81.4	205	133
10	cyclohexene	TBHP/O_2	**5**	8	1023	15.6	84.4	204	128
11	cyclohexene	TBHP/O_2	fluorous recovered phase from entry 10	8	13	–	100	12	8
12	cyclohexene	TBHP/O_2	$[Cu(CH_3CN)_4]PF_6$ + R_f-bipy	8	681	12.1	87.9	136	85
13	cyclohexene	TBHP/O_2	CuCl + R_f-bipy	8	590	13.8	86.2	113	74
14	cyclohexene	TBHP/O_2	fluorous recovered phase from entry 13	8	62	–	100	12	8
15	cyclohexane	TBHP/O_2	**7**	24	39	43.3	56.7	7.5	5
16	toluene	TBHP/O_2	**7**	24	87	48.4	51.6	17	13

[a] Conditions: Hydrocarbon phase: Substrate (S) = 40 mmol; *o*-dichlorobenzene (internal standard) = 2 mmol; 70% *t*BuOOH (O) = 500 μmol. Fluorocarbon phase: precatalyst (8 μmol, see experimental section) in perfluoroheptane (2 mL). Molar ratio S/O/C 5000:62.5:1. T = 298 K. Reactions were carried out in the dark in the presence of molecular oxygen. Products were identified by comparison with authentic samples by GC. [b] Determined by GC using the internal standard method. [c] μmol product/μmol converted substrate. [d] Based on the added *t*BuOOH. [e] μmol converted substrate/μmol precatalyst.

Oxidation of alcohols: The oxidation of alcohols to aldehydes or ketones under FBC conditions has been performed under an oxygen atmosphere both by Knochel et al. with a catalytic system consisting of $CuBr \cdot SMe_2$ and **2**, prepared in situ, at 90 °C[8] and by Uemura et al.[9] with $Pd(OAc)_2$ and fluoroponytailed pyridines prepared in situ at 80 °C. In the first example, the initiator was TEMPO and in the second case, they used 3 Å molecular sieves. However, while the Cu system used a small amount of fluorous ligand (2 mol %),[8] the Pd system needed a much larger amount of fluorous ligand (20 mol %).[9] Benzylic and allylic alcohols reacted faster than aliphatic alcohols for both systems and, in general, high yields were obtained.

The recyclability of the Cu system was demonstrated for the oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde. The reaction was performed eight times without a major loss of catalytic activity. In the Pd system, the recyclability of the precatalyst was demonstrated for six runs. It should also be noted that no mechanistic information was available for this transformation nor for the role of TEMPO in this FBC oxidation reaction. More importantly, we believed that the reported reaction between Cu^I salts and **2** also gave Cu^{II} complexes during the reaction, while the oxidation of alcohols with $TEMPO/O_2$ with Cu^I and Cu^{II} salts in a homogeneous system also suggested that Cu^{II} ions were responsible for initiating the oxidation.[18] We then decided to study the Cu^{II} complex **4** under single-phase FBC reaction conditions[4f] at 90 °C with 4-nitrobenzyl alcohol in the FBC oxidation to 4-nitrobenzaldehyde (Scheme 2).



Scheme 2. FBC oxidation of 4-nitrobenzylacohol with precatalyst, complex **4**.

The initial FBC mode at room temperature (Scheme 2) includes **4** in the lower perfluoroheptane layer, while the substrate alcohol, chlorobenzene, and TEMPO were in the upper organic layer (Table 2). At 90 °C, in a now single homogeneous phase, under an oxygen atmosphere for four hours, conversion to the aldehyde was at 63 % (entry 1) and 61 % (entry 2) in the first and second runs, respectively, showing that catalytic activity did not change during the second run. This preliminary experiment helped to optimize the FBC reaction conditions (entries 3–5). We found it was necessary to increase the amount of catalyst to 3.5 mol % and the reaction time from 4 to 8 hours to obtain a 96 % conversion to the benzaldehyde product.

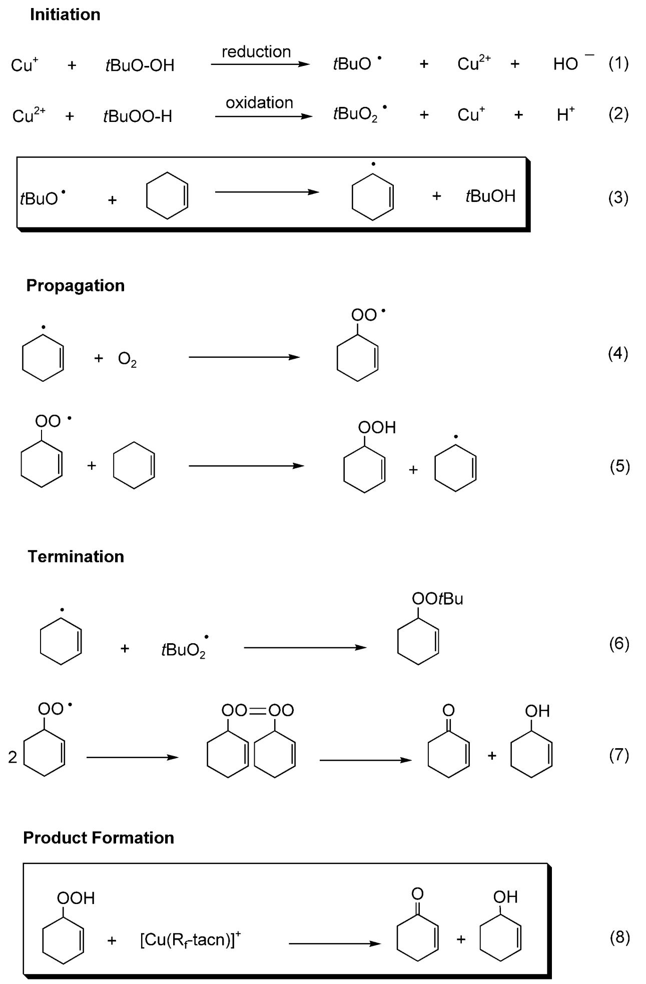
Table 2. Oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde under FBC conditions using **4** as precatalyst.[a]

