Asymmetric Epoxidation of Terminal Alkenes with Hydrogen Peroxide Catalyzed by Pentafluorophenyl Pt^{II} Complexes

Marco Colladon,[†] Alessandro Scarso,[†] Paolo Sgarbossa,[‡] Rino A. Michelin[‡] and Giorgio Strukul^{*,†}

[†]Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137, 30123, Venice, (Italy)

[‡]Dipartimento di Processi Chimici dell'Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padova, (Italy)

Supporting Information Available: Full experimental procedures and characterization data for complexes **1a**, **1b** and **1d**.

Experimental Section

General

¹H NMR and ³¹P{¹H} NMR spectra were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 and 121.50 MHz, respectively, while ¹⁹F{¹H} were recorded on a Bruker AC200 operating at 188.25 MHz. δ values in ppm are relative to SiMe₄, 85% H₃PO₄ and CCl₃F. GC measurement were taken on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector (gas carrier He). All reactions except propene oxidation were monitored on a 25 m HP-5 capillary column I.D. 0.32 mm, film 0.25 μ m. Product yields were calculated using the internal standard method. Identification of products was made with GLC, GC-MS and NMR by comparison with authentic samples. Elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of Università di Padova. Enantiomeric excess was determined as reported in Table S1.

Table S1. Enantiomeric excess and absolute configuration assignment of terminal epoxides.

Substrate	ee determination	Abs. Config. assignment
A	H
A	I
B	J
A	I
A	I
A	I
A	I
C	K
D	M
E	N
F	L
G	L
A	I

A	I
A	I

A) e.e. determined by $^1\text{H-NMR}$ integration with the chiral shift reagent Europium *tris*-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] ($\text{Eu}(\text{hfc})_3$) at RT. B) e.e. determined by CSP-GC on a 25 m β -cyclodex column I.D. 0.25 mm, film 0.25 μm , $T_{\text{inj}}=250^\circ\text{C}$ $T_{\text{det}}=300^\circ\text{C}$, carrier He 1 mL/min, $45^\circ\text{C} \times 30$ min then $5^\circ\text{C}/\text{min}$ up to 200°C ; t_{S} 18.1 min, t_{R} 19.3 min. C) e.e. determined by chiral HPLC analysis on a Chiracel-ODH column, 100% hexane, 0.6 mL/min, t_{S} 34.9 min, t_{R} 37.1 min. D) e.e. determined by chiral HPLC analysis on a Chiracel-ODH column, 97% hexane-3% 2-propanol, 1mL/min, t_{S} 7.7 min, t_{R} 8.3 min. E) e.e. determined by chiral HPLC analysis on a Chiracel-ODH column, 97% hexane-3% 2-propanol, 1mL/min, t_{S} 20.0 min, t_{R} 22.3 min. F) e.e. determined by chiral HPLC analysis on a Chiracel-ODH column, 97% hexane-3% 2-propanol, 1mL/min, t_{S} 33.0 min, t_{R} 38.1 min. G) e.e. determined by chiral HPLC analysis on a Chiracel-ODH column, 99.3% hexane-0.7% 2-propanol, 1mL/min, t_{S} 16.4 min, t_{R} 17.3 min. H) Absolute configuration determined by addition of enantiomerically pure (*R*)-(+)-propene oxide to the enantioenriched epoxides in the presence of ($\text{Eu}(\text{hfc})_3$) at RT. I) Absolute configuration assigned from comparison to the deshielding effect in the presence of ($\text{Eu}(\text{hfc})_3$) at RT observed for propene oxide. J) Absolute configuration assigned from the GC elution order in β -cyclodex column. K) The absolute configuration was determined by comparing the sign of the measured optical rotations with literature data.¹ L) Absolute configuration determined by HPLC elution order on a Chiracel-ODH column compared to the other aromatic substrates above reported. M) The absolute configuration was determined by comparing the sign of the measured optical rotations with literature data.² N) The absolute configuration was determined by comparing the sign of the measured optical rotations with literature data.³

Materials

Hydrogen peroxide (35% and 60% Aldrich) as well as all the alkene substrates listed above are commercial products (Aldrich or Fluka) and were used without further purification. The chiral complex $[(S,S)\text{-chiraphosPt}(\text{C}_6\text{F}_5)(\text{H}_2\text{O})]\text{OTf}$ **1c** was prepared following the procedure reported in the literature,⁴ while complexes **1a**, **1b**, **1d** were prepared with similar procedures.

