

Review

Chiral-at-iron compounds with phosphanes

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The design of chiral iron compounds is one of the main current research lines in the field of asymmetric synthesis and catalysis due to the low price, high abundance in the earth's crust, and low toxicity of iron. Because of the interesting electronic and structural properties of phosphanes and their stereochemical rigidity, combining iron with optically pure phosphanes is promising. It has been recently applied in asymmetric transformations. However, the development of chiral iron compounds with achiral phosphanes, which bear the iron atom as the only stereocenter, has been mainly focused on their synthesis and characterization. Although there is a long history and diversity of chemical strategies for the preparation of these chiral-at-iron compounds, in most cases, the stereochemistry (including chirality at metal) of the iron compounds has not been studied in detail, and there is a lack of rational design for targeted chiral compounds and structural analysis.

In this review, a description of the synthetic strategies and structure of chiral-at-iron compounds bearing symmetric or asymmetric phosphanes is presented. The structure of the iron compounds is analyzed based on NMR and X-ray diffraction results, with special emphasis on their configurational analysis based on the denticity and hapticity of phosphane ligands, chelate rings and conformations, and the additional donor atoms present in such phosphanes.

Abbreviations: ammpy, 2-acylmethyl-6-methoxymethoxy-pyridine; aqpn, N-[2-(di-*iso*-propylphosphino)ethyl]quinolin-8-amine; bdt, 2-benzenedithiolate; bmpbb, (1*R*,2*R*)-1,2-bis(methylphenylphosphino)benzene; bnpe, (*R,R*)-1,2-bis(binaphthylphosphino)-ethane; bppp, bis(2-picolyl)phenylphosphane; dbap, [2-(di-*tert*-butylphosphinomethyl)-6-diethylaminomethyl]pyridine; dbmpy, 2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine.; dbpe, 1,2-bis(dibutylphosphino)ethane; dedtc, diethyldithiocarbamate; depe, 1,2-bis(diethylphosphino)ethane; depma, bis[(diethylphosphino)methyl]methylamine; dfepe, 1,2-bis[di(pentafluoroethyl)-phosphino]ethane; DFT, density functional theory; dipp, 6-(di-*iso*-propylphosphino)methyl-2,2'-bipyridine; dippe, 1,2-bis(di-*iso*-propylphosphino)ethane; dippp, bis(2-di-*iso*-propylphosphino-phenyl)-phenylphosphane; dmbz, 1,2-bis(dimethylphosphino)-benzene; dmdep, bis[2-(dimethylphosphino)ethyl][(3-dimethylphosphino)propyl]-phosphane; dmdpe, [(3-dimethylphosphino)ethyl]bis[2-(dimethylphosphino)propyl]-phosphane; dmdtc, dimethyldithiocarbamate; dmea, bis(dimethylphosphinoethyl)amine; dmeoprpe, 1,2-bis(di(methoxypropyl)phosphino)ethane; dmpe, 1,2-bis(dimethylphosphino)ethane; dmpm, bis(dimethylphosphino)methane; dmpp, 1-phenyl-3,4-dimethylphosphole; dpbz, 1,2-bis(diphenylphosphino)benzene; dpmp, (2-diphenylphosphinomethyl)-pyridine; dpmp, N-diphenylphosphino-2-aminopyridine; dppadp, [(*iso*-propylphosphanediy)l-bis(1,2-dihydro-acenaphthylene-6,5-diyl)]bis(di-*iso*-propylphosphane); dppba, N-[(2-diphenylphosphino)benzylidene]-2-(2-pyridyl)-ethanamine; dppe, 1,2-bis(diphenylphosphino)ethane; dppe, *cis*-1,2-(diphenylphosphino)ethylene; dpmpy, 2,6-bis(di-*iso*-propylphosphino-methyl)-pyridine; dppp, 1,3-bis(diphenylphosphino)-propane; dpppp, bis(2-diphenylphosphino-phenyl)phenylphosphane; dppq, 2-(diphenylphosphino)methyl-quinoline; dppsH, (2-diphenylphosphino)ethane-thiol; dprpe, 1,2-bis(di-*n*-propylphosphino)ethane; dpvp, diphenylvinylphosphane; dvpp, divinylphenylphosphane; edabt, 1,2-ethanediamine-*N,N'*-bis(2-benzenedithiolate)(2-); ehpt, 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)1,4-diphosphabutane; etxant, ethyl xanthate; Hbpin, pinacolborane; mabt, 2-({[2-(Methylthio)phenyl]-methylene}amino)benzenedithiolate; meoprpe, 1,2-bis(methoxypropylphosphino)ethane; meoprpp, 1,3-bis(methoxypropylphosphino)propane; mhpt, 1,1,3,3-tetrakis(2-diphenylphosphino-ethyl)1,3-diphosphopropane; mppe, 1,2-bis(phenylphosphino)-ethane; mppp, 1,3-bis(phenylphosphino)propane; mps, bis(2-mercaptophenyl)-sulphide(2-); Np, naphthylenide; nppnpp, 4,7,13,16-tetraphenyl-1,10-dipropyl-1,10-diaza-4,7,13,16-tetraphosphacyclo-octadecane; pdmp, *o*-phenylenebis-(dimethylphosphino); pnoH, 2-(diphenylphosphino)benzaldehyde-benzoylhydrazone; prophos, propane-1,2-diylbis(diphenylphosphane); tdmep, tris(dimethylphosphinoethyl)-phosphane; tdmme, 1,1,1-tris(dimethylphosphino-methyl)ethane; tdpme, 1,1,1-tris(diphenylphosphino-methyl)ethane; tdppm, tris(diphenylphosphino)methane; tetraphos, 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane; tetraphosm, 1,1,4,6,9,9-hexaphenyl-1,4,6,9-tetraphosphanonane; tippm, tris[2-(di-*iso*-propylphosphino)phenyl]methane; tmdf, tetramethyldiphosphane; tmp, tris(pyridylmethyl)phosphane; tppos, Phosphinous acid,P,P-diphenyl-, bis[(diphenylphosphino)oxy]phenylsilyl ester; tppropyl, 1,5,9,13-tetraphenyl-1,5,9,13-tetraphosphatridecane; (*R,R*)-Me-DuPhos, (*R,R*)-1,2-Bis(2,5-dimethylphospholano) benzene; (*S,S*)-Me-DuPhos, (*S,S*)-1,2-Bis(2,5-dimethylphospholano)benzene.

