Iron complexes with polydentate phosphines as unusual catalysts for alcohol oxidation

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ABSTRACT

The iron(II) compounds [Fe(triphos)$(CH_3CN)_3$]$(OTf)_2$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; OTf = CF_3SO_3) (**1**), [Fe(dppm)$_2$$(CH_3CN)_2$]$(OTf)_2$ (dppm = bis(diphenylphosphino)methane) (**2**), [Fe(dppe)$_2$$(CH_3CN)_2$]$(OTf)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) (**3**), [Fe(dppp)$(CH_3CN)_4$]$(OTf)_2$ (dppp = 1,3-bis(diphenylphosphino)propane) (**4**) and [Fe(PSP)$(CH_3CN)_3$]$(OTf)_2$ (PSP = bis(2-(diphenylphosphino)ethyl)sulfide) (**5**) were synthesized and characterized by NMR and (**2**, **3** and **4**) also by X-ray crystallography. Such complexes catalyzed the selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. The catalytic reactions were performed in acetonitrile in mild experimental conditions (r.t. or 50 °C) using *tert*-butylhydroperoxide (TBHP) as oxidizing agent. By following the reaction of complex **4** with the oxidant by UV–visible spectroscopy, it was possible to evidence formation of the corresponding iron-peroxide intermediate. Comparison of ESI-MS spectra acquired on a solution of **1** or **4** before and after TBHP addition suggests ligand oxidation to iron-phosphine oxide complexes.

1. Introduction

The study of biomimetic iron catalysts for oxidation reactions has proved an intensely researched area in the last decade. Olefins, hydrocarbon, alcohols can be effectively and selectively oxidized, mostly by means of peroxides, in the presence of iron complexes with nitrogen polydentate ligands inspired by active sites of naturally occurring enzymes [1]. Thus, in several research groups efforts have been spent in the synthesis of novel nitrogen tri- or tetradentate ligands, which in association with iron might mimic the action of non-heme oxidation enzymes; on the other hand, heme enzymes having iron-porphyrin active sites seem less suitable to a biomimetic approach due to more restricted possible structural variations. Such wealth of studies has produced several examples of iron oxidation catalysts bearing nitrogen polydentate ligands: a considerable number of these have proved to be active for the selective oxidation of alcohols [2].

Notably, also simple Fe(II) or Fe(III) salts promote the oxidation of alcohols and alkanes (Fenton or Gif chemistry) [3], however such reaction generally follows a radical mechanism which leads to undesired overoxidation products. Moreover, iron salts are known to promote disproportionation of peroxides (catalase-like behaviour), an unwanted reaction which decreases the amount of available oxidant. Therefore, one major challenge concerning iron oxidation catalysis is precisely the suppression of their behaviour as radical initiators, in order to obtain controllable, selective reactions. Metal coordination to polydentate ligands can in principle produce catalyst precursors the activity of which is based on metal-centered, controllable and potentially selective oxidation, *i.e.* the desirable choice in opposition to radical chain mechanism.

We have recently been interested in the development of iron-based homogeneous catalysts for alcohol oxidation, with a specific attention towards use of simple bidentate nitrogen ligands [4]; in fact, examples of iron oxidation catalysts with bidentate ligands are not frequently found in the recent literature [5]. On the other hand, we showed that use of a tridentate nitrogen ligand resulted in selective iron catalyzed oxidation of glycerol [6].

To the best of our knowledge, use of phosphines as ligands for oxidation iron catalysis is so far unprecedented, but for the studies by Bauer, reporting use of phosphinooxazoline complexes [7], and Bhat who employed iron complexes with a Schiff base and triphenylphosphine [8]. Also with other metals, phosphines appear to have been rarely employed in oxidation reactions [9], very likely lest ligand oxidation occurs to the corresponding phosphine oxides. On the other hand, studies regarding catalytic properties of metal complexes with phosphine oxides as ligands have appeared in the literature [10], suggesting that, in oxidation promoted by phosphine complexes, potential

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ligand oxidation might still be compatible with catalysis. Such hypothesis is coherent with the studies performed by Bauer et al., who reported that oxidation of methylene groups of nitrogen ligands caused minor –if any – decrease in catalyst activity [2a].

Here we describe the results of our studies concerning the properties of iron complexes with bi- and tridentate phosphines as catalysts for the oxidation of alcohols. For these purpose the complexes [Fe(triphos)$(CH_3CN)_3](OTf)_2$ (triphos = 1,1,1-tris(diphenylphosphinomethyl) ethane; OTf = CF_3SO_3) (**1**), [Fe(dppm)$_2(CH_3CN)_2](OTf)_2$ (dppm = bis (diphenylphosphino)methane) (**2**), [Fe(dppe)$_2(CH_3CN)_2](OTf)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) (**3**), [Fe(dppp)$(CH_3CN)_4]$ $(OTf)_2$ (dppp = 1,3-bis(diphenylphosphino)propane) (**4**) and [Fe(PSP) $(CH_3CN)_3](OTf)_2$ (PSP = bis(2-(diphenylphosphino)ethyl)sulfide) (**5**) were synthesized and characterized by NMR and – with regard to complexes **2**, **3** and **4** - by X-ray crystallography. Such complexes proved to be effective catalysts for the investigated reaction in very mild reaction conditions, using *tert*-butylhydroperoxide (TBHP) as oxidizing agent. Spectroscopic studies provided interesting insight on the evolution of the iron species in the presence of the peroxide.

2. Experimental Section

2.1. General

All the chemicals employed were reagent grade and were used as received from the commercial suppliers.

2.2. Instrumental

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F NMR spectra were recorded on a Varian 400 spectrometer. Resonances were assigned with reference to COSY and HSQC spectra.

ESI-MS spectra were obtained by an ion-trap instrument (ESI-MS Bruker Esquire 4000) equipped with an electrospray ion source. The instrument performed with 10.0 psi nebulizer pressure, end-plate offset −500 V, capillary 4000 V and capillary exit at 113.3 V. The drying gas (N_2) flow was 5 L min^{-1} and the spectral range was from m/z = 100 to 1500.

UV–visible spectra were recorded on a Shimadzu UV-2450 spectrophotometer equipped with a TCC-240A Temperature-controlled cell holder.

The catalytic reactions were performed either in a thermostatted bath or using a CEM Discover Labmate microwave reactor.

The chemical yields of the catalytic reactions were determined by integration of the ^{1}H NMR signals and/or by GC analysis on an Agilent 6850 instrument with helium as carrier gas and a TCD detector. Samples from the reaction mixtures were injected without previous dilution at 100 °C into the cool on-column injector ("track-oven" programmed temperature) in a Restek Rtx®-Wax capillary column (30 m length, 0.32 mm ID, 0.5 μm film thickness) protected by a Restek Hydroguard® FS precolumn (5 m length, 0.53 mm ID).

The GC–MS analyses were carried out on a Shimadzu GCMS-QP2010 SE with helium as carrier gas. The system was equipped with an autosampler Shimadzu AOC-20i. Reaction mixture diluted in methanol was injected at 220 °C in split mode into a Supelco SLB-5 ms capillary column (30 m × 0.25 mm i.d. × 0.5 μm film thickness).

2.3. Synthesis of iron complexes

2.3.1. Synthesis of [Fe(triphos)$(CH_3CN)_3](OTf)_2$ (1)

A round-bottomed flask was charged with acetonitrile (30 mL) and $Fe(OTf)_2$ (200 mg, 0.56 mmol), the pale yellow solution so obtained turned red upon addition of triphos (352 mg, 0.56 mmol). The reaction mixture was stirred at r.t. for 1 h and then concentrated to 1/4 of the initial volume. Addition of diethylether caused precipitation of a pink red solid, which was filtered and washed with ether. Yield 78%. ^{1}H NMR (CD_3CN, 25 °C) δ 7.5–7.2 (m, 30H, Ph), 2.58 (m, 6H, CH_2), 1.95 (CH_3CN), 1.76 (m, 3H, Me). ^{31}P{^{1}H} NMR (CD_3CN, 25 °C) δ + 32.28. ^{19}F NMR (CD_3CN, 25 °C) δ −78.7.