Materials for Pt^{II} complexes Synthesis

All synthetic steps were carried out under dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified according to standard methods.⁵ The diphosphines (+)-1,2-*bis*((2*R*,5*R*)-2,5-di-*i*-propylphospholano)benzene, 98+% (*R,R*)-*i*-Pr-DUPHOS **2a**, (1*S*,1'*S*,2*R*,2'*R*)-(+)-1,1'-Di-*t*-butyl-[2,2']-diphospholane, 97% (*S,S,R,R*)-TANGPHOS **2b**, (2*R*,3*R*)-(-)-2,3-*bis*(diphenylphosphino)-bicyclo[2.2.1]hept-5-ene, min. 95% (*R,R*)-NORPHOS **2d** were commercially available from STREM chemicals and were used as purchased.

$[\text{Pt}(\text{C}_6\text{F}_5)(\mu\text{-Cl})(\text{tht})]_2$ ⁶ was synthesized following procedures reported in the literature. Hydrogen peroxide (35% Fluka), $\text{MgCl}\cdot\text{iPr}$, AgBF_4 , AgOTf , were commercial products and used without purification. The chiral complex $[(S,S)\text{-chiraphosPt}(\text{C}_6\text{F}_5)(\text{H}_2\text{O})]\text{OTf}$ **1c** was prepared following the procedure reported in the literature.⁴

Oxidation Reactions

These were carried out in a 2 mL vial equipped with a screw-capped silicone septum to allow sampling. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer (700 rpm). Constant temperature was maintained by water or alcohol circulation through an external jacket connected with a thermostat. The concentration of the commercial 35% H₂O₂ solution was checked iodometrically prior to use. Typically, the proper amount of catalyst **1a-d** (0.016 mmol) was placed in the vial, followed by the solvent (1 mL) and the internal standard (*n*-decane), then the vial was thermostatted. After stirring for 10 min, the substrate (0.83 mmol) was added and the mixture stirred for 10 min. To this, hydrogen peroxide was added in one portion (0.83 mmol) and time was started. All reactions (except propene oxidation which was followed by ¹H-NMR analysis) were monitored with GC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Prior quenching of the samples by adding an excess of LiCl was found to be unnecessary, except for propene AE.

Synthetic Procedures for **1a**, **1b** and **1d**

[PtCl(C₆F₅)((*R,R*)-*i*-Pr-DUPHOS)] **3a.** To a solution of [Pt(μ -Cl)(C₆F₅)(tht)]₂ (0.12 g, 0.12 mmol) in acetone (30 mL) at room temperature were added 0.10 g (0.24 mmol) of (*R,R*)-*i*-Pr-DUPHOS. The solution was stirred for 2 hours then concentrated and treated with *n*-pentane giving a white solid, which was filtered off and dried under vacuum. Yield 0.067 g, 35%. Anal. Calc. for C₃₂H₄₄ClF₅P₂Pt: C, 47.09; H, 5.43%; Found: C,

47.11; H, 5.40; %. ^1H NMR (δ , CD_2Cl_2): 7.86-7.50 (m, Ar), 3.37-2.70 (m, alkyl), 2.63-1.64 (m, alkyl), 1.18 (d, 6.1 Hz, *i*Pr), 1.08 (d, 6.4 Hz, *i*Pr), 0.97 (d, 6.4 Hz, *i*Pr), 0.89 (d, 6.4 Hz, *i*Pr), 0.79 (d, 6.7 Hz, *i*Pr), 0.72 (d, 6.4 Hz, *i*Pr), 0.70 (d, 6.4 Hz, *i*Pr), 0.62 (d, 6.7 Hz, *i*Pr); ^{31}P $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): 54.42 (d, $P_{\text{O-trans}}$, $^1J_{\text{Pt-P}} = 3732\text{ Hz}$, $^2J_{\text{P-P}} = 5.9\text{ Hz}$); 60.02 (m, $P_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2232\text{ Hz}$); ^{19}F $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): -116.20, -121.23 (m, *o*-F), -162.45 (t, *p*-F, $^3J_{\text{F-F}} = 20.3\text{ Hz}$), -164.15, -164.97 (m, *m*-F).