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1. Introduction

Asymmetric catalysis has been a developing area due to the need to prepare chiral compounds with high demand in pharmaceutical or cosmetic industries [1]. Metal complexes are generally used as catalysts and can produce large amounts of chiral compounds with small catalyst loadings [2–4]. Among transition metal complexes, chiral ligands, such as amines and phosphanes, are the most popular auxiliaries [5,6]. In this review, we have considered as “phosphane” the compounds of general formula PR_3 , irrespective of the composition of R, as these radicals can provide interesting properties to phosphanes.

Phosphanes contain soft σ -donor P atoms and substituents that modulate their electronic, steric, and stereochemical properties [7,8]. The great stereochemical rigidity of phosphanes (compared to analogous amines) makes the inversion of the P configuration an unlikely process [9]. This is very suitable for their use as ligands, and their combination with transition metals has been extensively used in organic synthesis and catalysis [6,10]. This combination has played a relevant role in asymmetric transformations. Since the discovery of Noyori and co-workers [11], numerous noble metal catalysts, such as Ru and Ir, containing chiral phosphanes have been developed. In the last years, the use of phosphanes for the preparation of complexes with Earth-abundant metals has increased and, among transition metals, iron has emerged as the rising star [6,12,13]. It has many advantages: it is abundant, cheaper, less toxic, environmentally benign, and forms complexes in diverse oxidation states and with a variety of ligands bearing P, N, S, or O as donor atoms and presents great flexibility to adopt different geometries and coordination numbers [14–17]. Mainly for these reasons, the development of chiral iron compounds has attracted attention for their application in asymmetric organic transformations in the field of green chemistry and catalysis, and this aspect has been reviewed on different occasions [14–18].