Entry	Catalyst	% mol catalyst	% mol TEMPO	*t* [h]	Conversion [%][b]	TON[c]
1	**4**	2	3.4	4	63	31
2	RFP[d] from entry 1	–	3.4	4	61	30
3	**4**	3.5	6	4	65	19
4	**4**	3.5	6	8	96	27
5	RFP from entry 4	–	6	8	94	27
6	RFP from entry 5	–	6	8	92	26
7	RFP from entry 6	–	6	8	90	26
8	RFP from entry 7	–	6	8	92	26
9	RFP from entry 8	–	6	8	51	14
10	RFP from entry 9	–	6	8	8	2

[a] Conditions: hydrocarbon phase: 4-nitrobenzyl alcohol, TEMPO; fluorous phase: **4** in perfluoroheptane (2 mL). Reactions were carried out at 90 °C in the presence of molecular oxygen. [b] Measured by ^1H NMR. [c] µmol converted substrate/µmol catalyst. [d] Recovered fluorous phase.

Autoxidation mechanism and the fate of the $[Cu(R_f\text{-tacn})]^+$ precatalyst in the oxidation of alkenes and alkanes

The $TBHP/O_2$ initiated oxidation reactions presented here are in agreement with an autoxidation mechanism involving alkoxy ($RO^\bullet$) or alkoxyperoxy ($ROO^{\bullet-}$) radicals, in which the reaction is initiated by tBuO$^\bullet$ or tBuO$_2^\bullet$ radicals produced from redox reactions (Haber–Weiss process with Cu^I/Cu^{II}). This mechanism is similar to that proposed by Fish et al. with the $[Mn(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ catalytic system.[7a,d] It has been previously reported that in the case of the substrate cyclohexene, the allylic radical that forms is then trapped by O_2 ($k > 1 \times 10^9\,M^{-1}s^{-1}$) to provide cyclohexenylperoxy radicals, which are able (ROO–H = 90 kcal mol^{-1}) to homolytically remove a hydrogen from benzylic or allylic C–H bonds (85 kcal mol^{-1}), and hence propagate the radical reactions.[19, 20] The secondary cyclohexenyl hydroperoxide that is formed then decomposes catalytically in the presence of the $[Cu(R_f\text{-tacn})Cl]$ precatalyst to give the alcohol and the ketone products. Scheme 3 defines the initiation, propagation, termination, and product-forming steps for the sequence of reactions [Eqs. (1)–(8)].[7a,d] Moreover, the lower yields observed in the case of cyclohexane are consistent with the stronger C–H bond (95 kcal mol^{-1}),[19] which implicates the cyclohexylperoxy radical and thus causes a lowering of the rate of the propagation step. The chain termination step presumably comes mainly from the coupling of two cyclohexenylperoxy radicals to give alcohol, ketone, and O_2 [Russell-type mechanism, Scheme 3, Eq. (7)].[7a,d]



Scheme 3. Haber–Weiss mechanism for the oxidation of cyclohexene with precatalyst, complex **7**.

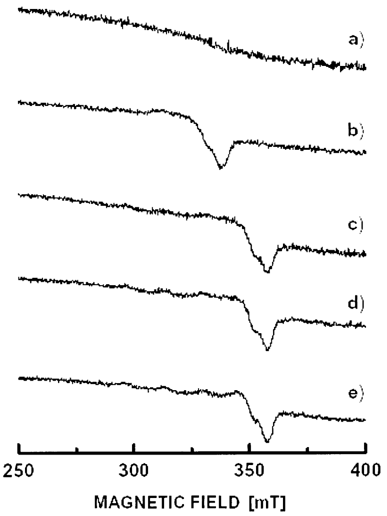


Figure 7. X-band EPR spectra of the perfluoroheptane layer during the course of the oxidation of cyclohexene with TBHP/O_2, **7** as precatalyst, measured at liquid nitrogen temperature. a) 2 h; b) 3.5 h; c) 6 h; d) 11 h; e) 23 h.

