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An Efficient and Selective Epoxidation of Olefins with Novel Methyltrioxorhenium/(Fluorous Ponytailed) 2,2′-Bipyridine Catalysts

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Abstract: Novel complexes between methyltrioxorhenium (MTO) and bis(fluorous-ponytailed) 2,2′-bipyridines (bpy-F_n) were synthesized and used for the oxidation of alkenes with hydrogen peroxide under fluorous catalysis. High conversions and yields of the corresponding epoxides were obtained.

Keywords: 2,2′-bipyridines; epoxidation; fluorous ponytails; homogeneous catalysis; hydrogen peroxide; methyltrioxorhenium

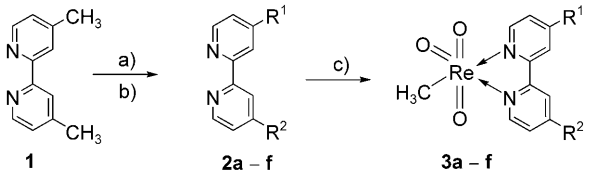
In the last few years the fluorous catalysis has become a novel synthetic strategy in the design and reuse of both homogeneous and heterogeneous metal catalysts.[1] Two branches have been developed in this field, namely the "heavy" and the "light" fluorous catalysis.[2] In both cases ligands bearing fluorous atoms are used to coordinate the active metal species. In the "heavy" fluorous catalysis, ligands bearing 39 or more fluorines are required to allow the complete solubility of the catalyst in the fluorinated solvents in biphasic transformations. The "light" fluorous catalysis typically is performed with 9–17 fluorines to increase the solubility of catalysts in common organic solvents. In this latter case the catalyst can be easily recovered at the end of the transformation by a fluorous solid-phase extraction technique (F-SPE).[3] Irrespective to the nature of the fluorine catalysis, 2,2′-bipyridines with 4,4′-bis(fluorous-ponytailed) substituents are commonly used as bidentate ligands in order to maintain the geometry at the metal center even when the metal is oxidized or reduced. Usually, methylene spacers of general formula $(CH_2)_m(CF_2)_nCF_3$ are used to insulate the active site from the electron-withdrawing fluorines.[4] Examples of redox processes catalyzed by metal/fluorous nitrogen ligands include manganese,[5] cobalt,[6] ruthenium,[7] and copper[8] oxidations under both "heavy" and "light" conditions.

Methyltrioxorhenium (MTO) is one of the most powerful catalysts for the activation of hydrogen peroxide in the oxidation of natural substances and fine chemicals. In these reactions the active catalytic forms are monoperoxorhenium [$MeRe(O)_2(O_2)$] and bisperoxorhenium [$MeRe(O)(O_2)_2$] complexes and/or their adducts with solvent molecules.[9] Among the synthetic applications of MTO, the epoxidation of olefins received greater attention. The most relevant drawback for this reaction is the concomitant ring opening of the newly formed oxiranyl ring to diols due to acidic properties of MTO. To date, different procedures have been developed to avoid this side reaction, including the use of ligands bearing one or more nitrogen atoms as mediators for the oxidation. In this case, adducts of MTO with Lewis bases, of general formula MTO/L_n [where L = ligand, $n = 1$ (monodentate) or 2 (bidentate)], are prepared by reaction with low molecular weight aromatic amines, such as pyridine, pyridine derivatives,[10] bipyridines[11] as well as easily available polymers bearing the pyridinyl moiety as anchorage site for the rhenium atom.[12] These adducts inhibit the formation of diols by tuning the electronic properties of MTO, their stability depending both on the physical and chemical properties of the ligand and of the reaction medium. Despite the large efforts devoted to the synthesis of novel MTO/L_n adducts, to the best of our knowledge there are no examples dealing with the synthesis of complexes between MTO and fluorinated nitrogen ligands. Recently, fluorinated rhenium(I)-bipyridine complexes bearing fluorinated alkyl ligands were prepared and their photochemical properties were investigated.[13]

In this paper we describe the hitherto unreported synthesis of complexes between MTO and bis(fluo-

rous-ponytailed) 2,2′-bipyridines (MTO/bpy-F_n) characterized by different values of fluorophilicity. These complexes are efficient and selective catalysts for the epoxidation of olefins with hydrogen peroxide (H_2O_2) under fluorous catalysis conditions.