The coordination of chiral phosphanes to the iron often generates a stereogenic metal centre to form chiral-at-metal catalysts [5]. Interestingly, this stereocenter can be generated with the absence of any chiral ligand in the coordination sphere. These compounds are known as stereogenic-only-at-metal compounds [19–27], and numerous chiral-at-metal compounds have been applied in catalysis [28–33]. This design of only-at-metal-centred stereogenicity is structurally simple because chirality is exclusively induced by the asymmetric coordination of ligands. Another advantage is that the chirality of the ligands is not necessary, which allows for a balance the electronic and steric features of the ligand with greater versatility. Often, the direct interaction between a stereogenic metal atom and a specific substrate fosters selectively an asymmetric transformation. Stereogenic-only-at-metal complexes are useful as chiral auxiliaries for the preparation of enantiopure sulfoxides, as well as inducers for asymmetric catalysis and autocatalysis [34–40]. Unexpectedly, the chiral-at-iron compounds with phosphanes have not been applied to stereoselective transformations until the present. The description of these compounds is limited to the synthesis, characterization, and, in a few cases, to their applications in non-stereoselective organic transformations. Chiral-only-at-iron phosphane compounds are usually obtained as a mixture of isomers and generally as racemic mixtures with no stereochemical description. In contrast, chiral-at-iron compounds with asymmetric phosphanes have been recently applied to enantioselective catalysis and have been successful in this field [12,41].

In the context of molecular design, the construction of chiral-at-iron catalysts including symmetric or asymmetric phosphanes envisages the coordination environment of the metal atom. Tetrahedral, pseudo-tetrahedral, square-pyramidal (SP), trigonal-bipyramidal (TB), and octahedral iron complexes containing phosphanes are the most developed compounds. The structure and type of donor atoms of the phosphane or other auxiliary ligands are crucial to determining these geometries, their stability, and stereoselectivity. Thus, the preparation of complexes bearing only monodentate ligands is cumbersome, and the

variety of possible enantiomers and diastereoisomers makes it difficult their separation, without considering that they can interconvert during the purification process step or after. In contrast, the presence of ligands with multiple denticity/hapticity limits the symmetry and decreases the number of diastereoisomers that can be formed.

Chiral-at-iron complexes can be stereogenic at iron and depending on the rigidity or flexibility of the polydentate ligand that can adopt different forms of binding to the metal, and different conformations of the cycles formed between the metal and the ligand. For 5 membered rings, two conformations are possible: λ and δ , to give two possible stereoisomers. Although the presence of substituents on the ring can prevent the interconversion, in most cases ring conformations interconvert easily and rapidly and are not normally distinguished in solution, while they can be observed in the crystal structures. The conformational interconversion of 6-membered cycles, which are more rigid than 5-membered ones, is more difficult. The existence of possible conformations has been verified in the solid state and we have no evidence of their resolution.

Concerning the coordination number of the Fe centre, in the case of coordination index 4, the tetrahedral metal complexes present the same possibility of stereoisomerism as in the case of a sp^3 C atom, with the difference of the inertness of the carbon compounds towards substitution reactions. For this reason, the development of tetrahedral complexes of iron including the scope of application to stereoselective transformations is limited to a few cases, and the presence of chelating/multidentate ligands is crucial to keep the configurational stability.

The stereochemistry of the complexes of other coordination indexes has been reviewed by different authors, in which it has been established which denticity/hapticity of ligands and which configurations can lead to the formation of chiral compounds [24,42–45]. Pentacoordinated complexes are often fluxional, so separation of the different isomers is not possible. Chiral-at-metal octahedral complexes belong to the most configurationally stable geometries, although these complexes can racemize.

Complexes bearing linear and non-linear polydentate phosphanes can result in compounds stereogenic at the iron depending on their disposition around the iron centre. Furthermore, in many cases, the coordination of P turns it into a stereogenic centre, which increases the number of isomers that can be formed.