In order to determine the redox chemistry occurring with the starting complex, [Cu(R_f-tacn)Cl] **7**, the best catalytic system we found for the oxidation of cyclohexene under FBC conditions, we carried out the following EPR experiments (Figure 7, spectra a–e). Compound **7** was dissolved in perfluoroheptane and then cyclohexene, *o*-dichlorobenzene (as internal standard), and TBHP were added. The reaction started in the presence of O_2 and an aliquot from the perfluoroheptane phase was removed and immediately frozen at liquid nitrogen temperature (LNT) in an EPR tube, after two hours of reaction. The EPR spectrum (measured at 77 K) is shown in Figure 7 (spectrum a). There was no indication of a Cu^{II} signal in this initial spectrum. This was in accordance with the oxidation state of the precatalyst **7**, whose Cu^I center had also been previously confirmed by an EPR spectrum of a solid sample (Figure 6, spectrum d).

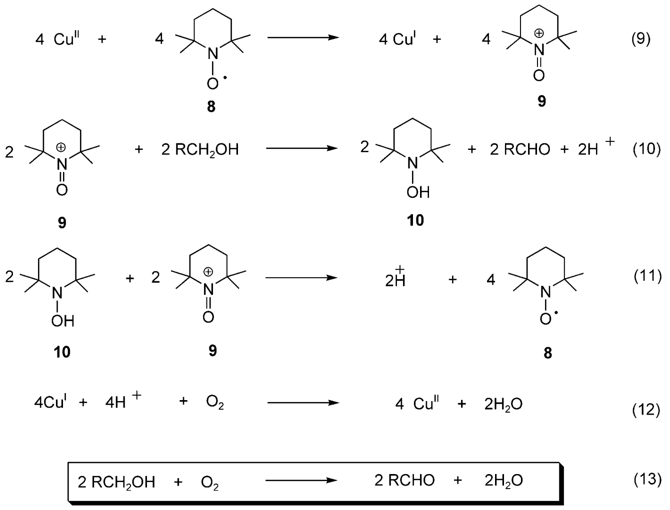
The reaction was further followed by EPR spectroscopy taking aliquots at different reaction times and after six hours (spectrum c), a Cu^{II} signal was observed. It could be described by an axial spin-Hamiltonian with a g tensor, $g_{\parallel} = 2.26(1)$ and $g_{\perp} = 2.05(1)$, as well as a Cu^{II} nuclei hyperfine interaction given by $A_{\parallel} = 520(5)$ MHz and $A_{\perp} < 50$ MHz. These EPR spectra are typical of a nearly square planar Cu^{II} complex. This EPR signal remains after 11 hours (spectrum d), and after 23 hours (spectrum e). After 3.5 h (spectrum b), the EPR spectrum showed some contribution of Cu^{II}, but the spectrum was not the same as the one after six hours. This fact could mean that a Cu^{II} complex was formed after addition of TBHP/O_2. What was clear was that it takes ≈3 h for the Cu^I precatalyst **7** to be oxidized to the Cu^{II} complex, which is consistent with a Haber–Weiss mechanism.[7a,d]

The catalytic results (Table 1, entry 1) have shown that the Cu^{II} complex with the R_f-TACN ligand, **4**, catalyzes the oxidation of cyclohexene, but to a smaller extent than **7**, or the Cu^{II} complex **5**. The reason for which **7** was a recoverable catalyst, while its catalytic activity in the second and third run decreases to 75 and 50%, respectively, could possibly be the formation of a Cu^{II} complex that could be easily reduced to a Cu^I complex, as designated by the Haber–Weiss process. In contrast, the low catalytic activity of the Cu^{II} catalytic system with **4** might be a consequence of not being able to efficiently generate the Cu^I complex [Scheme 3, Eq. (2)], because of a presumed kinetic effect [Scheme 3, Eq. (2)].[7a,d] The fact that Equation (1) (Scheme 3) involves the generation of the *tert*-butoxy radical implicates the Cu^I/Cu^{II} redox couple.

More importantly, the behavior of the Cu^{II} complex **5**, with ligand **2**, was quite different (Table 1, entries 10 and 11). In this example, the reduction to the Cu^I complex appears to be more facile, possibly because of the different electronic properties of the fluoroponytailed ligand **2**. Unfortunately, we were not able to isolate the corresponding Cu^I compound analogous to **7**. We also determined that **5** was not recoverable under FBC conditions and that after the reaction had taken place, the free ligand **2**, as well as Cu^{II} ions, could be observed in the organic phase, as analyzed by mass spectrometry.