2.3.2. Synthesis of [Fe(dppm)$_2(CH_3CN)_2](OTf)_2$ (2)

Same procedure as for **1** but with ligand dppm. Yield 52%. ^{1}H NMR (CD_3CN, 25 °C) δ 7.6–7.1 (m, 40H, Ph), 5.21 (br, 1H, CH_2), 2.99 (br, 1H, CH_2), 1.95 (CH_3CN). ^{31}P{^{1}H} NMR (CD_3CN, 25 °C) δ + 11.54. ^{19}F NMR (CD_3CN, 25 °C) δ −75.4.

2.3.3. Synthesis of [Fe(dppe)$_2(CH_3CN)_2](OTf)_2$ (3)

Same procedure as for **1** but with ligand dppe. Yield 50%. ^{1}H NMR (CD_3CN, 25 °C) δ 7.7–7.2 (m, 40H, Ph), 3.03 (br, 8H, CH_2), 1.95 (CH3CN). ^{31}P{^{1}H} NMR (CD_3CN, 25 °C) δ + 74.70. ^{19}F NMR (CD_3CN, 25 °C) δ −79.3.

2.3.4. Synthesis of [Fe(dppp)$(CH_3CN)_4](OTf)_2$ (4)

Same procedure as for **1** but with ligand dppp. Yield 73%. ^{1}H NMR (CD_3CN, 25 °C) δ 7.7–7.2 (m, 20H, Ph), δ 2.54 (br, 4H, PCH_2), δ 2.18 (br, 2H, CH_2), 1.95 (CH_3CN). ^{31}P{^{1}H} NMR (CD_3CN, 25 °C) δ + 39.10. ^{19}F NMR (CD_3CN, 25 °C) δ −78.6.

2.4. X-ray crystal structures analysis

Diffraction data for complexes **3** and **4** were collected at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron of Trieste (Italy), with a Pilatus 2 M image plate detector. The experiment was performed at 100(2) K (nitrogen stream supplied by an Oxford Cryostream 700) with a monochromatic wavelength of 0.700 Å through the rotating crystal method. The diffraction data were indexed, in-tegrated and scaled using program XDS [11]. The structures were solved by direct methods using SIR2014 [12]. Fourier analysis and refinement with the full-matrix least-squares method based on F^2 were performed with SHELXL-2014 [13]. Residuals in the difference Fourier of **4** were interpreted as two disordered diethyl ether molecules (one on an inversion center) and both were refined with fixed occupancy of 0.5. Hydrogen atoms were placed at calculated positions with isotropic U factors equal to 1.2/1.5 times the equivalent U factor of the bonded atom.

Crystallographic data:

(**3**) $C_{58}H_{54}F_6FeN_2O_6P_4S_2$, M = 1232.88, monoclinic, space group $P2_1/c$, a = 11.712(2), b = 20.417(4), c = 12.495(3) Å, β = 111.40(3)°, V = 2781.8(11) Å^3, Z = 2, Dc = 1.472 g/cm^3, μ(Mo-Kα) = 0.535 mm^{-1}, F(0 0 0) = 1272, θ range = 1.84–29.76°. Final R1 = 0.0286, w$R2$ = 0.0835, S = 1.073 for 508 parameters and 54,827 reflections, 8205 unique [R(int) = 0.0340], of which 7951 with $I > 2\sigma(I)$, max positive and negative peaks in ΔF map 0.472 and −1.050e. Å^{-3}.

(**4**) $C_{37}H_{38}F_6FeN_4O_6P_2S_2$.0.75($Et_2O$) M = 986.21, triclinic, space group $P\bar{1}$, a = 11.085(2), b = 13.933(3), c = 16.064(3) Å, α = 79.23(3), β = 81.17(3), γ = 76.86(3)°, V = 2357.7(9) Å^3, Z = 2, Dc = 1.389 g/cm^3, μ(Mo-Kα) = 0.549 mm^{-1}, F(0 0 0) = 1019, θ range = 1.28–30.96°. Final R1 = 0.0594, w$R2$ = 0.1797, S = 1.048 for 562 parameters and 50,083 reflections, 14,486 unique [R (int) = 0.0359], of which 13,523 with $I > 2\sigma(I)$, max positive and negative peaks in ΔF map 2.823, −1.023 e Å^{-3}.

CCDC 1910864-1910865 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.5. Catalytic reactions

2.5.1. Oxidation of alcohols using conventional heating

For a typical catalytic oxidation, in a round-bottomed flask the solvent (CD_3CN or acetone-d_6, 0.65 mL) and the catalyst (either

preformed **1** or **2–5** prepared *in situ*, 0.010 mmol) were introduced, followed by the substrate (0.50 mmol). For reactions performed at temperatures higher than r.t., the resulting solution was heated in a thermostatted bath to the desired temperature. Slow addition of the oxidant (1.0 or 2.0 mmol) was then carried out under stirring. After the desired time the reaction mixture was cooled at −18 °C and subsequently analyzed by ^{1}H NMR.

2.5.2. Oxidation of alcohols using microwave heating

A MW vial was charged with the solvent (CD_3CN, 0.65 mL), the catalyst (either preformed **1** or **2–5** prepared *in situ*, 0.010 mmol), the substrate (0.50 mmol) and finally the oxidant (2.0 mmol). The vial was then immediately placed into the microwave reactor and heated at the fixed temperature (60, 80 or 100 °C) under magnetic stirring; the target temperature was reached after about 1 min, after which time the power remained at values below 3 W. After the desired time the reaction mixture was cooled at r.t. and subsequently analyzed by ^{1}H NMR.

2.5.3. Oxidation of alcohols in the presence of radical trap

In a typical reaction carried out with added radical trap, in a round-bottomed flask the solvent (CD_3CN, 0.65 mL) and the catalyst (either preformed **1** or **2–5** prepared *in situ*, 0.010 mmol) were introduced, followed by the substrate (0.50 mmol) and the radical trap 2,6-di-*tert*-butyl-4-methylphenol (0.50 mmol). For reactions performed at temperatures higher than r.t., the resulting solution was heated in a thermostatted bath to the desired temperature. Slow addition of the oxidant (0.50 mmol) was then carried out under stirring. After the desired time the reaction mixture was cooled at −18 °C and subsequently analyzed by ^{1}H NMR.

2.6. Analysis of the reaction mixtures

Qualitative and quantitative analysis were accomplished by ^{1}H and ^{13}C NMR, by GC and GC/MS measurements; the NMR resonances and the GC retention times were compared to those of authentic samples obtained either by conventional routes or by commercial suppliers. Formation of other possible oxidation products (*e.g.* carboxylic acids) was ruled out due to absence of GC peaks of known retention times, obtained from authentic samples. Quantitative evaluation of product yields was performed by integration of ^{1}H NMR signals and, when appropriate, by GC *via* internal standard method (naphthalene or hexamethylbenzene). All reactions reported were repeated at least three times, showing a reproducibility of the quantitative results within ± 1%.

3. Results and discussion

3.1. Oxidation of 1-phenylethanol catalyzed by Fe/L complexes prepared in situ

As initial approach, we chose to carry out a series of oxidation reactions in the presence of a catalyst prepared *in situ* from $Fe(OTf)_2$ and one equivalent of a bi- or tridentate phosphine chosen within a selection of 10 ligands (see Fig. 1). The reactions were performed using 1-phenylethanol as model secondary alcohol and TBHP as oxidant, whereas CD_3CN was chosen as solvent with the purpose of analyzing by NMR the composition of the crude reaction mixtures.

