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20 steps, and the overall yield is 0.65% starting from D-(+)mannitol. The synthetic route features regioselective macrolactonization of a disaccharide bearing a 19-membered ring and a one-pot glycosidation for construction of a macrolactone tetrasaccharide.

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Fluorous Biphasic Catalysis: Complexation of 1,4,7- $[C_8F_{17}(CH_2)_3]_3$ -1,4,7-Triazacyclononane with $[M(C_8F_{17}(CH_2)_2CO_2)_2]$ (M = Mn, Co) To Provide Perfluoroheptane-Soluble Catalysts for Alkane and Alkene Functionalization in the Presence of *t*-BuOOH and O_2^{**}

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Recently, Horváth and Rábai published a seminal paper on a new homogeneous catalysis concept—Fluorous Biphasic Catalysis (FBC)—that entailed the use of a fluorocarbon as one phase containing a modified catalyst with polyfluorinated alkyl side chains (fluoroponytails), while the substrate and the product were soluble in a second hydrocarbon phase.^[1] It is also important to note that low-boiling, perfluorinated solvents are immiscible both in water and many organic solvents.^[2] Therefore, separation of the product from the catalyst occurred by solubility differences between the hydrocarbon and fluorocarbon phases; this process thus represents a potentially interesting new concept for the industrial synthesis of important chemicals.^[1, 3, 4]

In this communication, we present the synthesis of a new fluoroponytailed ligand (4), namely, tris-N-(4,4,5,5,6,6,7,7,8,8, 9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacy-

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clononane (R_fTACN), that is soluble in perfluoroalkanes, and new R_fMn^{2+} and R_fCo^{2+} fluoroponytailed carboxylate synthons 5 and 6, as well as our initial results on the functionaliza-

 $[Mn(O_2C(CH_2)_2C_8F_{17})_2]$ 5

 $[Co(O_2C(CH_2)_2C_8F_{17})_2]$ 6

tion of alkanes and alkenes, using in situ generated $[R_f Mn^{2+}-(R_f TACN)]$ and $[R_f Co^{2+}(R_f TACN)]$ complexes (7 and 8, respectively) as catalysts that are totally soluble in the fluorous phase (Scheme 1). In contrast to the new FBC concept, the oxidation



Scheme 1. Fluorous biphasic oxidation catalysis with cyclohexene as the substrate and complex 7 formed in situ with 4 and 5.

of alkanes with *tert*-butyl hydroperoxide (TBHP) in acetonitrile and epoxidation of alkenes with H_2O_2 in acetone were previously achieved in one homogeneous phase by the in situ preparation of Mn^{2+} catalysts containing 2,2'-bipyridine and tris-N-methyl-TACN ligands, respectively, and separation of the Mn catalyst from the product is relatively difficult or impossible.^[5] We will demonstrate that this novel FBC approach for separation of the catalyst from the substrate appears viable for oxidation of alkanes and alkenes in the presence of the necessary oxidants, TBHP and O_2 gas, and that these oxidation reactions occur by an autoxidation mechanism under our FBC conditions.^[6, 7]

One key component of the FBC approach includes the new fluoroponytailed ligand 4, synthesized by the sequence of reactions shown in Scheme 2. It is important to note that the threemethylene spacer in 3 is 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 that predominately occurs when a two-carbon spacer is used



Scheme 2. Synthesis of 4

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during the formation of **4**. The first step to the new perfluoroalkyl iodide **3** proceeds by a free radical addition of a perfluoroalkyl iodide (R_rI) to allyl alcohol that was initiated with AIBN to provide the perfluoroalkylated iodohydrin **1**.^[8] Compound **1** was then reduced to the perfluoroalkyl alcohol **2** by using tributyltin hydride in dry benzotrifluoride.^[9] Iodination of **2** to form **3** was achieved with 85% phosphoric acid in the presence of phosphorous pentaoxide and potassium iodide in 85% yield.^[110] Finally, ligand **4** was obtained from TACN and **3** in DMSO/K₂CO₃ in 60% yield after recrystallization (Scheme 2; see Experimental Section). Compound **4** is soluble in cold perfluorohexane and perfluoromethylcyclohexane, and represents, to our knowledge, the first example of an R_f -amine ligand that is soluble in a perfluorocarbon solvent.