Bis(fluorous-ponytailed) 2,2′-bipyridines **2a–f** (bpy-F_n) were prepared according to literature procedures starting from commercially available 4,4′-dimethyl-2,2′-bipyridine.[14] Briefly, compound **1** was treated with lithium diisopropylamide (LDA) in dry THF at low temperature (−78 °C) followed by alkylation with perfluoroalkyl iodides of general formula $C_nF_{2n+1}CH_2CH_2I$ ($n=5$, 7 and 9) to afford desired mono- and bis(fluorous-ponytailed) nitrogen ligands (bpy-F_n) in acceptable yield [(Scheme 1, *steps a)* and *b)*]. Freshly prepared bpy-F_n **2a–f** (0.18 mmol) were successively added to a solution of MTO (0.18 mmol) in diethyl ether (5.0 mL) at room temperature for 4 h (Scheme 1, *step c)*. The corresponding MTO/bpy-F_n catalysts **3a–f** were easily recovered in quantitative yield as yellow powders by cooling down to 0 °C.



1 **2a – f** **3a – f**

2a, 3a: $R^1 = (CH_2)_3(CF_2)_5CF_3$; $R^2 = CH_3$
2b, 3b: $R^1 = (CH_2)_3(CF_2)_7CF_3$; $R^2 = CH_3$
2c, 3c: $R^1 = (CH_2)_3(CF_2)_9CF_3$; $R^2 = CH_3$
2d, 3d: $R^1 = R^2 = (CH_2)_3(CF_2)_5CF_3$
2e, 3e: $R^1 = R^2 = (CH_2)_3(CF_2)_7CF_3$
2f, 3f: $R^1 = R^2 = (CH_2)_3(CF_2)_9CF_3$

a) LDA, THF_{dry}, −78 °C, 3 h
b) $C_nF_{2n+1}(CH_2)_2I$, n = 6, 8, 10, THF_{dry}, −78 °C to 25 °C overnight
c) MTO, Et_2O, 25 °C, 4 h

Scheme 1.

Nuclear magnetic resonance analysis (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) confirmed the assigned structures. In particular, we observed a downfield shift for Re*CH*$_3$ protons in fluorinated catalysts **3a–f** compared to the complex between MTO and 4,4′-dimethyl-2,2′-bipyridine as a reference ($\Delta\Delta = 0.23$–0.30 ppm, see Table 1). Downfield shifts for H-3,3′, H-5,5′ and H-6,6′ protons in ^{1}H NMR spectra of **3a–f** compared to ligands **2a–f** were also observed in accordance with the general behaviour previously reported for MTO complexes (*ΔΔ* Ar-*H 3,3′*, *ΔΔ* Ar-*H 5,5′*, *ΔΔ* Ar-*H 6,6′*, see Table 1).[15]

Ligands **2a–f** were further characterized by evaluation of typical parameters for fluorinated species, such as the percent of fluorine content (F), the fluorous partition coefficient (FPC) and the fluorophilicity[16,17] $f = \ln[\mathrm{FPC}]$. As a usual procedure, FPCs were calculated for a biphasic mixture (1:1 v/v) of perfluorooctane (FC77) and CH_2Cl_2. These parameters are reported in Table 2.

Table 1. Chemical shifts (δ, ppm) and *ΔΔ* Ar-*H 3,3′*, *ΔΔ* Ar-*H 5,5′*, *ΔΔ* Ar-*H 6,6′* of ligands **2a–f** and catalysts **3a–f**.

Entry	Ligand/Catalyst	Re*CH*$_3$	*ΔΔ* Ar-*H 3,3′*	*ΔΔ* Ar-*H 5,5′*	*ΔΔ* Ar-*H 6,6′*
1	MTO/bpy	1.04	–	–	–
2	**2a**	–	0.21	0.29	0.29
3	**3a**	1.28			
4	**2b**	–	0.09	0.27	0.31
5	**3b**	1.27			
6	**2c**	–	0.10	0.25	0.24
7	**3c**	1.28			
8	**2d**	–	0.10	0.20	0.24
9	**3d**	1.33			
10	**2e**	–	0.13	0.12	0.16
11	**3e**	1.33			
12	**2f**	–	0.05	0.09	0.10
13	**3f**	1.34			