Interconversion between configurational isomers in solution or even in the solid state provides crucial information for the development of well-defined and configurationally stable catalysts, which is the key to achieving high stereoselectivities in an organic transformation. In our review, we have confirmed that this information is not commonly described for iron-phosphane complexes. We have found that not always the crude product is identified and we suspect that after a work-up, other possible formed stereoisomers are removed from the reaction mixtures to lead to a single isomer. In addition, the structural description of the iron complexes in their crystalline form does not always match the structure in the solution.

This review reports the preparation and characterization details of chiral-at-iron compounds with chiral and achiral phosphanes reported until present, and we classify them according to the characteristics of ligand rather than the geometry or the oxidation state of metal. We illustrate a wide collection of iron compounds found in the Cambridge Structural Database and the Chemical Abstracts Service (Scifinder) in which metal stereogenicity was identified through structural and NMR analyses. In general, in the case of compounds that differ only in a monodentate ligand (halide, alkyl, aryl, etc.) or in the P substituents and have the same structure, we have only considered one. Often, we illustrate the complexity of ligand coordination to provide selectively a specific isomer, that does not necessarily correspond to a chiral-at-iron isomer. Despite the vast majority (or even all) of the chiral iron compounds directed to asymmetric catalysis including asymmetric phosphanes, our study has revealed that the chelation of achiral phosphanes often induces a stereogenic metal. This characteristic should be

considered for the design of low-cost iron-phosphane catalysts bearing readily accessible and cheap ligands.

Among the objectives of this review, it is, firstly, to promote the application of stereogenic-only-at-iron complexes, formed from simple achiral (symmetric or non-symmetric) phosphanes, in enantioselective organic transformations [37,39,46]. Efforts must be made to the resolution of racemic mixtures of chiral-at-iron compounds and the deep knowledge of the conformational and configurational stability of iron complexes depending on their oxidation state and coordination sphere. Some experimental (NMR, IR, X-Ray) and computational techniques are useful for these studies. Secondly, the use of optically pure chiral phosphanes as a useful strategy in the preparation of chiral-at-iron complexes in their enantiopure form is also directed to asymmetric catalysis. The application of racemic phosphanes is also considered since enantiopure iron complexes can be obtained by chiral resolution.

This work is organized, firstly, considering the number of P atoms in the ligand and secondly, by the denticity of the ligand and the type of donor atoms other than phosphorus. The different coordination geometries of iron compounds are contemplated in each subsection for a better comprehension of the symmetry of the compounds. The contents of this review are distributed in three chapters, which envisage the chiral-at-iron compounds including mono-, di- and polydentate phosphanes, respectively. The chapter dedicated to diphosphanes only contains complexes with chelating diphosphanes, with no donor atoms other than the two P. The study of polynuclear compounds is not included in this review, since in these compounds the polydentate ligands can present different forms of coordination and the presence of chirality limited to a single metal centre is unlikely. Other areas of interest, such as bioinorganic, medicinal chemistry, or nonlinear optics have also not been considered.

2. Iron compounds with monophosphanes

2.1. Monodentate phosphanes

In general, the reaction of iron with different monodentate ligands provides a mixture of chiral-at-iron stereoisomers. The synthesis directed to one specific isomer can be controlled in half-sandwich (or piano-stool) iron compounds, *i.e.* bearing a cyclic conjugate polyhaptocarbon ligand in *fac* disposition, and in compounds bearing one tripodal ligand or chelating ligands, in both cases with appropriate monodentate ligands arrangement around the iron centre.

2.1.1. Tetrahedral and pseudo-tetrahedral complexes

Tetrahedral complexes of the type $[\text{FeL}_1\text{L}_2\text{L}_3\text{L}_4]$, with four different monodentate L_x ligands, are chiral in the same way as in tetrahedral carbon compounds. Since, in general, metal complexes are labile, equilibria between different species and/or configurations are likely to occur and there are few species prepared from this kind of complexes. Brunner *et al.* described $[\text{FeL}_1\text{L}_2\text{L}_3\text{L}_4]$ compounds from $[\text{Fe}(\text{CO})_2(\text{NO})_2]$, by replacement of one NO by a three-electron donor ligand as an aryl-diazenyl group and a CO by a phosphane.[47] Using a pure enantiomer of a phosphane, the resulting two iron diastereoisomers were separated either by fractional crystallization or by chromatography. In the case of the compound represented in Fig. 1, the corresponding diastereoisomers did not epimerize at room temperature.