The other important components were the new $R_f Mn^{2+}$ and $R_f Co^{2+}$ complexes **5** and **6** synthesized by reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ or $Co(ClO_4)_2 \cdot 6H_2O$ in acetone with two equivalents of the triethylammonium salt of the 3- R_f -alkylpropanoic acid, $C_8F_{17}CH_2CH_2CO_2H$; elemental analysis of **5** and **6** provide a metal-to-carboxylate ligand ratio of 1:2, while **5** was found to be slightly soluble in perfluorocarbons, exhibits an intense and broad ESR signal at g = 2 (9 K), and displays the characteristic 6-line hyperfine structure (J = 90 G) of a mononuclear Mn^{2+} complex.^[11] Interestingly, when one equivalent of **4** was added to a solution of **5** in perfluoroheptane, a UV absorption band appears at 320 nm, tentatively suggesting that a new $[R_fMn(R_fTACN)]^{2+}$ complex (7) was formed in situ. Similarly, when ligand **4** and complex **6** were combined the complex $[R_fCo(R_fTACN)]^{2+}$ (**8**) resulted.

The FBC oxidation results for several substrates are presented in Table 1. All the experiments were carried out under biphasic conditions, generating complexes 7 or 8 in situ in perfluoroheptane (Scheme 1), while the upper phase was the substrate itself. Importantly, the oxidation products were detected only in the colorless upper phase after decantation (GC), while the colored perfluoroheptane lower phase contains only traces (<5%) of product. Clearly, a facile and rapid separation of the products from the catalyst was achieved with this FBC approach.

Table 1 demonstrates that the olefin with allylic hydrogens, cyclohexene, provides the highest yield of oxidation products (650% with TBHP in 3 h), while alkane oxidation was much lower (cyclohexane: 12% cyclohexanol (CyOH)/cyclohexanone (CyONE) with TBHP in 24 h; toluene: 65% PhCH₂OH/PhCHO with TBHP in 24 h). In the presence of a vigorously stirred mixture of 7, TBHP, and oxygen gas (1 atm), cyclohexene was converted into a product ratio of 2-cyclohexen-1-one (CyenONE, about 65%), 2-cyclohexen-1-ol (CyenOH, about

Table 1. Functionalization of alkenes and alkanes under fluorous biphasic catalysis conditions [a].

Cat.	Substrate	Oxidant	Product (µmol)	Yield[b] [%]	Time [h]
7	cyclohexene	TBHP	CyenOH (<2), CyenONE (<2)		7
7	cyclohexene	O ₂	CyenOH (<1), CyenONE (<1)		24
5	cyclohexene	TBHP/O ₂	CyenOH (130), CyenONE (160)	360	12
7	styrene	TBHP/O ₂	no epoxide		24
7	toluene	TBHP/O ₂	PhCHO (15), PhCH ₂ OH (30)	65	24
7	cyclohexane	TBHP/O ₂	CyOH (5), CyONE (3.5)	12	24
8	cyclohexene	TBHP/O ₂	CyenOH (185), CyenONE (360)	750	20
8	cyclohexane	$TBHP/O_2$	CyOH (7), CyONE (5.5)	17	24

[a] Conditions: 5 or 6 (3.5 μ mol) and 4 (3.5 μ mol) were dissolved in hot perfluoroheptane (3 mL) and then the substrate (2 mL) was added. The reaction starts after the addition of TBHP (90%, 72 μ mol) under an O₂ atmosphere when required. [b] Total yield was based on TBHP added.

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35%), and a small amount of cyclohexene oxide (<2%), while with complex **8** similar oxidation results were obtained. Styrene, with no allylic hydrogens, is not converted into styrene epoxide under these biphasic conditions. In the absence of O_2 or TBHP, only negligible amounts of 2-cyclohexen-1-ol and 2-cyclohexen-1-one were detected, indicative of an autoxidation reaction; that is, *both* were necessary for oxidation to proceed. At the end of the reaction the upper phase was removed, and new aliquots of cyclohexene and TBHP were added to provide a 400% yield after 5 h, showing that the catalyst, after decantation, was only present in the lower fluorocarbon phase.