With all ligands tested, after 3 h at 50 °C the substrate was oxidized to acetophenone as the only reaction product (see Scheme 1), with yields in the range 80–99 %. In Table 1 are reported the results obtained with two tridentate ligands (triphos and ttp), four bidentate phosphines (dppm, dppe, dppp, dppbz) and two ligands which may coordinate in either a bi- or a tridentate fashion (PSP, PNP). No data relative to the ligands dppb and dppe-F are here reported, due to their limited solubility in acetonitrile which was likely to cause formation of mixtures of different iron compounds in solution. With regard to the soluble ligands, use of triphos and PSP along with the bidentate phosphines dppm, dppe and dppp gave rise to 1-phenylethanol oxidation in yields close to 100%, whereas somewhat lower conversions were obtained with ttp, PNP and dppbz. From then on, we limited our studies to the series of five ligands which had provided more promising results. Notably, with the latter series of ligands conversions after 2 h already reached values in the range 89–93%.

Further experiments were carried out in conditions similar to those reported in Table 1, but in the presence of a double amount of ligand (*i.e.* [L]/[Fe] = 2): lower reaction yields were observed with all phosphines (53–85%), with a more pronounced decrease in the case of dppm and dppe. With regard to the oxidant employed, a decrease in the amount of TBHP ([ox]/[sub] = 2) gave slightly lower conversions, *e.g.* in such conditions the reaction yields were 93% with both triphos and dppp (to be compared with 96 and 99%, respectively, using [ox]/[sub] = 4, see Table 1, entries 1 and 7).

Substitution of TBHP with hydrogen peroxide as oxidizing agent caused a significant decrease of acetophenone yields, which did not exceed 50%. Other attempts at using H_2O_2 were carried out in the mixed reaction medium acetonitrile/acidic buffer (pH = 1.0), in order to verify whether the known stabilizing effect of low pH on hydrogen peroxide with regard to disproportionation [14] would lead to higher conversions: unfortunately, no such effect was observed, as reaction yields with and without buffer turned out to be comparable.

Interestingly, all the catalysts proved to be effective in promoting 1-phenylethanol oxidation also at room temperature. Selected results reported in Table 1 show that in the presence of the catalyst formed with either triphos (entry 9) or dppp (entry 13), after 24 h at 25 °C yields of acetophenone were 96 and 99%, respectively, whereas somewhat lower conversions were obtained with the other ligands tested.

The effect of the iron precursor was examined by substituting iron (II) triflate with the chloride, sulphate and acetate salts. The nature of the iron salt appears to be very relevant from the data obtained with all ligands: the results regarding Fe/triphos catalysts, reported in Table 2, show the superiority of triflate upon the other salts tested.

3.2. Synthesis and spectroscopic characterization of the iron complexes

The next target in our studies was represented by isolation and characterization of the most active catalyst precursors among those tested so far, *i.e.* the iron complexes with the ligands triphos, dppp, dppe, dppm and PSP.

By treatment of an acetonitrile solution of iron(II) triflate with one equivalent of triphos, formation of a red solution was observed. After reducing its volume under reduced pressure, slow addition of diethylether caused precipitation of a pink solid. The ^{1}H NMR spectrum of this product recorded in CD_3CN showed, aside the aromatic signals at δ 7.5–7.2, a multiplet at δ 2.58 assigned to methylene protons and a methyl resonance at δ 1.76 ppm (see Table 3). In the ^{31}P NMR spectrum one single resonance was observed at δ + 32.28. All assignments were supported by COSY and HSQC spectra. Moreover, the ^{19}F NMR narrow signal at δ −78.7 indicated that triflate ion was neither coordinated to iron nor involved in dynamic processes. The spectral data allowed identification of the complex as $[Fe(triphos)(CH_3CN)_3](OTf)_2$ (**1**), a species previously reported in the literature and identified by resolution of its X-ray structure, albeit with a different anion [15]. The isolated compound **1** showed a reasonably good stability both in acetonitrile solution and as a solid sample, and was employed as catalyst precursor in the latter form thereafter.

By the same procedure we also isolated the iron complexes with the ligands dppm, dppe and dppp (compounds **2**, **3** and **4**). The NMR data of these compounds (see Table 3) indicated formation of single, highly symmetrical species, which showed good stability in acetonitrile solution. On the other hand, unfortunately, their stability in the solid state as pink-red powders was rather poor, giving rise within few hours to

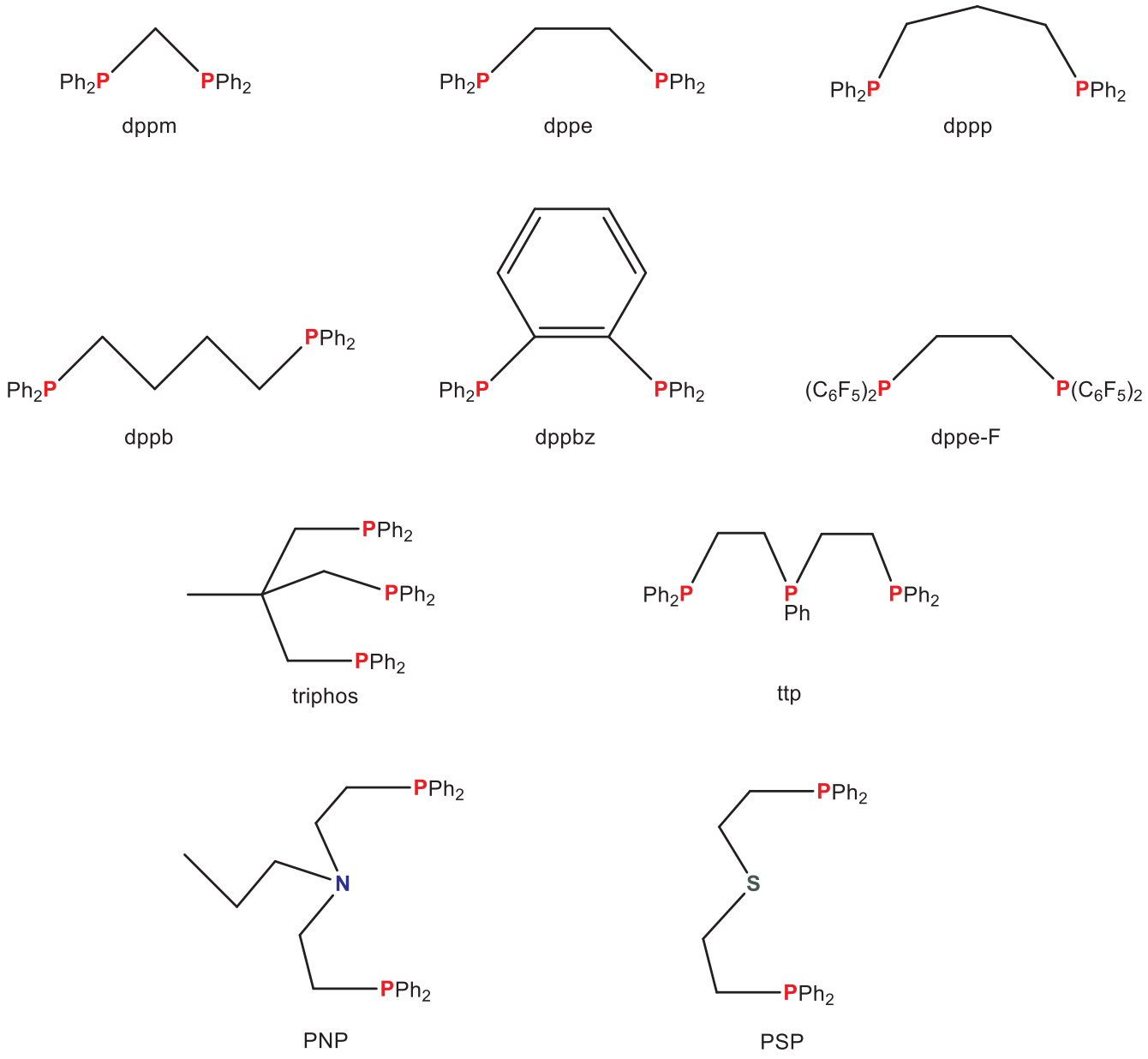
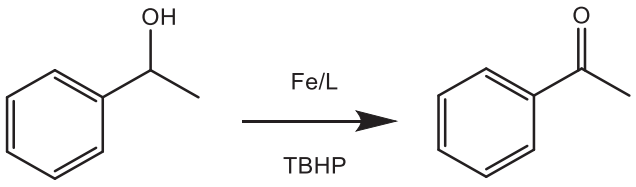


Fig. 1. Ligands employed in this study.