When one of the ligands is a Cp ring, we have $[\text{Fe}(\text{Cp})\text{L}_1\text{L}_2\text{L}_3]$ chiral-at-metal compounds with a pseudo-tetrahedral structure. Although these compounds could be easily prepared by CO/phosphane substitution from $[\text{Fe}(\text{CO})_2(\text{Cp})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), phosphanes preferentially displace the halide forming achiral compounds of formula $[\text{Fe}(\text{CO})_2(\text{Cp})(\text{P})\text{X}]$ [48,49]. The $[\text{Fe}(\text{CO})_2(\text{Cp})(\text{P})]^+$ complex is prochiral, and the substitution of one of the CO ligands would give rise to two enantiomers. When the substitution takes place with a pure enantiomer of a ligand, the $[\text{Fe}(\text{CO})(\text{COOC}_{10}\text{H}_{19})(\text{Cp})(\text{PPh}_3)]$ was obtained as a mixture of two diastereoisomers (Fig. 2) [50,51].

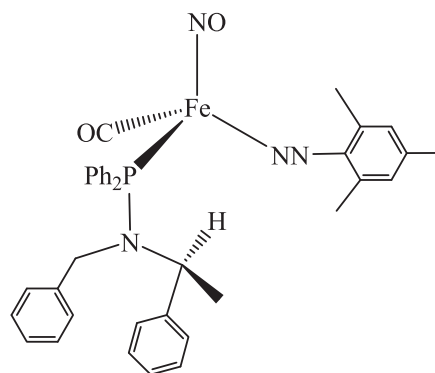


Fig. 1. Schematic representation of one diastereoisomer of a tetrahedral iron complex with four different ligands.

Surprisingly, the carbonyl substitution reaction of $[\text{Fe}(\text{CO})_2(\text{Cp})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with phosphite afforded the chiral $[\text{Fe}(\text{CO})(\text{Cp})(\text{phosphite})\text{X}]$ compounds [52]. The reaction of $[\text{Fe}(\text{CO})_2(\text{Cp})\text{I}]$ with dienephosphanes, such as dmpp or dvpp, or enephosphane, as dpvp gave the chiral-at-metal $[\text{Fe}(\text{CO})(\text{Cp})(\text{dienephosphane})\text{I}]$ complexes in good yields (Fig. 3a) [53].

Shejwalkar *et al.* obtained the piano-stool chiral iron (II) phosphoramidite complexes, through monocarbonyl substitution in $[\text{Fe}(\text{CO})_2(\text{Cp})\text{X}]$ ($\text{X} = \text{Br}, \text{I}$) by an optically active phosphoramidite $(\text{RO})_2\text{PNR}'$ ($\text{R} = \text{binaphthyl}$, $\text{R}' = \text{CH}_3, \text{benzyl}, i\text{Pr}$) ligand [54]. A mixture of two diastereoisomers was generally obtained, and the *iso*-propyl compound was detected in the crude reaction mixture as a single diastereomer, but not isolated in analytical purity.

The $[\text{Fe}(\text{CO})_2(\text{Cp})\text{X}]$ ($\text{X} = \text{acyl}$) compounds reacted with phosphanes to form $[\text{Fe}(\text{CO})(\text{Cp})(\text{P})(\text{X})]$ (Fig. 3a) racemic mixtures [55,56]. Their derivatization led to similar iron racemates, which were used as catalysts in asymmetric syntheses [57]. If the radical X is optically active in $[\text{Fe}(\text{CO})_2(\text{Cp})\text{X}]$, the substitution of a carbonyl by a phosphane led to a compound with two chiral centres, the metal and the ligand, that exist as two diastereomerically related pairs of enantiomers. Among others, the $[\text{Fe}(\text{CO})(\text{Cp})(\text{PPh}_3)(\text{X})]$ diastereoisomers were separated by physical techniques [58–60]. Subsequent exchange of X by a non-chiral radical generally provided enantiomerically pure compounds [59]. These compounds insert SO_2 in the metal–carbon σ -bond which, under suitable conditions, are highly stereospecific, maintaining the stereochemistry of iron (Fig. 3b) [61,62].