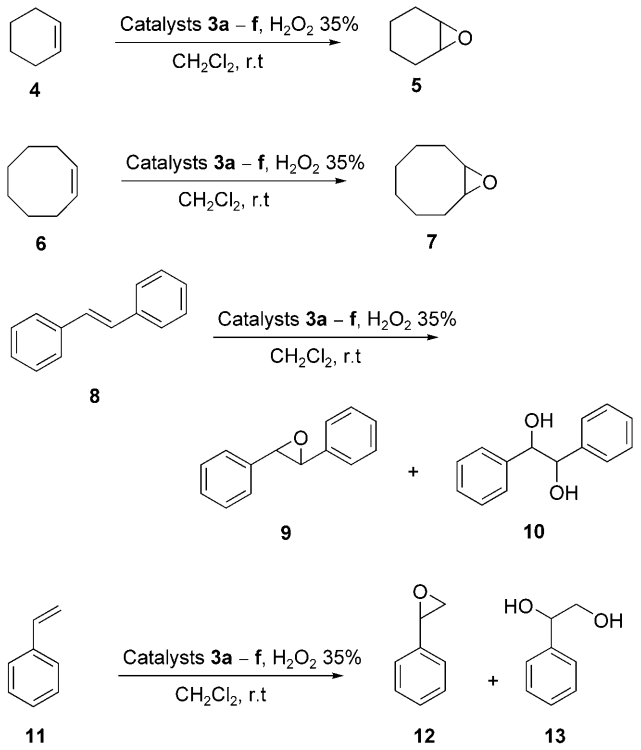
Table 2. Parameters of the ligands **2a–f**.

Entry	Ligand	F [%]	FPC[a]	*f*
1	**2a**	46.7	0.01	−4.60
2	**2b**	51.3	0.04	−3.20
3	**2c**	54.6	0.09	−2.40
4	**2d**	56.4	0.25	−2.40
5	**2e**	60.0	0.41	−0.90
6	**2f**	62.5	2.60	+0.95

[a] $\mathrm{FPC} = c_{i\ \text{fluorous phase}}/c_{i\ \text{organic phase}}$; c_i is the concentration of fluorinated species*i* expressed in mol/L; fluorous phase was FC77 and organic phase was dichloromethane.

On the basis of these data, ligands **2a–f** should be useful for "light fluorous catalysis" in accordance with previous trends observed for fluorocarbon modified organics (and, in principle, the ligand **2f**, with F > 60%, is also useful for "heavy fluorous catalysis").

Epoxidations with MTO/bpy-F_n catalysts **3a–f** and H_2O_2 (35% aqueous solution) were investigated with cyclic aliphatic olefins, cyclohexene **4** and *cis*-cyclooctene **6** (0.26 mmol) and low reactive aromatic olefins, *trans*-stilbene **8** and styrene **11**, as representative model substrates (Scheme 2*)*. All reactions were performed applying the "light fluorous catalysis" strategy in CH_2Cl_2 (2.5 mL) at room temperature using 2% in weight of **3a–f**. The epoxidation of **4** with the complex MTO/bpy was also performed as reference. The reactions were monitored by GC-MS analysis (see Experimental Section for more details). In the absence of the catalyst, less than 5% conversion of substrates took place under otherwise identical conditions. The results are summarized in Table 3. Noteworthy, irre-



Scheme 2.

spective of the presence of one or two fluorinated chains and number of fluorine atoms, MTO/bpy-F_n **3a–f** were highly efficient and selective catalysts in the epoxidation reaction of olefins **4** and **6** and the corresponding epoxides **5** and **7** were isolated in quantitative conversions and yields after only 2–5 h (Table 1, entries 2–7, 9–14). The MTO/bpy catalyst showed a similar behaviour in terms of yield and reaction time suggesting that the presence of fluorine atoms in the side-chains did not interfere with the reactivity of the MTO active species (Table 3, entries 1, 8, 15 and 22).

Catalysts **3a–f** were also efficient systems in the oxidation of the aromatic olefins *trans*-stilbene **8** and styrene **11** (Table 1, entries 16–21 and 23–28). In particular, in the oxidation of *trans*-stilbene **8**, the epoxide **9** was again obtained as the main reaction product in 64–92% conversion and 45–82% yield (Table 3, entries 16–21). According to the known high reactivity of stilbene epoxide to give nucleophilic ring-opening reactions, a significant amount of the corresponding diol **10** was observed (Table 3, entries 16-21). Noteworthy, the selectivity in the oxidation of **8** was tuned by the nature of the ligand, MTO/bpy-F_n **3b** being the most efficient catalyst (Table 3, entry 17). In the oxidation of styrene **11**, the epoxide **12** was obtained as the main product in 83–90% conversion and 80–87% yield (Table 1, entries 23–28), besides unreacted substrate and traces of diol **13**. As expected, longer reaction times were required for the oxidation of **11** due to the known lower reactivity of aromatic olefins with respect to aliphatic ones (Table 1, entries 16–21 and 23–28 *versus* entries 2–7 and 9–14). As a general trend, the fluorophilicity *f* of the catalysts did not influenced the selectivity of the epoxidation, with the only exception of *trans*-stilbene **8**, in which case, catalysts **3a–c** bearing mono(fluorous-ponytailed) nitrogen ligands were more selective than the corresponding bis(fluorous-ponytailed) systems **3d–f** (see, for example, Table 3, entries 16–18 *versus* entries 19–21).