Scheme 1. Oxidation of 1-phenylethanol.

amorphous solids, the NMR spectra of which showed very broad signals, suggesting formation of iron(III) species. Therefore, for the purpose of catalytic studies we preferred to continue with the preparation *in situ* of compounds **2**, **3** and **4**. For the complete identification of such compounds, resolution of their crystal structure was in order.

Finally, isolation of the iron compound with the ligand PSP was unsuccessful, therefore we suggest its structure on the basis of the NMR spectra (see Table 3). Observation of a single ^{31}P resonance, aside with the number and multiplicity of ^{1}H NMR signals and the ^{19}F spectrum indicating a non-coordinated triflate anion, all concur to propose that

Table 1
Oxidation of 1-phenylethanol with TBHP catalyzed by $Fe(OTf)_2$ + L.

Entry	L	T (°C)	t (h)	Conversion (%)
1	triphos	50	3	96
2	ttp	50	3	82
3	PSP	50	3	98
4	PNP	50	3	87
5	dppm	50	3	96
6	dppe	50	3	99
7	dppp	50	3	99
8	dppbz	50	3	88
9	triphos	25	24	96
10	PSP	25	24	92
11	dppm	25	24	86
12	dppe	25	24	88
13	dppp	25	24	99

Experimental conditions: [Fe] = $1.5x10^{-2}$M; [L]/[Fe] = 1; [sub]/[Fe] = 50; [ox]/[sub] = 4; solvent = CD_3CN; TBHP 70% aqueous solution.

Table 2
Oxidation of 1-phenylethanol with TBHP catalyzed by an iron salt + triphos.

Entry	Iron salt	T (°C)	t (h)	Conversion (%)
1	$Fe(OTf)_2$	50	3	96
2	$FeCl_2$	50	3	47
3	$FeSO_4$	50	3	5
4	$Fe(OAc)_2$	50	3	14

Experimental conditions: see Table 1.

Table 3
NMR data (CD_3CN, 25 °C) of the free ligands and of their iron complexes 1–5.

	^1H	^{31}P	^{19}F
triphos	7.5–7.2 (m, 30H, Ph), 2.45 (br, 6H, CH_2) 0.98 (s, 3H, Me)	−26.95	–
complex **1**	7.5–7.2 (m, 30H, Ph), 2.58 (m, 6H, CH_2) 1.95 (CH_3CN), 1.76 (m, 3H, Me)	+32.28	−78.7
dppm	7.5–7.3 (m, 20H, Ph), 2.95 (t, 2H, CH_2)	−23.20	–
complex **2**	7.6–7.1 (m, 20H, Ph), 5.21 (br, 1H, CH_2) 2.99 (br, 1H, CH_2), 1.95 (CH_3CN)	+11.54	−75.4
dppe	7.35 (m, 20H, Ph), 2.09 (dd, 4H, CH_2)	−13.73	–
complex **3**	7.7–7.2 (m, 20H, Ph), 3.03 (br, 4H, CH_2) 1.95 (CH_3CN)	+74.70	−79.3
dppp	7.4–7.3 (m,20H, Ph), 2.24 (t, 4H, PCH_2) 1.51 (m, 2H, CH_2)	−17.90	–
complex **4**	7.7–7.2 (m, 20H, Ph), 2.54 (br, 4H, PCH_2) 2.18 (br, 2H, CH_2), 1.95 (CH_3CN)	+39.10	−78.6
PSP	7.5–7.3 (m, 20H, Ph), 2.55 (m, 4H, PCH_2) 2.26 (m, 4H, SCH_2)	−17.76	–
Complex **5**	7.9–7.3 (m, 20H, Ph), 3.82 (m, 2H, PCH_2) 3.60 (m, 2H, PCH_2), 2.81 (pst, 2H, SCH_2) 2.43 (pst, 2H, SCH_2), 1.95 (CH_3CN)	+61.30	−79.3

compound **5** can be formulated as $[Fe(PSP)(CH_3CN)_3](OTf)_2$. Moreover, the large low field shift of the ^{31}P signal of complex **5** with respect to that of the free ligand suggests formation of five-membered chelate rings, compatible with sulfur coordination to the metal [16]. A selection of NMR spectra is reported in the Supporting Information.

3.3. Characterization of the iron complexes: X-ray structures

For a thorough characterization of compounds **2**, **3** and **4** resolution of their X-ray structure was needed. Crystals suitable for the purpose were grown by slow ethyl ether diffusion into an acetonitrile solution containing equimolar amounts of $Fe(OTf)_2$ and dppm, dppe or dppp, respectively. All attempts to use the same - or other - techniques to grow suitable crystals of compound **5** were unsuccessful.

In the following, the molecular structures for **2**, **3** and **4** are described; more details regarding the resolution of the crystal structures are reported in the Section 2.

Red, long-shaped crystals of compound **4**, of reasonable quality for the X-ray analysis, were obtained after several attempts. Its molecular structure indicates that coordination of one dppp ligand to iron has taken place, together with four acetonitrile molecules. The NMR data of **4** above discussed are compatible with complex $[Fe(dppp)(CH_3CN)_4](OTf)_2$ (Fig. 2) being the main species present also in solution. A selection of bond lengths and angles of **4** is reported in Table 4. The Fe-N distances of trans located CH_3CN are slightly shorter (mean value 1.920 Å) than those trans to the phosphorous donors that average to 1.965 Å. It is worth noting that the complex formed contains only one dppp, likely due to the bite angle for this ligand (92.10(3)°. As a matter of fact, a search of CCDC retrieved almost 20 octahedral complexes of M $(dppp)_2X_2$ stoichiometry but of transition metals of second and third row having larger ionic radius [17].

The iron complex with dppe (**3**) formed well defined, red crystals suitable for X-ray analysis. The structural analysis showed a centrosymmetric structure where two phosphines were coordinated in a

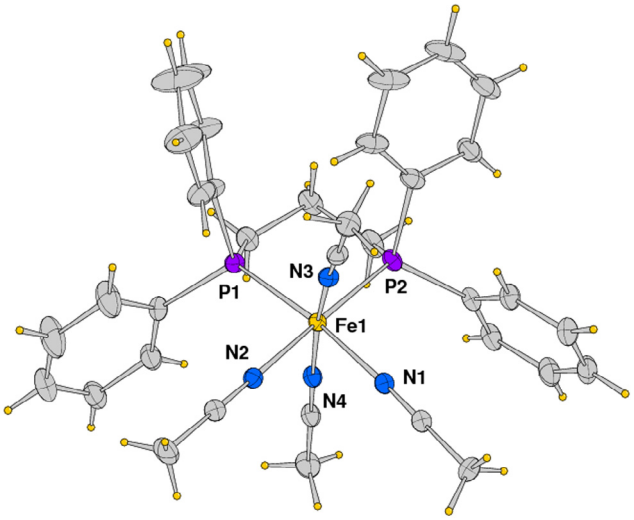


Fig. 2. Molecular structure (ORTEP drawing, ellipsoid probability at 50%) of complex cation $[Fe(dppp)(CH_3CN)_4]^{2+}$ of (**4**).