Mayer and Hossain described that half-sandwich iron compounds with a Cp ring tethered to a terminal diphenylphosphinite group afforded a $\eta^5\text{-}\eta^1$ -cyclopentadienyl-phosphinite iron compounds, as a mixture of two diastereoisomers (Fig. 3c) [63].

2.1.2. Penta- and hexacoordinated complexes

The interest in developing model complexes of the active site of the mono-iron hydrogenase, which is capable of catalyzing the H_2 metabolism in a variety of microorganisms, has promoted the synthesis of some chiral iron chelates with monophosphanes, which are not related to half-sandwich and tripodal iron compounds. This is the case of the chiral air-stable iron chelate compound represented in Fig. 4, which is obtained by a ligand exchange reaction between the *mer,cis*- $[\text{Fe}(\text{ammpy-}\kappa^3\text{C},\text{N},\text{O})(\text{CO})_2\text{I}]$ and triphenylphosphane. Among the possible isomers that could be isolated, only the compound with iodine *trans* to phosphorous atom was structurally elucidated by X-ray diffraction, which appears as a racemic mixture in the crystal [64].

Not only 18 electron species constitute the chiral-at-metal models of the hydrogenase. For example, the pentacoordinate iron (II) dicarbonyl compounds with chelating 2-amidothiophenolate (atph) ligands, such as $[\text{Fe}(\text{atph})(\text{CO})_2(\text{P})]$ ($\text{P} = \text{PCy}_3, \text{PPh}_3$ and $\text{P}(\text{OEt})_3$) (Fig. 5) [65]. These compounds were prepared in a one-pot reaction from $[\text{Fe}(\text{CO})_3\text{I}_2(\text{P})]$, 2-aminothiophenol, and two equivalents of sodium *tert*-butoxide, and

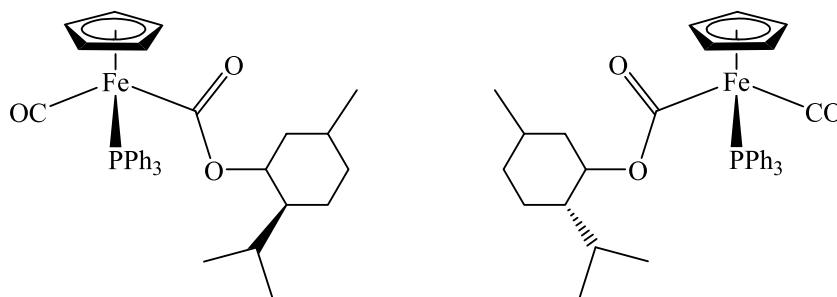


Fig. 2. Diastereoisomers of $[\text{Fe}(\text{CO})(\text{COOC}_{10}\text{H}_{19})(\text{Cp})(\text{PPh}_3)]$.

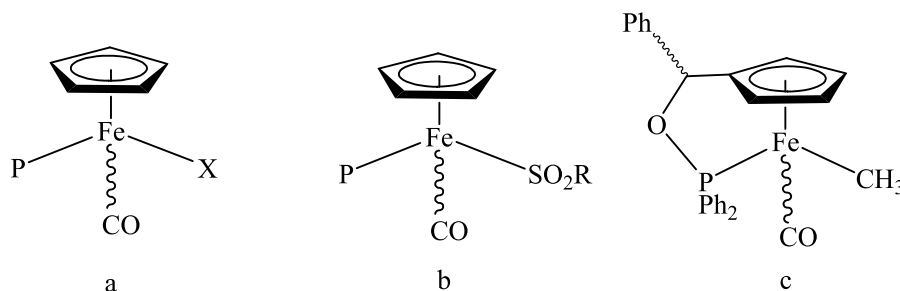


Fig. 3. Chiral half-sandwich iron compounds: a) P = phosphite, X = Cl, Br, I; P = di- or ene-phosphane, X = I; P = phosphoramidite, X = Br, I; P = phosphane, X = alkyl, acyl. b) Insertion of SO_2 (R = alkyl); c) compound from alkyl iron and diphenylphosphinite.