Mechanism and fate of the [Cu($C_8F_{17}(CH_2)_2CO_2)_2$(R_f-tacn)] (4) precatalyst in the oxidation of 4-nitrobenzyl alcohol

We have shown that an isolated R_f-Cu^{II} complex **4** can be a recyclable and efficient precatalyst for the oxidation of alcohols under FBC conditions at 90 °C with TEMPO/O_2. The mechanism of this reaction was thus of interest. Moreover, several years ago Semmelhack et al.[17] reported on the oxidation of alcohols to aldehydes with oxygen and Cu^{II} ions, mediated by a nitrosonium ion that was generated from the TEMPO radical. The catalytic cycle proposed by these authors is shown in Scheme 4. The Cu^{II} ions are reduced to Cu^{I} in a one-electron oxidation of TEMPO **8** to the nitrosonium ion **9** [Scheme 4, Eq. (9)]. The alcohol is then oxidized by **9** [Eq. (10)], generating the aldehyde and hydroxylamine **10**; rapid *syn*-proportionation of **10** with **9** regenerates **8** [Eq. (11)]. Finally, Cu^{II} is regenerated by oxygen gas, in a process that consumes protons and provides Cu^{II} and water [Eq. (4)], following a general method for recycling Cu^{II} ions.[17] This catalytic cycle was based on the reactions and electrochemical studies that indicated that Cu^{II} could indeed oxidize **8** to **9**.



Scheme 4. Semmelhack mechanism for the oxidation of alcohols to aldehydes mediated by Cu^{II}, TEMPO, and O_2.

In order to verify the Semmelhack mechanism,[17] we used EPR spectroscopy to follow the redox chemistry of the starting fluorous catalyst **4** during the oxidation of 4-nitrobenzylic alcohol with TEMPO/O_2 at 90 °C under FBC conditions. To reiterate, precatalyst **4** was recoverable and recyclable, while its catalytic activity did not decrease over the course of five runs. We carried out an EPR catalytic experiment (Figure 3, spectra a–d) as was described above for the oxidation of cyclohexene. Precatalyst **4** was dissolved in perfluoroheptane, and then chlorobenzene, TEMPO, and 4-nitrobenzyl alcohol were added to the reaction mixture. The reaction started at 90 °C in the presence of O_2, and after 30 min, followed by cooling to room temperature, an aliquot was removed from the perfluoroheptane phase and immediately frozen at 77 K in an EPR tube. The EPR spectrum is shown in Figure 8 (spectrum a, at LNT). The spectrum shows a narrow central signal at about $g = 2.006$, which can be associated with the TEMPO radical. This was further confirmed by measuring this radical in perfluoroheptane at 77 K. The spectrum of the reaction mixture also has a Cu^{II} signal, with $g_{\parallel} = 2.26(1)$ and $g_{\perp} = 2.06(1)$, $A_{\parallel} = 520(5)$ MHz and $A_{\perp} < 50$ MHz.[18] After 3.5 h, both signals decrease (spectrum b), and after 6 h the signals have decreased further (spectrum c). After 8 h, we observed a recovery of the signal corresponding to the Cu^{II} species (spectrum d). An EPR spectrum of the upper phase (chlorobenzene layer), after the reaction had taken place, showed a EPR signal that can be assigned to the TEMPO radical. Thus, TEMPO appears to be regenerated as was proposed in Scheme 4. It is clear from the silent EPR spectrum after 3.5 h (Figure 8, spectrum c) that the initial Cu^{II} complex **4** is reduced to the Cu^{I} complex and is then regenerated to a Cu^{II} complex (spectrum d). This is in accordance with the mechanism proposed by Semmelhack et al.[17] (Scheme 4) and with the catalytic results reported in this paper (Table 2). After 4 h, a 65 % yield of aldehyde was obtained; however, by leaving the reaction for longer periods of time, a nearly 100 % yield of aldehyde (Table 2) was formed, concomitant with a full recovery of **4**. We believe that the TEMPO was also regenerated, but probably ended up in the organic phase where it was destroyed during the work-up procedure; TEMPO was then replenished during the next catalytic run.

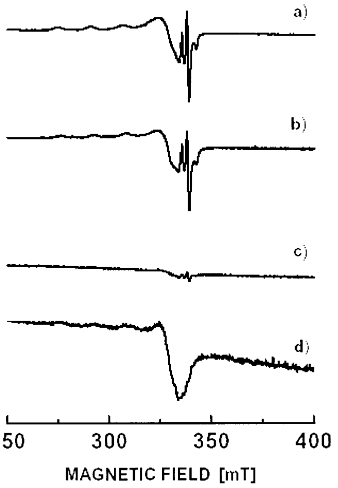
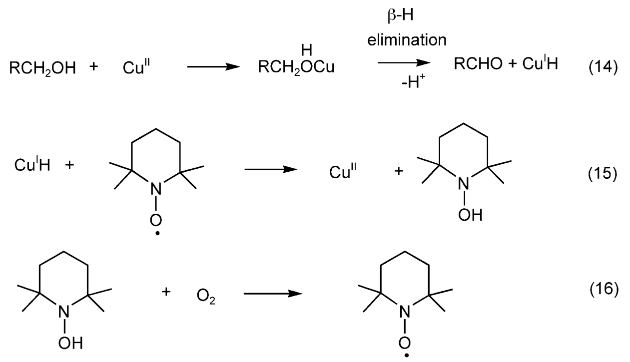


Figure 8. X-band EPR spectra of the perfluoroheptane layer during the course of the oxidation of 4-nitrobenzyl alcohol with TEMPO/O_2, at 90 °C, **4** as precatalyst measured at liquid nitrogen. a) 0.5 h; b) 3.5 h. c) 6 h; d) 8 h.