[PtCl(C₆F₅)((S,S,R,R)-TANGPHOS)] 3b. This compound was prepared using a similar procedure to that described above for complex **3a** starting from [Pt(μ -Cl)(C₆F₅)(tht)]₂ (0.165 g, 0.17 mmol) in chloroform (30 mL) and 0.10 g (0.35 mmol) of (S,S,R,R)-TANGPHOS. Yield 0.148 g, 63%. Anal. Calc. for C₂₂H₃₂ClF₅P₂Pt: C, 38.63; H, 4.72%. Found: C, 38.72; H, 4.60%. ^1H NMR (δ , CD_2Cl_2): 2.75-1.86 (m, alkyl), 1.80-1.55 (m, alkyl), 1.41 (d, 14.3 Hz, *t*Bu), 1.04 (d, 14.3 Hz, *t*Bu); ^{31}P $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): 86.30 (d, $P_{\text{O-trans}}$, $^1J_{\text{Pt-P}} = 3670\text{ Hz}$, $^2J_{\text{P-P}} = 3.1\text{ Hz}$); 96.17 (m, $P_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2228\text{ Hz}$); ^{19}F $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): -117.42, -122.11 (m, *o*-F), -162.91 (t, *p*-F, $^3J_{\text{F-F}} = 19.1\text{ Hz}$), -163.80, -165.67 (m, *m*-F).

[PtCl(C₆F₅)((R,R)-NORPHOS)] 3d. This compound was prepared using a similar procedure to that described above for complex **3a** starting from [Pt(μ -Cl)(C₆F₅)(tht)]₂ (0.15 g, 0.15 mmol) in chloroform (30 mL) and 0.15 g (0.31 mmol) of (R,R)-NORPHOS. Yield 0.220 g, 83%. Anal. Calc. for C₃₇H₂₈ClF₅P₂Pt: C, 51.67; H, 3.28%; Found: C, 51.88; H, 3.09%. ^1H NMR (δ , CD_2Cl_2): 8.24-7.68 (m, Ar), 7.65-7.37 (m, Ar), 7.36-7.22 (m, Ar), 7.15-6.95 (m, Ar), 6.23 (dd, J 3.3 Hz, 5.2 Hz, aryl), 6.11 (dd, J 3.3 Hz, 5.2 Hz, aryl), 5.39 (m, aryl), 3.50-3.21 (m, alkyl), 3.16 (s, alkyl), 3.04 (s, alkyl), 2.87 (s, alkyl), 2.70 (s, alkyl), 2.35 (m, alkyl), 1.05-0.70 (m, alkyl); ^{31}P $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): 12.52 (d, $P_{\text{O-trans}}$, $^1J_{\text{Pt-P}} = 3784\text{ Hz}$, $^2J_{\text{P-P}} = 9.8\text{ Hz}$), 11.47 (d, $P_{\text{O-trans}}$, $^1J_{\text{Pt-P}} = 3790\text{ Hz}$, $^2J_{\text{P-P}} = 12.2\text{ Hz}$), 9.60 (m, $P_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2286\text{ Hz}$), 8.54 (m, $P_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2294\text{ Hz}$); ^{19}F $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): -120.14, -121.34 (m, *o*-F), -163.48 (t, *p*-F, $^3J_{\text{F-F}} = 20.3\text{ Hz}$), -165.09, -166.44 (m, *m*-F).

[Pt(C₆F₅)(H₂O)((R,R)-i-Pr-DUPHOS)][OTf] 1a. To a solution of [PtCl(C₆F₅)((R,R)-i-Pr-DUPHOS)] (0.066 g, 0.08 mmol) in dichloromethane (25 mL) were added 0.5 mL of an acetone solution of AgOTf (0.083 mmol). The suspension was stirred for an hour then the solid AgCl was filtered off and the solution was concentrated. Upon treatment with *n*-pentane a pale yellow solid was obtained, filtered off and dried under vacuum. Yield 0.051g, 66%. Anal. Calc. for C₃₃H₄₆F₈O₄P₂PtS: C, 41.82; H, 4.89%; Found: C, 41.70; H, 5.01%. ^1H NMR (δ , CD_2Cl_2): 7.90-7.61 (m, Ar), 3.09-2.87 (m, alkyl), 2.66-1.44 (m, alkyl), 1.25 (d, 6.6 Hz, *i*Pr), 1.16 (d, 6.6 Hz, *i*Pr), 1.04 (d, 6.6 Hz, *i*Pr), 0.92 (d, 6.6 Hz, *i*Pr), 0.85 (d, 6.6 Hz, *i*Pr), 0.76 (d, 6.3 Hz, *i*Pr), 0.74 (d, 6.3 Hz, *i*Pr), 0.66 (d, 6.6 Hz, *i*Pr); ^{31}P $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): 44.48 (d, $P_{\text{O-trans}}$, $^1J_{\text{Pt-P}} = 4348\text{ Hz}$, $^2J_{\text{P-P}} = 6.3\text{ Hz}$); 64.89 (m, $P_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2282\text{ Hz}$); ^{19}F $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): -79.34 (s, OTf), -120.91, -121.77 (m, *o*-F), -161.30 (m, *p*-F), -164.41, -165.02 (m, *m*-F).