The turnover frequencies (TOFs; moles of converted substrate per mole of catalyst per hour) of MTO/bpy-F_n catalysts **3a–f** calculated for the epoxidation of olefins **4**, **6**, **8** and **11** were found in the range of 1.0–25 depending on the experimental conditions and were similar to those of the parent MTO/bpy catalyst, confirming that the fluorinated chains did not modify the catalytic activity of the MTO active species.

Finally, our efforts were aimed at recycling the catalysts. The oxidation of cyclohexene **4** with **3f** was performed as a selected example. The thermomorphic method based on the temperature-dependent solubility of the fluorous catalysts in the organic solvent[16] was chosen as procedure to recover the catalyst. After the oxidation, the reaction mixture was directly cooled until $T = -60\,^{\circ}C$. A precipitate was observed and the supernatant phase containing the oxidation product was removed. The precipitate was washed and used for a successive oxidation (see Experimental Section). Unfortunately, the conversion of substrate and yield of epoxide **5** were dramatically decreased (25% and 20%, respectively).

A better result was obtained with the light catalyst **3a** by a fluorous solid-phase extraction technique (F-SPE). Fluorous silica gel as solid phase (commercially available as Fluoro*Flash* ®), a mixture of methanol/water as fluorophobic solvent and methanol as fluorophilic solvent were used experimentally.[3] Briefly, the reaction mixture dissolved in DMF was charged on column previously preconditioned with methanol/water (80:20). The column was eluted with methanol/water 80:20 to recover epoxide **5** followed by methanol to afford **3a** in appreciable yield (60%). Catalyst **3a** was used in a successive run without any further purification showing the expected reactivity (conversion: 75%; yield of epoxide **5**: 75%).

Thus, in our hands the F-SPE technique was the most efficient recycling procedure. However, a decrease of the reactivity of catalyst **3**a was observed during the successive run (conversion: 45%; yield of epoxide **5**: 45%).

In conclusion, in this paper mono- and bis(fluorous-ponytailed)/MTO catalysts were prepared for the first time in acceptable yield and applied for the activation of environmental friendly H_2O_2 in the epoxidation of aliphatic and aromatic olefins under fluorous catalysis. The epoxides were obtained in high yield and selec-

Table 3. Experimental data of oxidation of alkenes **4**–**8** with perfluoroalkylated catalysts **3a**–**f**.[a]

Entry	Substrate	Catalyst	Reaction time [h]	Conv. [%][b]	Yield [%][b]
1	cyclohexene **4**	**MTO/bpy**	5	98	**5**: 97
2		**3a**	5	97	**5**: 97
3		**3b**	5	>98	**5**: >98
4		**3c**	5	>98	**5**: >98
5		**3d**	2	96	**5**: 96
6		**3e**	3	>98	**5**: >98
7		**3f**	3	>98	**5**: >98
8	*cis*-cyclooctene **6**	**MTO/bpy**	5	>98	**7**: >98
9		**3a**	5	>98	**7**: >98
10		**3b**	3	>98	**7**: >98
11		**3c**	5	82	**7**: 82
12		**3d**	3	>98	**7**: >98
13		**3e**	4	>98	**7**: >98
14		**3f**	4	>98	**7**: >98
15	*trans*-stilbene **8**	**MTO/bpy**	24	65	**9**: 54; **10**: 11
16		**3a**	24	64	**9**: 52; **10**: 12
17		**3b**	24	92	**9**: 82; **10**: 10
18		**3c**	24	89	**9**: 76; **10**: 13
19		**3d**	24	85	**9**: 45; **10**: 40
20		**3e**	24	77	**9**: 65; **10**: 12
21		**3f**	20	82	**9**: 70; **10**: 12
22	styrene **11**	**MTO/bpy**	48	85	**12**: 80; **13**: 5
23		**3a**	48	83	**12**: 80; **13**: 3
24		**3b**	48	95	**12**: 85; **13**: 10
25		**3c**	48	90	**12**: 86; **13**: 4
26		**3d**	60	89	**12**: 86; **13**: 3
27		**3e**	48	85	**12**: 85
28		**3f**	48	87	**12**: 87

[a] *Reaction conditions:* substrate (0.26 mmol), catalyst (2%), hydrogen peroxide (35% water solution, 2 equiv.), dichloromethane (2.5 mL), room temperature.
[b] Calculated by GC-MS analysis.

tivity, values comparable to that of non-fluorinated MTO complex. With the only exception of *trans*-stilbene, the fluorophilicity of the ligand did not influence the reactivity, suggesting that three carbon units in the methylene spacer effectively insulated the bipyridyl ring and the rhenium center from the electron-withdrawing effect of the fluorinated alkyl chains. The MTO/bpy-F_n catalysts can be recovered by a fluorous solid-phase extraction technique and used in successive runs. Since MTO shows multifunctional catalytic properties including Lewis and Brönsted activity and metathesis properties,[18] these results are a promising entry to further exploiting the fluorine chemistry in the family of MTO-based organometallic species.