These results were in agreement with an autoxidation mechanism involving alkoxy (RO[•]) or alkylperoxy (ROO[•]) radicals, ^[12] where the reaction was initiated by $t \operatorname{BuO}^{\bullet}$ or $t \operatorname{BuO}^{\bullet}_{2}$ radicals produced from redox reactions (Haber–Weiss Process, Equations 2 and 3 with $\operatorname{Mn}^{2+}/\operatorname{Mn}^{3+}$). In the case of the substrate

$$Mn^{2+} + RO-OH \xrightarrow{\text{Reduction}} RO^{-} + Mn^{3+} + HO^{-}$$
 (1)

 $Mn^{3+} + ROO-H \xrightarrow{Oxidation} RO_2' + Mn^{2+} + H^+$ (2)

cyclohexene, the allylic radical formed was then trapped by O_2 ($k > 10^9 \text{ M}^{-1} \text{ sec}^{-1}$) to provide cyclohexenylperoxy radicals, which were able to homolytically remove a hydrogen (bond energy of RCOO-H 90 kcal mol⁻¹) from benzylic or allylic C-H bonds (85 kcal mol⁻¹), and hence, propagate the radical reactions. The secondary cyclohexenyl hydroperoxide that was formed then decomposes catalytically in the presence of the Mn catalyst to give the alcohol and the ketone products.^[13]

The lower yields observed in the case of cyclohexane are consistent with the stronger C-H bond strength (95 kcal mol⁻¹),^[12] 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 O₂ (Russell-type mechanism).^[12]

The R_fMn complex, formed during the oxidation of 7, was plausibly a R_fMn³⁺Mn⁴⁺ dimer. Therefore, when TBHP was added to the reaction mixture, the solution turns brown and exhibits intense UV-Vis absorptions (ε per Mn atom is approximately 9000 and 1130 M⁻¹ cm⁻¹ at 300 and 500 nm, respectively, after 1 h) characteristic of dinuclear Mn³⁺Mn³⁺, Mn³⁺Mn⁴⁺, or Mn⁴⁺Mn⁴⁺ complexes.^[14] The occurrence of such a putative R_fMn³⁺Mn⁴⁺ dimer from starting complex 7, under oxidation conditions, was unambiguously confirmed by ESR studies at 9 K. Thus, a strong, distinctive 16-line signal of an antiferromagnetically coupled R_fMn³⁺Mn⁴⁺ dimer complex at g = 2 was observed in the perfluoroheptane phase, after 1 h of reaction. Indeed, it has recently been shown that the decomposition of TBHP in the presence of a dinuclear Mn³⁺₂(2-OHsalpn)₂ complex (salpn = bis(salicylidene)propylenediamine dianion) resulted in the formation of *t*BuO' radicals and a dinuclear Mn³⁺(μ -O)₂Mn⁴⁺ complex.^[15]

Furthermore, reaction 2 was favored over reaction 3 with complex 7 for two important reasons: 1) It has been previously shown that in nonpolar solvents equation 3 was very slow,^[16] and 2) the $R_rMn^{3+}Mn^{4+}$ dimeric species formed upon the addition of TBHP to complex 7 was not very efficient in the oxidation of TBHP. Interestingly, after three hours, the 16-line ESR signal had almost disappeared, which suggests that this $R_rMn^{3+}Mn^{4+}$ dinuclear mixed valent species might be involved in the catalytic decomposition of the cyclohexenyl hydroperoxide intermediate to provide the alcohol and ketone products.