Table 4
Selected bond lengths (Å) and angles (°) of $[Fe(dppp)(CH_3CN)_4]^{2+}$ (4).

Fe-N(1)	1.9699(17)	Fe-N(4)	1.9208(17)
Fe-N(2)	1.9596(18)	Fe-P(1)	2.2660(9)
Fe-N(3)	1.9199(17)	Fe-P(2)	2.2468(9)
N(3)-Fe-N(4)	172.44(7)	N(2)-Fe-P(2)	178.63(5)
N(3)-Fe-N(2)	88.83(7)	N(1)-Fe-P(2)	91.70(5)
N(4)-Fe-N(2)	88.99(7)	N(3)-Fe-P(1)	98.99(5)
N(3)-Fe-N(1)	86.91(7)	N(4)-Fe-P(1)	88.19(5)
N(4)-Fe-N(1)	85.76(7)	N(2)-Fe-P(1)	88.70(5)
N(2)-Fe-N(1)	87.39(7)	N(1)-Fe-P(1)	172.86(5)
N(3)-Fe-P(2)	92.15(6)	P(2)-Fe-P(1)	92.10(3)
N(4)-Fe-P(2)	89.92(6)		

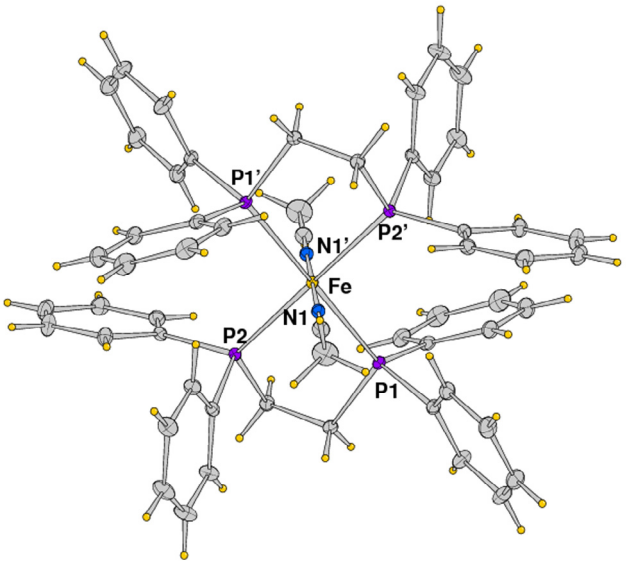


Fig. 3. Molecular structure (ORTEP drawing, ellipsoid probability at 50%) of complex cation *trans*-$[Fe(dppe)_2(CH_3CN)_2]^{2+}$ of (**3**).

trans stereochemistry to the iron center, which completes the coordination environment with two acetonitrile molecules, thus forming *trans*-$[Fe(dppe)_2(CH_3CN)_2](OTf)_2$. The molecular structure of **3** and a selection of its bond lengths and angles is reported in Fig. 3 and Table 5, respectively. Here the Fe-P bond distances are longer by ca. 0.1 Å and

Table 5
Selected bond lengths (Å) and angles (°) of $[Fe(dppe)_2(CH_3CN)_2]^{2+}$ (3).

Fe-N(1)	1.9079(9)	Fe-P(2)	2.3237(6)
Fe-P(1)	2.3702(4)		
N(1)-Fe-P(2)	91.74(3)	N(1)-Fe-P(1)	91.12(3)
N(1)-Fe-P(2)#1	88.26(3)	P(1)-Fe-P(2)	83.34(3)
N(1)-Fe-P(1)#1	88.88(3)	P(2)-Fe-P(1)#1	96.66(3)

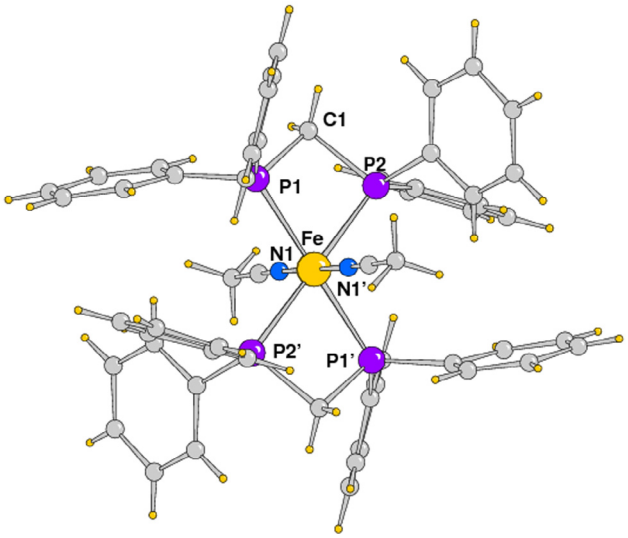


Fig. 4. Molecular structure of *trans*-$[Fe(dppm)_2(CH_3CN)_2]^{2+}$ (**2**).

with a narrower P-Fe-P angle (83.34(3) vs 92.10(3)°) than the values measured in **4**, indicating a strain upon coordination of phosphine ligand to the metal center. These data agree with those of two complexes reported with BF_4^- [18a] and $[Fe_2(dppe)Cl_6]^{2-}$ [18b] as counteranions where the P-Fe-P chelating angle is of 83.20 and 82.66°, respectively.

The ligand dppm forms the iron complex **2** similar to that of dppe, *i.e.* *trans*-$[Fe(dppm)_2(CH_3CN)_2](OTf)_2$ (see Fig. 4). Although orange crystals obtained from an acetonitrile/diethyl ether solution of **2** were of poor quality, the X-ray diffraction analysis unambiguously indicated the structure of the complex cation as reported in Fig. 4. Since the refinement of this was very poor due to a heavy crystal disorder, we do not report the crystallographic results, which anyway confirm a trans configuration of CH_3CN ligands analogously to that detected for complex 3. In the literature, the same complex, reported with different anions [19] exhibits Fe-P and Fe-N bond lengths of comparable values to those here reported, with a very narrow P-Fe-P angle in the range 72.64–73.17°.

3.4. Oxidation of 1-phenylethanol catalyzed by Fe(triphos)$(CH_3CN)_3](OTf)_2$ (1)

The only iron-phosphine complex which proved to be stable as a solid, *i.e.* $[Fe(triphos)(CH_3CN)_3](OTf)_2$ (**1**), was employed as catalyst precursor for the oxidation of 1-phenylethanol with TBHP. Both at 25 and 50 °C the catalytic reactions gave the same yields of acetophenone – single product formed - previously obtained with the $Fe(OTf)_2$/triphos catalyst prepared *in situ*.

In order to ascertain the robustness of the catalytic system an oxidation reaction was performed at 25 °C, in which after 24 h and complete substrate oxidation a new load of 1-phenylethanol and TBHP was added: once more quantitative formation of acetophenone was observed. Addition of another load of substrate and oxidant gave the same result; finally, the fourth alcohol load was oxidized with 80% conversion.

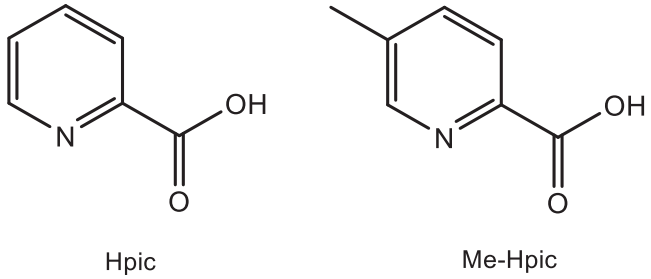


Fig. 5. Additives.

With the aim of further exploring the catalyst behaviour we decided to investigate the effect of the addition of selected components to the reaction mixture. In a first series of experiments, we repeated some previously reported reactions under an argon atmosphere, in order to verify whether atmospheric oxygen plays a role in the oxidation reaction. In all cases the reaction yields were identical both in air and under inert atmosphere, thus indicating that atmospheric oxygen does not participate in the catalytic reaction, either as oxidating agent or as activator of the catalyst precursor.