We also wish to propose an alternative mechanism to Semmelhack's, described above for the oxidation of alcohols to aldehydes, that can reasonably fit the experimental data presented, and is favored by Sheldon et al.[19] This is shown in Scheme 5. It entails the coordination of the alcohol to the Cu^{II} center, followed by a β-hydrogen elimination, which forms the Cu^{I} hydride, the aldehyde, and a proton.[19] The regeneration of the Cu^{II} center is now the role of the TEMPO radical, which abstracts hydrogen from $Cu^{I}H$ to give TEMPOH, while the TEMPO radical can be regenerated by O_2. Both mechanistic Schemes 4 and 5 indicate that the presence of Cu^{II} is critical for the oxidation of the alcohol to the aldehyde. The mechanistic differences are in the role of the TEMPO radical, and we are in the process of attempting to differentiate between the two pathways.



Scheme 5. Alternative mechanism for the oxidation of alcohols to aldehydes mediated by Cu^{II}, TEMPO, and O_2.

Conclusions

In summary, we have prepared and fully characterized by several standard spectroscopic techniques new Cu^{I} and Cu^{II} complexes with fluoroponytailed amine ligands. To the best of our knowledge, the reported Cu^{I} and Cu^{II} fluoroponytailed derivatives were previously unknown, as the previously reported fluoroponytailed Cu^{I} complexes had been prepared in situ and their characterization was incomplete or nonexistent. More importantly, in many previously reported Cu complexes that were studied, in their synthesis or catalytic reactivity, there was no information concerning the oxidation state of the resulting Cu complexes. We have now rectified this situation by isolating and fully characterizing all of the Cu^{I} and Cu^{II} compounds reported in either synthesis or under catalytic reactivity, in this FBC contribution.

All of the reported novel Cu^{I} and Cu^{II} complexes were evaluated in the FBC oxidations of hydrocarbons and olefins with TBHP/O_2. The most promising catalytic systems were the [Cu(R_f-tacn)Cl] **7**, as well as the Cu^{I} and Cu^{II} complexes with the R_f-bpy ligand **2**. However, only **7** could be totally separated from the organic phase by a simple decantation process and thus recycled for three runs. EPR experiments showed that the oxidation process occurs by an autoxidation mechanism, with formation of alkenyl or alkyl hydroperoxides as the key intermediates, which are then catalytically decomposed by the $[Cu(R_f\text{-tacn}]^+$ catalyst, probably at the solvent interface, to provide the alcohol and ketone products.[7a,d] However, this precatalyst was found to be less efficient after the third run, possibly because of the concentration of the Cu^{II} complex that could not be readily reduced to the initial Cu^{I} complex under the normal Haber–Weiss reaction conditions.

Furthermore, the Cu^{II} complex $[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ **4** was an efficient and recoverable precatalyst for the oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde with TEMPO/O_2, under single phase FBC conditions at 90 °C, with catalytic activity being maintained even after five runs. The EPR experiments can be interpreted in two ways. In one mechanism, this Cu^{II} complex was reduced to Cu^{I} by the TEMPO radical and then oxidized again to the initial Cu^{II} complex by O_2, while also regenerating TEMPO, and producing the aldehyde. The other mechanism involves the Cu^{II} mediated β-hydrogen elimination providing a $Cu^{I}H$, which reacts with TEMPO to recycle Cu^{II} and TEMPO-H, while regenerating TEMPO with O_2. Future FBC studies will focus on gas to liquid technology, as well as further studies on FBC oxidation mechanisms.

Experimental Section

All manipulations involving organolithium reagents and hygroscopic TACN were performed under an inert atmosphere of dry argon, using Schlenk techniques, and all solvents were dried and degassed before use. R_f-TACN **1** was prepared as described previously from a nitrogen atom alkylation reaction between commercial TACN and $C_8F_{17}(CH_2)_3I$.[7a,d] Carboxylic acid, $CF_3(CF_2)_7CH_2CH_2CO_2H$, was generously donated by Elf Atochem. The fluorocarbon solvents and some starting perfluoro derivatives were purchased from ABCR., while 4,4′-dimethyl-2,2′-bipyridine, alkenes, alkanes, and alcohols were from Aldrich. *tert*-Butyl hydroperoxide (70% TBHP) was purchased from Aldrich, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) from Avocado, and were used without further purification. $[Cu(CH_3CN)_4]PF_6$ was prepared as previously reported.[21] ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were obtained on a 300 MHz Varian-GEMINI 2000 apparatus in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (external, ^1H and $^{13}C\{^1H\}$) and $CFCl_3$ (external $^{19}F\{^1H\}$). GC analyses were performed on a Hewlett Packard (HP) 5890 Series II instrument. C,H,N elemental analyses were performed with a Perkin Elmer 2400 microanalyzer, while mass spectra (LSIMS, 3-nitrobenzyl alcohol as matrix) were obtained on a VG Autospec spectrometer using a Cesium gun. The IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR instrument in a Universal ATR Sampling Accessory. The UV/Vis spectra were recorded on a Unicam-Vision 32 instrument with accompanying V1.02 software. The diffuse reflectance spectra were recorded on a Cary 500 scan UV/Vis-nir spectrophotometer. The Electron Paramagnetic Resonance (EPR) spectra were measured on a Bruker ESP380E spectrometer working at X-band using a PPPP cavity. Powdered samples as well as solutions were introduced in a standard EPR quartz tube (707-SQ from Wilmad). The spectra of powdered samples were recorded at room temperature (RT). To follow catalytic experiments, aliquots of the perfluoroheptane layer were removed and immediately frozen at liquid nitrogen temperature (LNT). These frozen solutions were measured at LNT using an immersion quartz Dewar. The microwave frequency was determined with a Hewlett Packard HP5350B frequency counter. For detecting Cu^{II} complexes, the conditions were as follows: 3320 ± 125 mT scan range, 2 mW microwave power, 9.51 GHz microwave frecuency, RT or LNT temperature, 0.4 mT modulation amplitude, 100 KHz modulation frequency, conversion time, 163.84 msg (see below).