Experimental Section

All chemicals and Fluoro*Flash*® were purchased from Aldrich Company. Solvents were of the hightest commercially available quality. Dry tetrahydrofuran was prepared according to classical procedures. Silica gel was commercially available (Merck). Thin layer chromatography was carried out using Merck platen Kieselgel 60 F254. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (200 MHz) spectrometer; ^{19}F NMR were taken on a Bruker AMX 400 MHz. Chemical shifts are reported in δ values. Mass spectra were recorded on a VG 70/250S spectrometer with an electron beam of 70 eV and a CP-SIL 8 CB-MS column (25 m × 0.25 mm and 0.25 mm film thickness). GC analysis were performed using an isothermal temperature profile of 40 or 80 °C for 5 min, followed by a 10 °C min^{-1} temperature gradient to 250 °C for 10 min. The injector temperature was 280 °C.

Preparation of 4-(Perfluoroalkyl)-4′-methyl-2,2′-bipyridines (2a–c) and 4,4′-Bis(perfluoroalkyl)-2,2′-bipyridines (2d–f)

The preparation was performed according to that reported in the literature.[14] Into a dry round-bottom flask, 20 mL of dry THF were added. After cooling to −78 °C, LDA 2 M (0.3 mL, 2.3 mmol) and a 0.5 M solution of 4,4′-dimethyl-2,2′-bypiridine **1**, (0.198 g, 1.08 mmol) in 2 mL of dry THF were added. The mixture was kept under stirring for 3 h. To the dianion obtained, the perfluoroalkyl iodide $C_nF_{2n+1}CH_2CH_2I$ (2.3 mmol) was added and the mixture was

kept under stirring for 1 h at −78 °C, then warmed up to room temperature and kept under stirring overnight. The reaction was quenched with brine (20 mL); the residue was extracted with diethyl ether (3×20 mL) and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure, afforded a crude mixture. After crystallization and, if necessary, chromatographic purification on silica gel (eluent: dichloromethane/methanol), 4-(perfluoroalkyl)-4′-methyl-2,2′-bipyridines **2a–c** and 4,4′-bis(perfluoroalkyl)-2,2′-bipyridines **2d–f** were respectively isolated in 20–40% yield. Spectroscopic data are reported below.

4-(1H,1H,2H,2H,3H,3H-Perfluorononyl)-4′-methyl-2,2′-bipyridine (2a): Yield: 36%. Light brown solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.61–8.54 (m, Ar-H 6,6′), 8.33–8.29 (m, 2H, Ar-H 3,3′), 7.23–7.18 (m, 2H, Ar-H 5,5′), 2.84–2.63 (m, 2H, Ar-CH_2), 2.46 (s, 3H, Ar-CH_3), 2.22–1.95 (m, 4H, -$CH_2CH_2CH_2CF_2$-); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 156,6 (C-2′), 155.8 (C-2), 150.5 (C-4), 149.3 (C-6′), 149 (C-6), 148.2 (C-4′), 122.1(C-3′), 121.1 (C-3), 34.5 (-$CF_2CH_2CH_2CH_2$-Ar), 30.4 (-$CF_2CH_2CH_2CH_2$-Ar), 21.1 (CH_3-Ar), 21.0 (-$CF_2CH_2CH_2CH_2$-Ar); ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −131.4 (CF_2, 2F), −128.6 (CF_2, 2F), −128.1 (CF_2, 2F), −127.2 (CF_2, 2F), −119.1 (CF_2, 2F), −86.0 (CF_3, 3F).