Finally, as pointed out recently by Pozzi et al.,^[17] despite the apparent simplicity of the FBC concept the concrete demonstration of this strategy is still a difficult challenge, since the solubilization of the fluoroponytailed metal complexes used in perfluorocarbons is one limiting step along with catalyst stability and the favorable recycling of the catalyst system. We now have been able to solubilize complexes 7 and 8 successfully in perfluoroheptane, using both the new R_cTACN ligand 4 and the new $R_f Mn^{2+}$ and $R_f Co^{2+}$ complexes 5 and 6, with fluoroponytailed carboxylate ligands. Moreover, we have been able to perform alkane and alkene oxidations under FBC conditions in the presence of TBHP and O₂ as oxidant, and hence, separate the products from the catalyst by a simple decantation process. The oxidation process occurs by an autoxidation mechanism, with formation of alkenyl or alkyl hydroperoxides as the key intermediates, which then are catalytically decomposed by the R_fMn- or R_fCoR_fTACN catalyst, probably at the solvent interface, to provide the alcohol and ketone products. Future studies will attempt to ascertain the unequivocal structures of complexes 5-8 by single-crystal X-ray crystallography, define the role of the dinuclear R_fMn³⁺Mn⁴⁺ complex in the decomposition of the alkyl and alkenyl hydroperoxide intermediates and determine its full structure, as well as further the scope of the FBC approach to oxidation chemistry.

Experimental Section

4: TACN (88.4 mg, 0.73 mmol), K₂CO₃ (423 mg, 3:1 mmol), and R_iCH₂CH₂CH₂L₁ (1.41 g, 2.41 mmol) were dissolved in DMSO (10 mL, distilled over CaH₂) and heated at 90 °C for 24 h. Then perfluoroheptane (20 mL) was added to the reaction mixture, and the brown fluorous lower phase was separated and then filtered. After removing the solvent, compound 4 was obtained as a brown oil. After crystallization from hot hexane, compound 4 was isolated as a yellowish powder in 60% yield. FAB/MS: m/z 1510 [M + H⁺]. Elemental analysis calcd for C₃₉H₃₀F₅₁N₃: C 31.03, F 64.20, H 1.98, N 2.78; found: C 30.74, F 64.31, H 2.02, N 2.70. ¹H NMR (400 MHz, CDCl₃, 25°C): $\delta = 2.71$ (s, 12H, NCH₂CH₂N), 2.55 (t, 6H, NCH₂CH₂), 2.17 (m, 6H, CH₂CH₂CH₂), 1.58 (m, 6H, CH₂CH₂R_f).

5: CF₃(CF₂)₇CH₂CH₂CO₂H (1.35 g, 2.80 mmol) was dissolved in acetone (15 mL) and to this solution was added triethylamine (380 mL, 2.80 mmol). This resulting solution was added dropwise to $Mn(ClO_4)_2$ ·6H₂O (500 mg, 1.37 mmol) dissolved in acetone (30 mL). The sticky precipitate that formed was vigorously stirred for 2 h. After filtration, 5 was obtained as a white powder in 75% yield. Elemental analysis calcd for C₂₂F₃₄H₁₂O₆Mn: C 24.61, F 60.19, H 1.12, Mn 5.12; found: C 25.37, F 59.77, H 0.94, Mn 5.50.

6: The same procedure as for complex 5 was used for the synthesis of 6, except with $Co(ClO_4)_2$ ·6H₂O. A pink precipitate formed immediately, and after filtration, a pink powder was obtained in 100% yield. Elemental analysis calcd for $C_{22}H_{12}F_{34}CoO_6$: C 24.53, H 1.11, F 59.98, Co 5.46; found: C 25.05, H 1.27, F 60.15, Co 5.35.

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- [9] Compound 2 was recrystallized from hexane. EI-MS: m/z: 477 [M +]. Elemental analysis calcd for C₁₁H₇F₁₇O: C 27.63, H 1.46; found: C 27.72, H 1.63.
 ¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.75 (m, 2H, CH₂OH), 2.20 (m, 2H, Rf-CH₂), 1.88 (m, 2H, CH₂CH₂CH₂), 1.57 (s, OH).
- [10] Compound 3 can be recrystallized from methanol. EI-MS: m/z: 588 [M +]. Elemental analysis calcd for C₁₁F₁₇H₆I: C 22.47, H 1.02; found: C 22.80, H 1.26. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.26 (t, 2H, ICH₂), 2.16 (2m, 4H, CH₂CH₂R_f).
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A 1,3,5-Triphosphinantriium Ion**