Preparation of fluoroponytailed ligands and their copper complexes

4,4′-Diheptadecafluoroundecyl-2,2′-bipyridine (R_f-bpy, 2): LDA, prepared in situ from bisisopropylamine (2.37 mmol, 0.33 mL) and *n*BuLi (2.42 mmol, 1.21 mL) in dry THF (60 mL) at −78 °C, was treated with 4,4′-dimethyl-2,2′-bipyridine (0.95 mmol, 0.17 g). The temperature was allowed to rise from −78 to 0 °C over 1 h. After cooling down again to −78 °C, $C_8F_{17}(CH_2)_3I$ (2.08 mmol, 1.21 g) in dry THF (5 mL) was added. The reaction mixture was stirred at this temperature for 5 h and then warmed up to room temperature overnight. After total removal of the THF, the residue was extracted with CH_2Cl_2/Et_2O (50 mL, 1:1) and washed with H_2O (3×15 mL). The organic layer was dried over Na_2SO_4, and all solvents were concentrated to ≈ 1 mL. Subsequent addition of cold *n*-pentane (6 mL) afforded pure **2** as a beige powder (0.361 g, 35%). ^1H NMR ($CDCl_3$, 25 °C): $\delta = 8.57$ (d, $^2J(H,H) = 5.1$ Hz, 2H; $H_{1,1'}$), 8.24 (s, 1H; $H_{3,3'}$), 7.13 (d, $^2J(H,H) = 5.1$ Hz, 2H; $H_{2,2'}$), 2.74 (t, $^2J(H,H) = 7.5$ Hz, 4H; -CH_2CH$_2$-), 2.08 (m, 4H; -CH$_2$$CH_2CH_2$-), 1.73 (dd, 8H; -CH$_2CH_2$$CH_2CH_2$-$C_8F_{17}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 156.2$, 155.6, 149.15, 123.8 (d), 121.1 (d), 120–108 (4m, vbr), 34.8, 30.4 (t), 29.6, 19.7, 0.7 (t); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = -81.7$ (3F; CF_3), −115.4 (2F; CF_2), −123.0 (6F; CF_2), −123.8 (2F; CF_2), −124.6 (2F; CF_2), −127.3 (2F; CF_2); LSIMS-MS: *m/z* (%): 1105 (5) $[M]^+$, 645 (100) $[M - \{(CH_2)_3C_8F_{17}\}]^+$;

elemental analysis calcd (%) for $C_{34}H_{22}F_{34}N_2$: C 36.97, H 2.00, N 2.54; found C 36.64, H 1.95, N 2.69.

$[Cu(C_8F_{17}(CH_2)_2CO_2)_2]$ (3): Triethylamine (0.39 mL, 2.80 mmol) was added to a solution of $CF_3(CF_2)_7CH_2CH_2CO_2H$ (1.35 g, 2.80 mmol) in acetone (15 mL). This solution was added dropwise to a suspension of $CuSO_4 \cdot 5H_2O$ (0.342 g, 1.37 mmol) in acetone (30 mL). After 24 h stirring at room temperature, complex **3** precipitated as a blue powder, which was collected by filtration and washed with Et_2O to give the title compound (0.098 g, 69 %). Complex **3** was totally soluble in trifluorotoluene, partly soluble in dichloromethane, and insoluble in acetone, Et_2O, *n*-hexane, MeOH, H_2O, and perfluoroheptane. IR: $\nu = 1573$, 1420 cm^{-1} (C=O); UV/Vis (diffuse reflectance): $\lambda = 666$ nm (28 %); elemental analysis calcd (%) for $C_{22}H_8F_{34}O_4Cu$: C 25.27, H 0.77; found C 25.44, H 0.81.