Then, it seemed interesting to probe the effect of additives on the catalytic reaction. Some Authors [20] reported that a series of heteroaromatic aminoacids can behave as effective cocatalysts in oxidations promoted by iron complexes with nitrogen polydentate ligands; actually, also we recently described a positive effect of some aminoacids on oxidation catalysis by iron in association to nitrogen bidentate ligands [4b]. Therefore, in order to ascertain the influence of such additives on the reactions promoted by complex **1**, we performed some tests of catalytic oxidations in the presence of **1** together with either 2-pyridinecarboxylic acid (Hpic) or 5-methyl-2-pyrazinecarboxylic acid (Me-Hpca) (see Fig. 5). Surprisingly, not only did the additives fail to increase the reaction yields, but their presence nearly completely suppressed the oxidation reaction both at 25 and 50 °C, giving conversions in the range 7–22% to be compared with 96% yields of the same reactions performed in the absence of additive (see Table 1, entries 1 and 9). In fact, the nature of the effect of this class of additives on iron oxidation catalysis has often proved to be unpredictable, and it is presently the object of intense debate.

Finally, the effect of microwave irradiation in replacement to conventional heating in thermostatted bath was investigated: as a matter of fact, some recent studies regarding iron-promoted oxidation reported that microwave irradiation favorably influenced the catalytic reactions [4b,21]. When oxidation of 1-phenylethanol in the presence of complex **1** was performed in a microwave reactor at T = 60, 80 and 100 °C for t = 15, 30 and 60 min, yields of acetophenone obtained were in the range 60–72% with TBHP as oxidant (to be compared with 96% with conventional heating, see Table 1 entry 1); use of hydrogen peroxide in the place of TBHP gave even lower conversions. Such findings indicate that the catalytic reactions under investigation do not take advantage of microwave irradiation.

3.5. Oxidation of alcohols catalyzed by Fe(triphos)$(CH_3CN)_3](OTf)_2$ (1)

The studies on the catalytic properties of the iron-phosphines compounds were extended to oxidation of other primary and secondary alcohols. For this purpose catalysts **1** and **4** were investigated: complex **1** was synthesized and used as preformed sample, whereas compound **4** was formed *in situ* due to its poor stability as isolated solid. Both catalysts gave similar results in the oxidation of various alcohols, either at r.t. or at 50 °C: in Table 6 are reported the reaction yields obtained when using complex **1** as catalyst precursor.

From a perusal of Table 6, a lower efficacy in the oxidation of both primary and secondary alcohols other than 1-phenylethanol stands out.

Table 6
Oxidation of alcohols with TBHP catalyzed by 1.

Entry	Substrate	Product	T (°C)	t (h)	Conversion (%)
1	1-phenylethanol	acetophenone	25	24	96
2	1-phenylethanol	acetophenone	50	3	96
3	benzyl alcohol	benzaldehyde	25	24	51
4	benzyl alcohol	benzaldehyde	50	3	55
5	*p*-methoxy benzyl alcohol	*p*-methoxy benzaldehyde	25	24	48
6	*p*-methoxy benzyl alcohol	*p*-methoxy benzaldehyde	50	3	49
7	cinnamyl alcohol	cinnamaldehyde	25	24	58[a]
8	cinnamyl alcohol	cinnamaldehyde	50	3	57[b]
9	3-phenyl-1-propanol	3-phenyl propanal	25	24	1
10	3-phenyl-1-propanol	3-phenyl propanal	50	3	1
11	Butan-1-ol	butanal	25	24	2
12	Butan-1-ol	butanal	50	3	1
13	Butan-2-ol	2-butanone	25	24	54
14	Butan-2-ol	2-butanone	50	3	46
15	cyclohexanol	cyclohexanone	25	24	46
16	cyclohexanol	cyclohexanone	50	3	49
17	cyclopentanol	cyclopentanone	25	24	43
18	cyclopentanol	cyclopentanone	50	3	49

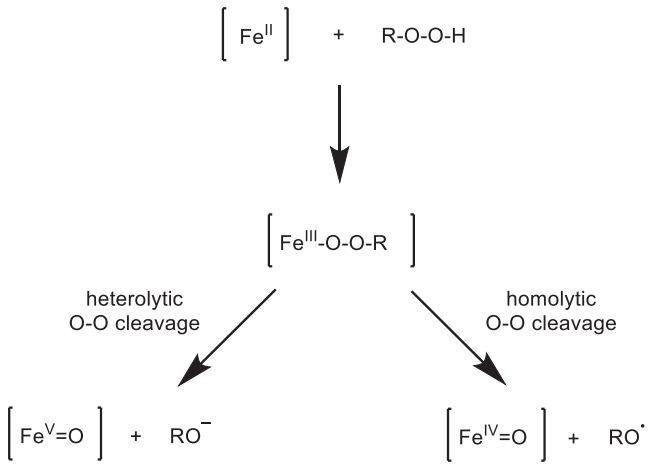
Experimental conditions: [Fe] = $1.5x10^{-3}$M; [sub]/[Fe] = 50; [ox]/[sub] = 4; solvent = CD_3CN; TBHP 70% aqueous solution. (a) byproduct = benzaldehyde 12%; (b) byproduct = benzaldehyde 15%.

As a matter of fact, oxidation yields of both phenylmethanol (benzyl alcohol) and of its *p*-methoxy derivative hardly exceeded 50% (Entries 3–6), whereas 3-phenylprop-2-en-1-ol (cinnamyl alcohol) was oxidized to 3-phenylprop-2-en-al (cinnamaldehyde) with conversions close to 60% (see Entries 7 and 8): in the latter case formation of 12–15% benzaldehyde was also observed.

Aliphatic secondary alcohols were oxidized with yields around 50% (Table 6, entries 13–18), in contrast to primary alcohols, oxidation of which occurred only in traces (see entries 9–12).

3.6. Catalytic reactions in the presence of radical traps

According to the commonly accepted mechanism for iron catalyzed oxidation of alcohols using peroxides [2a,5a,22], activation of the latter takes place by formation of the key intermediate Fe(III)OOR. Such compound, itself a poor catalyst, may undergo either homolytic or heterolytic O—O cleavage (see Scheme 2). The former reaction path leads to formation of hydroxyl radicals, which behave as initiators for a radical chain oxidation; on the other hand, by heterolytic O—O cleavage



Scheme 2. Proposed mechanism for the reaction of iron complexes with a peroxide.

an iron(V) oxo species is probably formed, which is considered to be the active catalyst for metal-centered oxidation. Studies aimed at discriminating between the two alternatives – homolytic vs. heterolytic path – are of current interest in the field of iron oxidation, as they may provide valuable information for the design of effective and selective iron catalysts.

In this perspective, we further explored the behaviour of our iron-phosphines catalysts with the aim of gaining information about the reaction mechanism. Our approach included on one hand use of radical traps in the oxidation reactions, aimed at intercepting possible radical initiators which contribute to the catalytic reactions, and on the other investigations on catalyst evolution by means of UV–visible spectroscopy as well as MS.

In order to detect the occurrence of a radical mechanism, we ran selected catalytic reactions replacing the usual solvent acetonitrile with acetone, which is known to intercept radical species [23]. Thus, we found that the reactions performed in acetone either with the preformed compound **1** or with catalyst **4** prepared *in situ* gave the same yields as the corresponding reactions in acetonitrile: for example, oxidation of 1-phenylethanol in the presence of 1 at 25 °C (t = 24 h) gave acetophenone yields of 96 and 95% in acetonitrile and acetone, respectively.