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Dedicated to Professor Hans Georg von Schnering

In 1976 we prepared the spherical, negatively charged $[P_{12}S_{12}N_{14}]^{6-}$ ion by reaction of P_4S_{10} with potassium cyanate.^[1] In spite of the spatial proximity of the charge carriers, the anion is both thermally stable and stable to hydrolysis. The 1,1,3,3,5,5hexakis(dimethylamino)- $1\lambda^5$, $3\lambda^5$, $5\lambda^5$ -triphosphinantriium cation 2 has also proved to be thermally stable. The charge carriers in the six-membered ring are separated from one another by just a single CH₂ group. Cyclic phosphonium salts with two positively charged phosphorus atoms and symmetrically arranged phosphorus-carbon units have been described previously [2-7] However, in the quadruply charged P-C heterocycles known to date, three or four methylene groups separate the individual phosphorus atoms and thus 16-membered or 20membered rings are present.^[4] A cyclic dication prepared by Karsch that contains two phosphonium centers and a phosphane center in the 1,3,5 positions could not be quaternized to the 1,3,5-trication; instead, ring-opening occurred.^[8]

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Compound 2 is formed by the reaction of 1,1,3,3,5,5-hexakis(dimethylamino)-1,3,5-triphosphinine (1) with HBF₄·Et₂O in diethyl ether with a yield of 79.3%. The colorless crystalline compound melts at 211–212 °C and is soluble in acetonitrile.



The singlet at $\delta = 45.21$ in the ³¹P{¹H} NMR spectrum of **2** indicates that a planar ring is present within the scope of the NMR time scale. The position of the singlet is-compared with the position of the signal of the ylidic PCP triad of the starting material 1-shifted upfield by 20.2 ppm in the region of the $\hat{\lambda}^{5}$ -1,3-diphosphetes.^[9] The base of the singlet has a narrow line width and is flanked by two pairs of ¹³C satellites.^[10] Together with the triplet observed in the ${}^{13}C{}^{1}H$ NMR spectrum at $\delta = 18.26$, which displays individual lines with different structures, these four ¹³C satellites permit the full evaluation of the A, BX spin system of the $[{}^{13}C_1]$ isotopomer of 2. A ${}^{13}C$ -DEPT experiment confirmed unequivocally the presence of the endocyclic CH₂ groups. The small geminal P-P coupling constant of 4.0 Hz is characteristic for a $P-CH_2-P$ group.^[11] The ²J(P,P) coupling constant of the P=C-P triad in the starting material 1 was determined to be 73 Hz. As is the case in 1, a small negative vicinal P-C coupling constant is found in the ring $(-1.8 \text{ Hz}).^{[12]}$

The crystal structure analysis of **2** in the solid state revealed a six-membered heterocycle; the atoms P1, P3, C2, and C3 lie almost in a plane (Figure 1). P2 and C1 are both located above



Figure. 1. Molecular structure of the cation **2** in the crystal (thermal ellipsoids at 50 % probability, H atoms not shown for clarity). Selected distances [pm] and angles [°]: P1-C1 178.9 (3), P1-C3 180.6(3), P2-C1 180.2(3), P2-C2 181.2(3), P3-C2 180.7(3), P3-C3 181.7(3); P1-C1-P2 114.3(2), P1-C3-P3 117.4(2), C1-P2-C2 108.32(13), P2-C2-P3 119.9(2), C2-P3-C3 108.90(14), C3-P1-C1 103.8(2).

this plane; their positions in the ring are characterized by greatly different bond angles (P2-C2-P3: 119.9°, C1-P1-C3: 103.8°) and by distances between 178.9 and 181.2 pm, which are typical for P-C single bonds.^[13] The nitrogen atom environments are approximately planar. The P-N bond lengths (160.7– 162.0 pm) are about 7 pm shorter than those found in the starting material 1 and in $1\lambda^5, 3\lambda^5$ -diphosphinines.^[14, 15] There are no interactions between the triply positively charged six-membered ring and the tetrafluoroborate ions, and there is no H… F bridging. The peaks of the singly and doubly charged cations

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