4-(1H,1H,2H,2H,3H,3H-Perfluoroundecyl)-4′-methyl-2,2′-bipyridine (2b): Yield: 33%. Light brown solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.59–8.56 (dd, ^5J = 0.7 Hz, ^3J = 5.7 Hz 1H, Ar-H 6′), 8.53–8.50 (dd, ^5J = 0.5 Hz, ^3J = 5.0 Hz, 1H, Ar-H 6), 8.23–8,19 (m, 2H, Ar-H 3,3′), 7.14–7.11 (2dd, ^4J = 1.69 Hz, ^3J = 6.6 Hz, 2H, 5,5′) 2.88–2.66 (m, 2H, Ar-CH_2-), 2.42 (3H, s, Ar-CH_3), 2.19–2.02 (m, 4H, -$CH_2CH_2CH_2CF_2$-); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 156.6 (C-2′), 155.8 (C-2), 150.6 (C-4), 149.3 (C-6′), 149.0 (C-6), 148.2 (C-4′), 124.8 (C-5′), 123.6 (C-5), 121.1 (C-3′), 121.0 (C-3), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 30.4 (-$CF_2CH_2CH_2CH_2$-Ar), 21.2 (CH_3-Ar), 21.0 (-$CF_2CH_2CH_2CH_2$-Ar): ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −131.1 (CF_2, 2F), −128.3 (CF_2, 2F), −128.0 (CF_2, 2F), −127.7 (CF_2, 2F), −126.9 (CF_2, 4F), −119.1 (CF_2, 4F), −85.7 (CF_3, 3F).

4-(1H,1H,2H,2H,3H,3H-Perfluorotridecyl))-4′-methyl-2,2′-bipyridine (2c): Yield: 25%. Light brown solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.59–8.57 (dd, ^5J = 0.7 Hz, ^3J = 5.0 Hz, 1H, Ar-H 6′), 8.54–8.51 (dd, ^5J = 0.7 Hz, ^3J = 5.0 Hz, 1H, Ar-H 6) 8.26–8.23 (m, 2H, Ar-H 3,3′), 7.15–7.11(2dd, ^4J=1.56 Hz, ^3J = 6.5 Hz, 2H, 5,5′), 2.82–2.75 (m, 2H, Ar-CH_2), 2.43 (s, 3H, Ar-CH_3), 2.15–2.02 (m, 4H, -$CH_2CH_2CH_2CF_2$-); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 157.9 (C-2′), 154.5 (C-2), 151.4 (C-4), 149.1 (C-6′), 147.8 (C-6), 148.2 (C-4′), 125.2 (C-5′), 124.1(C-5), 122.8 (C-3′), 121.8 (C-3), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 30.6 (-$CF_2CH_2CH_2CH_2$-Ar), 21.4 (CH_3-Ar), 20.9 (-$CF_2CH_2CH_2CH_2$-Ar); ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −131.0 (CF_2, 4F), −128.0 (CF_2, 4F), −126.8 (CF_2, 4F), −122.5 (CF_2, 2F), −119.0 (CF_2, 4F), −85.7 (CF_3, 3F).

4,4′-Bis(1H,1H,2H,2H,3H,3H-perfluorononyl)-2,2′-bipyridine (2d): Yield: 40%. White solid. Spectroscopic data were in accord to those reported in the literature.[14]

4,4′-Bis(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-2,2′-bipyridine (2e): Yield: 37%. White solid. Spectroscopic data were in accord to those reported in the literature.[14]

4,4′-Bis(1H,1H,2H,2H,3H,3H-perfluorotridecyl)-2,2′-bipyridine (2f): Yield: 30%. White solid. Spectroscopic data were accord to those reported in the literature.[14]

Preparation of MTO Complexes (3a–f)

0.18 mmol of perfluoroalkyl bipyridines **2a–f** were added to a solution of MTO (0.045 g, 0.18 mmol) in diethyl ether (5.0 mL). The mixture was kept under stirring for 2 h at room temperature. After cooling down to 0 °C, a yellow precipitate was formed. The solid was filtered off, washed with pentane and dried under a flow of nitrogen until constant weight. Spectroscopic data are described below.

MTO/4-(1H,1H,2H,2H,3H,3H-perfluorononyl)-4′-methyl-2,2′-bipyridine (3a): Yield: 98%. Yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.91–8.88 (d, J = 5.4 Hz, 1H, Ar-H 6′), 8.85–8.82 (d, ^3J = 5.4 Hz, 1H, Ar-H 6). 8.11 (s, 2H, Ar-H 3,3′), 7.36–7.33 (m, 2H, ArH 5,5′), 2.92–2.85 (m, 2H, Ar-CH_2), 2.54 (s, 3H, Ar-CH_3), 2.27–2.00 (m, 4H, -$CH_2CH_2CH_2CF_2$-), 1.28 (3H, MTO-CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 154.7 (C- 2′), 152.3 (C-2), 150.7 (C-4), 150.0 (C-4′), 149.2 (C-6′), 148.8 (C-6) 127.4 (C-5′), 126.2-(C-5), 124.3 (C-3′), 123.4 (C-3), 34.5 (-$CF_2CH_2CH_2CH_2$-Ar), 30.4 (-$CF_2CH_2CH_2CH_2$-Ar), 28.0 (CH_3-Re), 21.4 (CH_3-Ar), 21.0 (-$CF_2CH_2CH_2CH_2$-Ar); ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −128.8 (CF_2, 2F), −126.0 (CF_2, 2F), −125.5 (CF_2, 2F), −124.5 (CF_2, 2F), −116.7 (CF_2, 2F), −83.4 (CF_3, 3F).