$[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-tacn})]$ (4): R_f-TACN (0.218 g, 0.14 mmol) was added to a suspension of **3**, (0.15 g, 0.14 mmol) in dichloromethane (10 mL). A green solid precipitated immediately and was collected by filtration. After drying under vacuum, **4** was obtained as a green powder (0.255 g, 80 %). Complex **4** was totally soluble in trifluorotoluene and perfluoroheptane, while being insoluble in acetone, dichloromethane, chloroform, Et_2O, *n*-hexane, MeOH, and H_2O. IR: $\nu = 1632$, 1403 cm^{-1} (C=O); UV/Vis (perfluoroheptane): $\lambda = 272$ nm, (diffuse reflectance): $\lambda = 1013$ (62 %), 700 nm (48 %); LSIMS-MS: *m*/*z* (%): 2063 (75) $[M - \{C_8F_{17}(CH_2)_2CO_2\}]^+$, 1572 (30) $[M - \{C_8F_{17}(CH_2)_2CO_2\}_2]^+$, 1508 (58) $[R_f\text{-TACN}]^+$; elemental analysis calcd (%) for $C_{61}H_{38}F_{85}O_4N_3Cu$: C 28.67, H 1.49, N 1.64; found C 29.01, H 1.60, N 2.03.

$[Cu(C_8F_{17}(CH_2)_2CO_2)_2(R_f\text{-bpy})]$ (5): R_f-bpy (0.110 g, 0.1 mmol) was added to a suspension of $[Cu(C_8F_{17}(CH_2)_2CO_2)_2]$ (0.104 g, 0.1 mmol) in dichloromethane (10 mL). A green solid precipitated immediately. This precipitate was collected by filtration, and after drying under vacuum, **5** was obtained as a pale green powder (0.086 g, 40 %). Complex **5** was totally soluble in trifluorotoluene, hot perfluoroheptane, or hot perfluoro-1,3-dimethylcyclohexane (PP3), partly soluble in dichloromethane, and insoluble in acetone, Et_2O, *n*-hexane, MeOH, and H_2O. IR: $\nu = 1569$, 1394 cm^{-1} (C=O); UV/Vis (perfluoroheptane): $\lambda = 246$ nm, (diffuse reflectance): $\lambda = 680$ nm (42 %); LSIMS-MS: *m*/*z* (%): 1541 (5) $[M - \{C_8F_{17}(CH_2)_2CO_2\}\text{-}\{C_2F_5\}]^+$, 1351 (33) $[M - \{C_8F_{17}(CH_2)_2CO_2\} - \{C_5F_{13}\}]^+$, 707 (100) $[M - \{C_8F_{17}(CH_2)_2CO_2\} - \{C_6F_{14}\}]^+$; elemental analysis calcd (%) for $C_{56}H_{30}F_{68}O_4N_2Cu$: C 31.28, H 1.40, N 1.30; found C 31.54, H 1.60, N 1.73.

$[Cu(R_f\text{-tacn})]PF_6$ (6): R_f-TACN (0.151 g, 0.1 mmol) was added to a solution of $[Cu(CH_3CN)_4]PF_6$ (0.037 g, 0.1 mmol) in dry dichloromethane (10 mL) under argon. After 2 h of stirring at room temperature, the solution became pale green. After removal of the CH_2Cl_2 and addition of Et_2O, a very pale green powder precipitated. This precipitate was collected by filtration, and after drying under vacuum, **6** was obtained as an almost off white powder (0.061 g, 36 %). Complex **6** was soluble in trifluorotoluene and insoluble in dichloromethane acetone, Et_2O, *n*-hexane, MeOH, H_2O, and perfluoroheptane. LSIMS-MS: *m*/*z* (%): 1753 (15) $[M+2H_2O]^+$, 1573 (60) $[M - PF_6]^+$, 1554 (100) $[M - PF_6 - F]^+$; elemental analysis calcd (%) for $C_{39}H_{30}F_{57}N_3PCu$: C 27.26, H 1.76, N 2.44; found C 27.66, H 1.82, N 2.09.

$[Cu(R_f\text{-tacn})Cl]$ (7): R_f-TACN (0.151 g, 0.1 mmol) was added to a suspension of excess [CuCl] (0.050 g, 0.5 mmol) in trifluorotoluene (5 mL). After 3 h of stirring at room temperature, the suspension was filtered through celite (to remove the excess CuCl), and the colourless solution was evaporated to 1 mL. The addition of *n*-hexane afforded **7** as an off-white powder (0.125 g, 78 %). This complex was totally soluble in trifluorotoluene and perfluoroheptane, partly soluble in dichloromethane and chloroform, and insoluble in acetone, Et_2O, *n*-hexane, MeOH, and H_2O. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 2.25$ (m, 6H; $\text{-}CH_2\text{-}\mathit{CH_2}\text{-}CH_2\text{-}C_8F_{17}$), 2.10 (s, 12H; $\text{-}N\text{-}\mathit{CH_2}\text{-}\mathit{CH_2}\text{-}N$), 1.57 (m, 6H; $\text{-}CH_2\text{-}CH_2\text{-}\mathit{CH_2}\text{-}C_8F_{17}$), 1.20 (m, 6H; $\text{-}CH_2\text{-}CH_2\text{-}\mathit{CH_2}\text{-}C_8F_{17}$); $^{19}F\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = -80.5$, -110.8, -111.2, -121.1, -121.7, -122.6, -125.9 (the $^{19}F\{^1H\}$ NMR spectrum in $CDCl_3$ of R_f-TACN (**1**) has signals at $\delta = -81.7$, -115.2, -122.9, -123.9, -124.7, -127.3); UV/Vis (perfluoroheptane): $\lambda = 212$, 260 nm; LSIMS-MS: *m*/*z* (%): 1573 (88) $[M - Cl]^+$, 1095 (100) $[M - Cl - (CH_2)_3C_8F_{17} - F]^+$; elemental analysis calcd (%) for $C_{39}H_{30}F_{51}N_3ClCu$: C 29.12, H 1.88, N 2.61; found C 29.45, H 1.97, N 2.43.