[Pt(C₆F₅)(H₂O)((S,S,R,R)-TANGPHOS)][OTf] 1b. This compound was prepared using a similar procedure to that described above for complex **1a** starting from [PtCl(C₆F₅)((S,S,R,R)-TANGPHOS)] (0.14 g, 0.20 mmol). Yield 0.12 g, 74%. Anal. Calc. for C₂₃H₃₄F₈O₄P₂PtS: C, 33.87; H, 4.20%; Found: C, 33.72; H, 4.33%. ^1H NMR (δ , CD_2Cl_2): 2.69-1.98 (m, alkyl), 1.90-1.55 (m, alkyl), 1.38 (d, 14.8 Hz, *t*Bu), 1.14 (d, 14.8 Hz, *t*Bu); ^{31}P $\{^1\text{H}\}$ NMR (δ , CD_2Cl_2): 77.15 (d, $P_{\text{O-trans}}$, $^1J_{\text{Pt-P}} = 4204\text{ Hz}$, $^2J_{\text{P-P}} = 3.1\text{ Hz}$); 99.76 (m, $P_{\text{C-trans}}$, $^1J_{\text{Pt-P}} = 2256\text{ Hz}$);

^{19}F { ^1H } NMR (δ , CD_2Cl_2): -79.36 (s, OTf), -116.75, -122.63 (m, *o*-F), -159.62 (m, *p*-F), -162.45, -164.12 (m, *m*-F).

[Pt(C₆F₅)(H₂O)((*R,R*)-NORPHOS)][OTf] 1d. This compound was prepared using a similar procedure to that described above for complex **1a** starting from [PtCl(C₆F₅)((*R,R*)-NORPHOS)] (0.202 g, 0.23 mmol). Yield 0.218 g, 93%. Anal. Calc. for C₃₈H₃₀F₈O₄P₂PtS: C, 46.02; H, 3.05%; Found: C, 45.89; H, 3.16%. ^1H NMR (δ , CD_2Cl_2): 8.18-7.91 (m, Ar), 7.74-7.44 (m, Ar), 7.37-7.28 (m, Ar), 7.16-7.02 (m, Ar), 6.23 (dd, *J* 3.3 Hz, 5.2 Hz, aryl), 6.12 (dd, *J* 3.3 Hz, 5.2 Hz, aryl), 5.47 (dd, *J* 2.7 Hz, 5.5 Hz, aryl), 5.36 (dd, *J* 2.7 Hz, 5.5 Hz, aryl), 3.44-3.25 (m, alkyl), 3.21 (s, alkyl), 3.04 (s, alkyl), 2.93 (s, alkyl), 2.91-2.78 (m, alkyl), 2.69 (s, alkyl), 2.34-2.11 (m, alkyl), 1.90-1.57 (m, alkyl), 0.95 (d, 9.1 Hz, alkyl), 0.90 (d, 6.6 Hz, alkyl), 0.87 (d, 6.6 Hz, alkyl), 0.77 (d, 9.1 Hz, alkyl); ^{31}P { ^1H } NMR (δ , CD_2Cl_2): 5.84 (d, *P*_{O-trans}, $^1J_{\text{Pt-P}}$ = 4410 Hz, $^2J_{\text{P-P}}$ = 13.5 Hz), 4.84 (d, *P*_{O-trans}, $^1J_{\text{Pt-P}}$ = 4410 Hz, $^2J_{\text{P-P}}$ = 13.5 Hz), 16.63 (m, *P*_{C-trans}, $^1J_{\text{Pt-P}}$ = 2388 Hz), 14.31 (m, *P*_{C-trans}, $^1J_{\text{Pt-P}}$ = 2388 Hz); ^{19}F { ^1H } NMR (δ , CD_2Cl_2): -79.23 (s, OTf), -120.66, -121.92 (m, *o*-F), -160.87 (m, *p*-F), -164.49, -165.05 (m, *m*-F).

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