MTO/4-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-4′-methyl-2,2′-bipyridine (3b): Yield: 98%. Yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.90–8.87 (d, J = 5.5 Hz, 1H, Ar-H 6′), 8.85–8.82 (d, ^3J = 5.5, 1H, Ar-H 6), 8.12(s, 2H, Ar-H 3,3′), 7.36–7.34 (2dd, ^4J = 1.69 Hz, ^3J = 5.5 Hz, 2H, 5,5′), 2.93–2.85 (m, 2H, $ArCH_2$-), 2.55 (s, 3H, $ArCH_3$), 2.15–2.00 (m, 4H, -$CH_2CH_2CH_2CF_2$-), 1.27 (s, 3H, MTO-CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 156.6 (C-2′), 155.8 (C-2), 150.6 (C-4), 149.3 (C-6′), 149.0 (C-6), 149.1 (C-4′), 124.8 (C-5′), 123.6(C-5), 121.1 (C-3′), 121.0 (C-3), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 30.4 (-$CF_2CH_2CH_2CH_2$-Ar) 28.0 (CH_3-Re), 21.2 (1C, CH_3-Ar) 21.0 (1C, -$CF_2CH_2CH_2CH_2$-Ar; ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −126.7 (CF_2, 2F), −123.9 (CF_2, 2F), −123.6 (CF_2, 2F), −123.3 (CF_2, 2F), −122.5 (CF_2, 4F), −114.7 (CF_2, 4F), −81.3 (CF_3, 3F).

MTO/4-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)-4′-methyl-2,2′-bipyridine (3c): Yield: 98%. Yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.83–8.76 (m, 2H, Ar-H 6,6′), 8.41–8.29 (m, 2H, Ar-H 3,3′), 7.42–7.34 (m, 2H, Ar-H 5,5′), 2.94–2.87 (m, 2H, $ArCH_2$-), 2.58 (s, 3H, $ArCH_3$), 2.13–2.07 (m, 4H, -$CH_2CH_2CH_2CF_2$-), 1.28 (s, 3H, MTO-CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 153.6 (C-2,2′), 150.9 (C-4), 149.1 (C-4′), 149.0 (C-6,6′), 126.6 (C-5′), 125.6 (C-5), 124.1 (C-3′), 123.0 (C-3), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 30.3 (-$CF_2CH_2CH_2CH_2$-Ar), 26.0 (CH_3-Re), 21.7 (CH_3-Ar), 20.9 (-$CF_2CH_2CH_2CH_2$-Ar; ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −126.7 (CF_2, 4F), −123.7 (CF_2, 4F), −122.5 (CF_2, 4F), −118.2 (CF_2, 2F), −114.7 (CF_2, 4F), −81.4 (CF_3, 3F).

MTO/4,4′-bis(1H,1H,2H,2H,3H,3H-perfluorononyl)-2,2′-bipyridine (3d): Yield: 98%. Yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.85 (d, 2H, J = 5.4 Hz, Ar-H 6,6′), 8.15 (s, 2H, Ar-H 3,3′), 7.33 (d, 2H, J = 5.5 Hz, Ar-H 5,5′), 2.92–2.84 (m, 4H, $ArCH_2$), 2.22–2.06 (m, 8H, -$CH_2CH_2CH_2CF_2$-), 1.3 (s, 3H, MTO-CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 154.0 (C-2,2′), 152.7 (C-4,4′), 149.5 (C-6,6′), 125.2 (C-3,3′), 122.1 (C-5,5′), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 30.1 (-$CF_2CH_2CH_2CH_2$-Ar), 23.9 (CH_3-Re), 20.9 (-$CF_2CH_2CH_2CH_2$-Ar); ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = −128.8 (CF_2, 4F), −126.0 (CF_2,

4F), −125.5 (CF_2, 4F), −124.6 (CF_2, 4F), −116.7 (CF_2, 4F), −83.3 (CF_3, 6F).