Reaction of CuCl and R_f-bpy (2): R_f-bpy (**2**; 0.110 g, 0.1 mmol) was added to a suspension of [CuCl] (0.010 g, 0.1 mmol) in trifluorotoluene (5 mL). A green solid started to precipitate immediately. After 1 h of stirring at room temperature, the trifluorotoluene was removed under vacuum to ≈1 mL. The addition of Et_2O (10 mL) afforded a deep green powder (0.065 g, 54 %). LSIMS-MS: *m*/*z* (%): 2271 (29) $[M+R_f - bpy - Cl - (CH_2)_3C_8F_{17} - F]^+$, 1167 (100) $[M - Cl]^+$, 707 (100) $[M - Cl - (CH_2)_3C_8F_{17} - F]^+$); elemental analysis calcd (%) for $C_{34}H_{22}F_{34}N_2ClCu$: C 33.93, H 1.84, N 2.33; found C 32.51, H 3.61, N 1.41.

Standard catalytic oxidation of alkanes and alkenes under FBC conditions: A Schlenk tube (previously purged with Ar) was filled with a perfluoroheptane solution (2 mL) of the precatalyst (8 µmol). The isolated Cu^{II} complexes **4** (0.020 g) and **5** (0.017 g) were used for the oxidation experiments. For the Cu^I complexes, the preferred method was preparation in situ from excess [CuCl] (16 µmol, 0.017 g) or $[Cu(CH_3CN)_4]PF_6$ (16 µmol, 0.059 g) and **1** (0.012 g, 8 µmol), or **2** (0.009 g), in perfluoroheptane (2 mL). After stirring for 1 h at RT, these suspensions were filtered through Celite (to remove the excess Cu^I salts). The resulting colourless (**1**) or green (**2**) solutions were placed in the Schlenk tube and used as precatalysts. The hydrocarbon phase (upper layer of the biphasic system) consists of 40 mmol of substrate (cyclohexene 4.05 mL, cyclohexane 4.32 mL, toluene 4.26 mL) and 2 mmol (0.23 mL) of *o*-dichlorobenzene (as internal standard). Then *t*BuOOH (70 %, 500 µmol, 69.2 µL) was added and the reaction mixture (protected from light exposure) was stirred under an O_2 atmosphere at ambient temperature (for 8 or 24 h, see Table 1). After the reaction had taken place, the two phases were separated by decantation and analyzed by GC. In some cases, the fluorous phase could be reused for further runs (see Table 1), in which case perfluoroheptane (0.5 mL) and a new load of substrate/oxidant/internal standard were added, and the oxidation reaction proceeded under the conditions described above.

Standard catalytic oxidation of alcohols under FBC conditions: For the preparation of 4-nitrobenzaldehyde, a 25 mL Schlenk tube (previously purged with Ar) was charged with a perfluoroheptane solution (2 mL) of 3.5 mol % of **4** (0.027 mmol, 0.070 g). The hydrocarbon phase (upper layer of the biphasic system) consisted of 4-nitrobenzylalcohol (0.120 g, 0.78 mmol) in chlorobenzene (2 mL). TEMPO (6 mol %, 0.04 mmol, 0.069 g) was then added, and the biphasic reaction mixture was stirred under an O_2 atmosphere at 90 °C (for 4 or 8 h, see Table 2). After the reaction, the Schlenk tube was cooled to room temperature and the two phases were separated by decantation. The fluorous phase was washed with chlorobenzene (3 × 2 mL), and the combined organic layers were diluted with Et_2O (30 mL) and washed successively with brine (40 mL), and water (40 mL). After drying ($MgSO_4$), filtration, and complete evaporation of the solvent under reduced pressure, the crude product was weighted and analysed by ^1H NMR. The fluorous phase was separated and used directly (after adding 0.5 mL of perfluoroheptane) for further reaction runs.

EPR-FBC experiment A: Using standard oxidation conditions for cyclohexene, as outlined in Table 1, with precatalyst **7**, generated in situ, aliquots of the perfluoroheptane layer were removed and immediately frozen at LNT in an EPR tube (Figure 7, EPR spectra a–e).

EPR-FBC experiment B: Using standard oxidation conditions for 4-nitrobenzylic alcohol, as outlined in the experimental section using **4** as the precatalyst, aliquots of the perfluoroheptane layer were removed (after cooling down the reaction mixture at RT) and immediately frozen at LNT in an EPR tube (Figure 8, EPR spectra a–d).

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