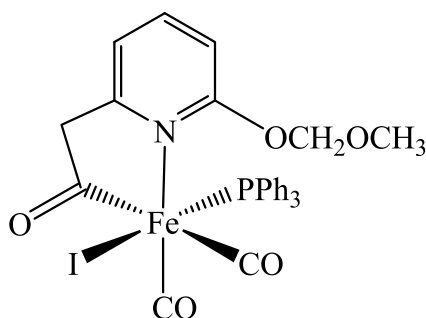


Fig. 4. Schematic representation of $\text{cis-}[\text{Fe}(\text{ampmy-}\kappa^2\text{C,N})(\text{CO})_2\text{I}(\text{PPh}_3)]$.

were obtained as racemic mixtures. They have a distorted SP structure and, surprisingly, only the PCy_3 compound crystallized in an enantiomorphic group.

2.2. P-Do phosphanes (Do = C, N, O, or S)

The synthesis of iron complexes with monophosphane ligands with an additional second donor atom can lead to the formation of chiral chelate compounds. Within these potential bidentate monophosphanes, we will consider only those ligands in which one of the donor atoms is P and the other donor atoms are C, N, O, or S. Half-sandwich iron (II) chiral complexes and other iron chelated compounds containing

isocyanide- and carbenephosphane (PC), aminophosphane (PN) and thiophosphane (PS) ligands are described in this section.

2.2.1. Pseudo-tetrahedral complexes

The chiral $[\text{Fe}(\text{CO})(\text{Cp})(\text{dpmp-}\kappa^2\text{N,P})]^+$ (Fig. 6a) was obtained from $[\text{Fe}(\text{CO})_2(\text{Cp})(\text{THF})]^+$ and dpmp and under light irradiation. Using the crystallographic identification, the iron centre shows a pseudo-tetrahedral geometry and both enantiomers appear in the crystal.[66] In contrast, when $[\text{Fe}(\text{CO})_2(\text{Cp})\text{I}]$ reacts with a more bulky NP ligand, such as dppq, the also chiral complex $[\text{Fe}(\text{CO})(\text{Cp})(\text{dppq-}\kappa^1\text{P})\text{I}]$ (Fig. 6b) was obtained as a racemic mixture, but in this case with a dangling ligand.

The reaction between $[\text{Fe}(\text{CO})_2(\text{Cp})\text{I}]$ and $\text{Ph}_3\text{P} = \text{N}(\text{CH}_2)_3\text{PPh}_2$ provided the chiral-at-metal $[\text{Fe}(\text{CO})(\text{Cp})(\text{PPh}_2(\text{CH}_2)_3\text{NC-}\kappa^2\text{C,P})]^+$ complex (Fig. 7a) [67]. This chiral complex shows a pseudo-tetrahedral geometry and the crystal structure contains both enantiomers. Chirality is preserved when these (bisphenyl)- or (bis-*tert*-butyl)-phosphane-isocyanide- $\kappa^2\text{C,P}$ piano-stool iron (II) complexes react with secondary amines to afford the (diamino)carbene-phosphane- $\kappa^2\text{C,P}$ iron (II) products in greater than 70 % yields [67,68]. Other cyclic and acyclic (oxy) (amino)-, cyclic (diamino)-, acyclic (phosphino)(amino)- and (silyl) (amino)carbene-phosphane chelated half-sandwich carbonyl iron analogues (Fig. 7b and c) can also be obtained from the (bisphenyl)-phosphane-isocyanide chelated iron precursor [68,69]. These complexes were characterized by NMR and IR techniques, and the pseudo-tetrahedral geometry of the iron centre is confirmed by the