Another series of experiments made use of the radical trap 2,3-di-*tert*-butyl-4-methylphenol, which is known to behave as scavenger for oxygen radicals [5d,24]; once more, the catalysts **1** and **4** were employed, the latter being prepared *in situ*. In a typical test two parallel reactions were carried out in acetonitrile, using [ox]/[sub] = 1, one with and the other without radical trap, and, in the former case, using equimolar amounts of oxidant and radical trap. Comparison of the two reactions gave ambiguous results, *e.g.* using **1** at 25 °C (t = 24 h) cyclohexanol oxidations occurred with conversions of 20 and 32% with and without radical trap, respectively. In all cases, in the presence of radical trap a decrease of reaction yields was observed, although partial alcohol oxidation always occurred. Such findings might be reasoned in terms of both mechanisms - homo and heterolytic O—O cleavage - simultaneously taking place in the catalytic reactions.

3.7. UV–visible studies

All the iron complexes under investigation formed intensely coloured solutions in acetonitrile, due to the presence in the UV–visible spectra of a MLCT absorption with a wavelength in the range 475–501 nm. In order to gain information about the evolution of the iron complexes upon oxidant addition, a series of UV–visible spectra was acquired following the reaction for the iron complexes **1–5** with TBHP. Due to low stability of complexes **2**, **3**, **4** and **5** in the solid state (see Section 3.2), such species were prepared from $Fe(OTf)_2$ and the appropriate ligand in acetonitrile solution.

A preliminary study verified that addition of the substrate (1-phenylethanol or benzyl alcohol) caused no change in the UV–visible spectra of all iron complexes **1–5**; coherently, also their NMR spectra remained unchanged upon substrate addition, suggesting that no significant alcohol coordination took place.

Afterwards, for each iron compound the following experiment was performed: the UV–visible spectrum of the complex in acetonitrile was acquired at 25 °C, then TBHP was added and the resulting evolution was followed by recording a series of spectra at suitable time intervals. By examining the spectra of complex **1** reported in Fig. 6, it can be noticed that, upon addition of the peroxide, the MLCT band at λ = 489 decreased in intensity with time; a similar behaviour was observed with complexes **2**, **3** and **5** (see SI for the complete series of spectra). No appreciable differences were observed when the experiments were repeated at 0 °C.

Conversely, the pink-red solution of complex **4**, which showed a MLCT absorption at 501 nm, upon TBHP addition at 25 °C underwent an immediate color change to purple, with appearance in the spectrum

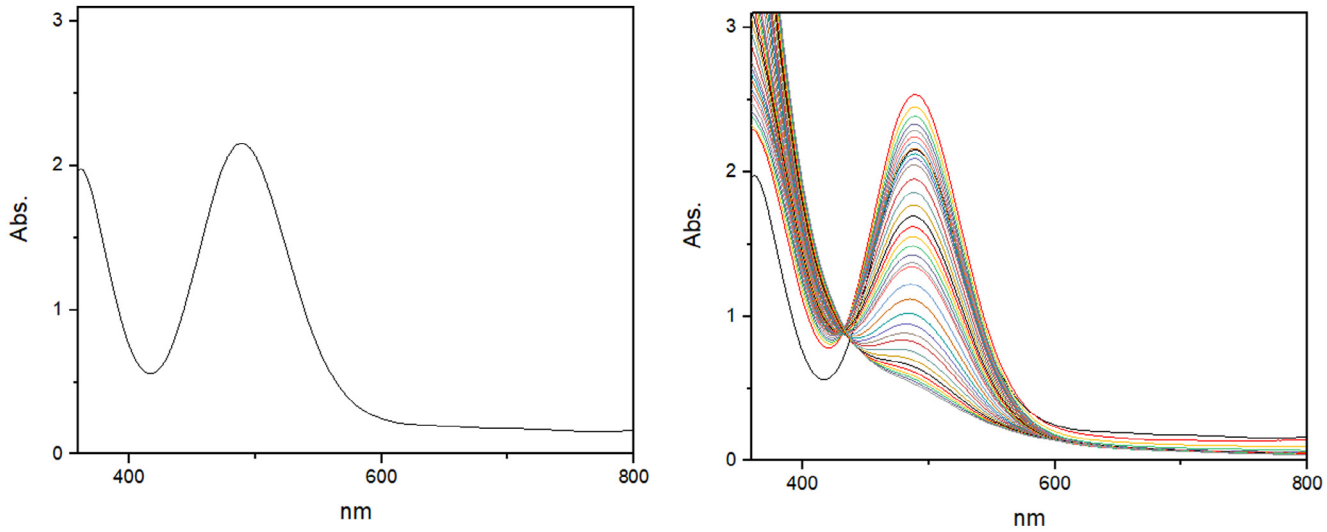


Fig. 6. UV–visible spectra of [Fe(triphos)$(CH_3CN)_3$](OTf)$_2$ (**1**) in acetonitrile at 25 °C before (left) and after (right) addition of TBHP.

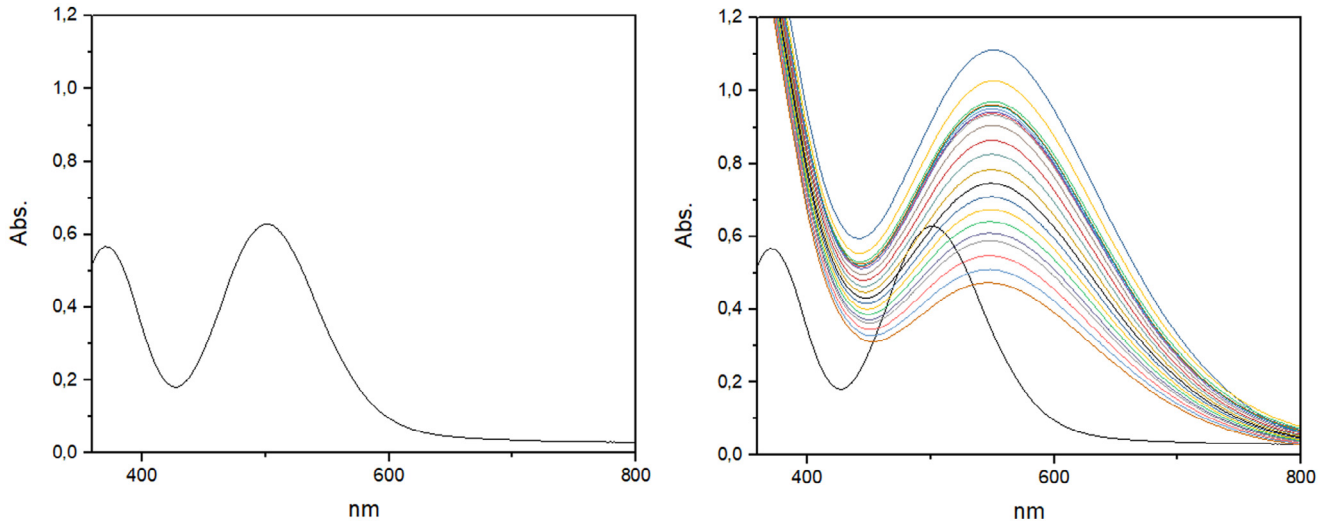


Fig. 7. UV–visible spectra of [Fe(dppp)$(CH_3CN)_4$](OTf)$_2$ (**4**) in acetonitrile at 25 °C before (left) and after (right) addition of TBHP.

of a new band at λ = 550 nm. This absorption was observed to decay with time (Fig. 7), and also visually a slow colour change from purple to yellow-grey could be noticed, which was complete after 10–30 min according to the [ox]/[Fe] ratio employed. According to the spectral data reported in the literature, which indicate that solutions of iron-peroxide species are coloured in violet and show an absorption in the range 480–590 nm [22a], we suggest that the purple intermediate observed is likely to be the corresponding Fe(III)-OOBu^t intermediate (see Scheme 2). Interestingly, although such peroxo intermediates have been spectroscopically detected in several cases [25], their formation has been only rarely observed at r.t. [26].