MTO/4,4′-bis(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-2,2′-bipyridine (3e): Yield: 98%. Yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.76$ (d, 2H, $J = 5.4$ Hz, Ar-H 6,6′), 8.18 (s, 2H, Ar-H 3,3′), 7.27–7.24 (m, 2H, Ar-H 5,5′), 2.91–2.65 (m, 4H, $ArCH_2$), 2.24–1.82 (m, 8H, -$CH_2CH_2CH_2CF_2$-), 1.33 (s, 3H, MTO-CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta =$ 156.1 (C-2,2′), 153.7 (C-4,4′), 149.4 (C-6,6′), 124.8 (C-3,3′), 122.8 (C-5,5′), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 33.8 (-$CF_2CH_2CH_2CH_2$-Ar), 30.3 (-$CF_2CH_2CH_2CH_2$-Ar), 23.9 (CH_3-Re), 20.9 (-$CF_2CH_2CH_2CH_2$-Ar); ^{19}F NMR (376.4 MHz, $CDCl_3$): $\delta = -126.7$ (CF_2, 4F), −124.0 (CF_2, 4F), −123.4 (CF_2, 4F), −122.6 (CF_2, 8F), −118.1 (CF_2, 4F), −114.8 (CF_2, 4F), −81.3 (CF_3, 6F).

MTO/4,4′-bis(1H,1H,2H,2H,3H,3H-perfluorotridecyl)-2,2′-bipyridine (3f): Yield: 98%. Yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.70$ (d, 2H, $J = 5.4$ Hz, Ar-H 6,6′), 8.20 (s, 2H, Ar-H 3,3′), 7.24–7.21 (m, 2H, Ar-H 5,5′), 2.90–2.68 (m, 4H, $ArCH_2$), 2.19–2.04 (m, 8H, -$CH_2CH_2CH_2CF_2$-), 1.54 (s, 3H, MTO-CH_3); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta =$ 156.2 (C-2,2′) 152.7 (C-4,4′), 149.5 (C-6,6′), 124.8 (C-3,3′), 122.8 (C-5,5′), 34.6 (-$CF_2CH_2CH_2CH_2$-Ar), 30.1 (-$CF_2CH_2CH_2CH_2$-Ar), 23.9 (CH_3-Re), 20.9 (-$CF_2CH_2CH_2CH_2$-Ar); ^{19}F NMR (376.4 MHz, $CDCl_3$): $\delta =$ −126.7 (CF_2, 4F), −124.0 (CF_2, 4F), −123.6 (CF_2, 4F), −122.5 (CF_2, 16F), −118.1 (CF_2, 4F), −114.8 (CF_2, 4F), −81.4 (CF_3, 6F).

Determination of the Partition Ratio of Ligands 2a–e

This parameter was determinated according to the literature.[15,16] A 5-mL bottom-flask was charged with the perfluoroalkyl ligand **2a–f** (0.015 mmol), FC77 (2.0 mL) and CH_2Cl_2 (2.0 mL). The mixture was vigorously stirred for 2 h. After separation of the two phases, gravimetric measurements were performed.

Epoxidation Reaction

In a typical procedure the catalyst (2% referred to the substrate) was solubilized in CH_2Cl_2 (2.5 mL). Then hydrogen peroxide (35% aqueous solution, 2 equiv, 45 μL) was added and finally the substrate (0.26 mmol). The reaction mixture was kept under stirring at room temperature for 4–72 h depending on the substrate. Each 2 h, a sample was extracted; a small amount of MnO_2 was added to destroy the unreacted hydrogen peroxide and the mixture was stirred for 15 min. After filtration, the sample was analyzed by TLC and GC-MS to evaluate the conversion of the substrate and the yields of the final products.

Recycling Experiments Using the Thermomorphic Mode

The crude mixture of the oxidation reaction of cyclohexene **4** with catalyst **3f** was cooled down to −60 °C. A precipitate was observed and the supernatant phase containing the oxidation product was removed. The precipitate was washed with a small amount of cold dichloromethane. Then, at room temperature a solution of substrate (0.26 mmol) in dichloromethane (2.5 mL) and hydrogen peroxide (35% aqueous solution, 2 equiv, 45 μL) were freshly introduced.

Recycling Experiments Using the Fluorous Biphasic Catalysis (FBC) Technique

To apply the F-SPE technique, we used fluorous silica gel as solid phase (commercially available as Fluoro*Flash*®) and a mixture of methanol/water as fluorophobic solvent and methanol as fluorophilic solvent. The oxidation of cyclohexene **4** catalyzed by **3a** was performed in dichloromethane at room temperature. The silica gel was washed with DMF. The reaction mixture was dissolved in DMF and charged in a column with the solid phase previously preconditioned with methanol/water (80:20). Firstly, the column was eluted with methanol/water 80:20 to recover the oxidation product (epoxide **9**); then with methanol to recover the fluorinated species (catalyst **3a**). Finally, the column was washed with acetone to regenerate the fluorous solid phase.

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