3.8. Iron phosphines or phosphine oxide catalysts? MS studies

A possible drawback in oxidation reactions catalyzed by transition metal complexes is represented by ligand oxidation. This process might in principle lead to less active or inactive species, therefore use of oxidizable ligands such as phosphines is frequently avoided. In fact, as mentioned in the Introduction, if on one hand ligand oxidation in some cases leads to no significant loss of catalytic activity [2a], on the other the development of processes catalyzed by complexes with phosphine oxides has been reported [10].

With regard to our studies on iron-phosphine catalysts, all the results so far reported clearly indicate that, upon addition of peroxide to the catalyst precursors, either the ligands were not oxidized, or ligand oxidation did take place, but in the latter case a catalytically active iron-phosphine oxide species was formed.

In order to shed light on the matter, we performed a series of experiments using mass spectrometry. Our purpose was, by comparison of MS spectra before and after oxidant addition, to ascertain whether the phosphines coordinated to iron were converted to the corresponding phosphine oxides. The iron complexes **1** and **4**, the former used as preformed sample and the latter prepared *in situ* from Fe(OTf)$_2$ and dppp, were therefore investigated.

The ESI-MS spectra of an acetonitrile solution containing [Fe(triphos)$(CH_3CN)_3$](OTf)$_2$ (**1**) showed in positive ion mode a signal at *m/z* 340 which was assigned to [Fe(triphos)]$^{++}$ and a weak signal at *m/z* 829 assigned to [Fe(triphos)(OTf)]$^+$. A very weak peak at *m/z* 625 [M + H] shows the presence of free triphos ligand, but much more intense signals at *m/z* 547 and *m/z* 439 were assigned to fragments obtained from free triphos upon loss of a phenyl and a "PPh_2" moiety, respectively. The presence of coordinated MeCN was never detected in all the series of spectra recorded, showing that acetonitrile ligand is promptly removed from the metal in the experimental conditions of

ESI-MS. When the acetonitrile solution of **1** was treated with 10 equivalents of TBHP, in the ESI-MS spectrum the peaks related to the original complex immediately disappeared, being replaced by a series of new peaks due to oxidized species: a signal at *m/z* 364 assigned to $[Fe(triphos\text{-}O_3)]^{++}$ and two signals at *m/z* 511 and *m/z* 527 due to loss of a "PPh_2" moiety and oxidation with 1 or 2 oxygen atoms, respectively. An intense peak at *m/z* 673 [M + H] was assigned to the fully oxidized free triphos ligand (triphos-O_3) and a much weaker signal at *m/z* 657 [M + H] was assigned to product of a double oxidation of the free ligand, triphos-O_2. Notably, upon addiction of TBHP all the signals related to both coordinated and free ligand belong to oxidized species, with a number of oxygen atoms even to the number of the phosphorous atoms, suggesting that iron-phosphine oxide complexes and free phosphine oxides were formed nearly quantitatively.

Another series of ESI-MS experiments were carried out to study the evolution of $[Fe(dppp)(CH_3CN)_4](OTf)_2$ (**4**) in oxidizing conditions. The spectra of an acetonitrile solution containing equimolar amounts of $Fe(OTf)_2$ and dppp showed in positive ion mode an intense signal at *m/z* 413 [M + H] which was assigned to the free dppp ligand; as we detected in the case of triphos ligand, two signals at *m/z* 335 and *m/z* 227 were assigned to fragments obtained from free dppp upon loss of a phenyl and a "PPh_2" moiety, respectively. Another series of signals were assigned to iron containing fragments, due to their characteristic isotopic distribution: a signal at *m/z* 617 was assigned to $[Fe(dppp)(OTf)]^+$, with two weak satellites at + 16 and + 32 (*m/z* 633 and *m/z* 649 respectively), suggesting the presence of traces of oxidized complexes.

When the same solution of **4** was treated with 10 equivalents of TBHP, acquisition of the ESI-MS spectrum showed the disappearance of most of the previous signals, which were replaced by a new set of signals. Immediately after the TBHP treatment, the signals related to the free ligand were steadily evolving with time towards the corresponding oxidized species: an intense signal at *m/z* 429 [M + H] (assigned to dppp-O) was promptly detected, but it was soon replaced by a signal at *m/z* 445 [M + H] (assigned to dppp-O_2); other signals were assigned to fragments related to oxidized dppp (*m/z* 367 (dppp-O_2 (-Ph)), 351 (dppp-O (-Ph)), 335 (dppp (-Ph)), 243 (dppp-O (-PPh_2)) and 227 (dppp (-PPh_2)). With regard to iron containing moieties, upon TBHP addition the signals of the original complex $[Fe(dppp)(OTf)]^+$ immediately disappeared to be replaced by signals at *m/z* 649 and 633 assigned to $[Fe(dppp\text{-}O_2)(OTf)]^+$ and $[Fe(dppp\text{-}O)(OTf)]^+$, respectively. Other signals were assigned to complexes with two dppp ligands coordinated to an iron atom: *m/z* 472 ($[Fe(dppp\text{-}O_2)_2]^{++}$), 464 ($[Fe(dppp\text{-}O_2)(dppp\text{-}O)]^{++}$) and 456 ($[Fe(dppp\text{-}O_2)(dppp)]^{++}$ or $[Fe(dppp\text{-}O)_2]^{++}$). In all cases, the intensity of the signals of fully oxidized species increased with time at the expenses of those of partially oxidized ones. After 30 min, the only signals detected were related to fully oxidized species (dppp-O_2, dppp-O_2 (-Ph), $[Fe(dppp\text{-}O_2)(OTf)]^+$ and $[Fe(dppp\text{-}O_2)_2]^{++}$) with the oxidized free ligand being by far the most intense. A selection of ESI-MS spectra is reported in the Supporting Information.

On the whole, the ESI-MS results here reported allow to draw some interesting conclusions. First of all, both complexes **1** and **4** give immediate and complete reaction with TBHP, as coherently observed both by UV–visible spectroscopy and ESI-MS measurements. Moreover, in the ESI-MS spectra recorded after oxidant addition the number of oxygen atoms in most of the fragments is even to the number of the phosphorous atoms, thus suggesting that oxidation of the ligand takes place, leading to iron-phosphine oxide species. On the other hand, unfortunately in the ESI-MS studies of complex **4** we never detected signals assignable to the iron-peroxo intermediate identified by UV–visible spectroscopy (see Section 3.7).

4. Conclusions

Iron complexes with the bi- or tridentate phosphines dppm, dppe, dppp, dppbz, PSP, PNP, triphos and ttp behaved as effective catalysts for the oxidation of 1-phenylethanol to acetophenone by TBHP, in mild experimental conditions. Other secondary alcohols were oxidized only in moderate yields, whereas oxidation of primary alcohols gave rise to low amounts of the corresponding aldehydes. Characterization of the most active catalyst precursors was performed by NMR spectroscopy and, in the case of derivatives with dppp, dppe and dppm, by resolution of X-ray structures.

UV–visible studies were performed to follow the evolution of the catalyst precursors in oxidizing conditions, allowing in the single case of $[Fe(dppp)(CH_3CN)_4](OTf)_2$ (**4**) to intercept formation at r.t. of the peroxo intermediate Fe(III)OOR. Further investigations regarding complexes $[Fe(triphos)(CH_3CN)_3](OTf)_2$ (**1**) and **4**, carried out by ESI-MS, evidenced that treatment of a solution of the iron complex with TBHP led to immediate formation of the corresponding phosphine oxide complexes, which are likely to be the real catalyst precursors; therefore, coherently with studies by other Authors, such results indicate that ligand oxidation does not necessarily imply catalyst inactivation.

CRediT authorship contribution statement

Erica Farnetti: Conceptualization, Supervision. **Corrado Crotti:** Methodology, Investigation. **Ennio Zangrando:** Investigation, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.119318.

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