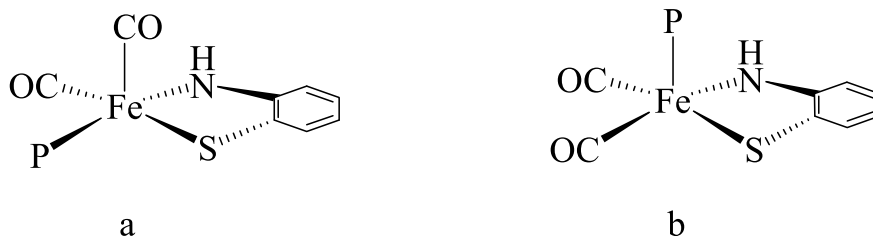


Fig. 5. Isomers of $[\text{Fe}(\text{atph})(\text{CO})_2(\text{P})]$: a) P = PPh_3 ; b) P = PCy_3 , $\text{P}(\text{OEt})_3$.

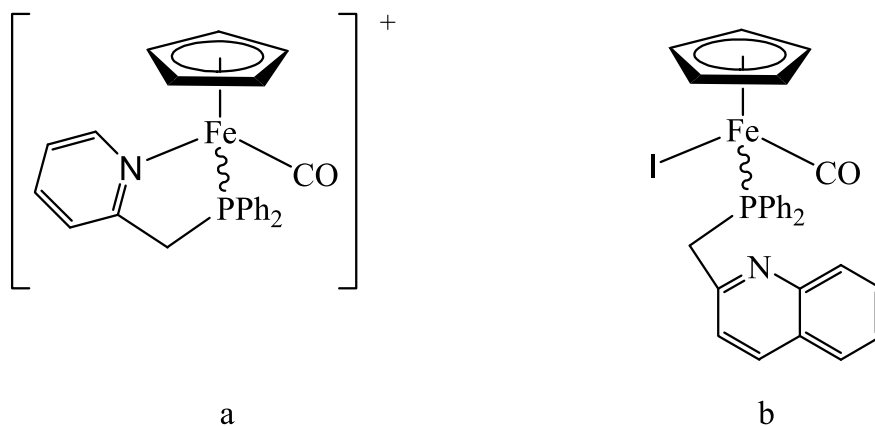


Fig. 6. Representation of half-sandwich chiral iron complexes with PN ligands.

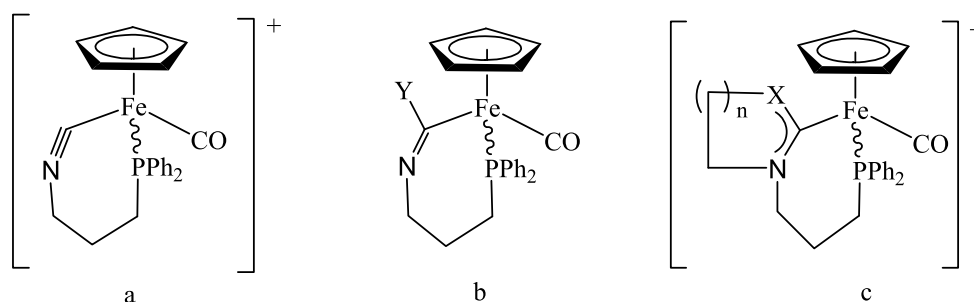


Fig. 7. Schematic representation of some carbene-phosphane- κ^2C,P iron (II) complexes: Y = NRR' (R = H, R' = *n*-Bu, R = R' = *n*-Hex), OR (R = alkyl), PPh₂, SiPh₃; X = O, NH, n = 1,2).

crystallographic structure elucidation of some of these complexes.

Other half-sandwich chiral iron (II) compounds with hybrid phosphanes can be found in the literature. The reaction of [FeBr(CO)₂(Cp)] with dppsH and NaH provided the chiral [Fe(CO)(Cp)(dpps- κ^2P,S)] compound (Fig. 8), the chelated structure of which is confirmed exclusively by mass spectrometry analysis [70].

The complex [Fe(CO)(Cp)(dmpp)I] reacted with PhSCH = CH₂ or PhS(O)CH = CH₂ through an intramolecular [4 + 2] Diels-Alder cycloaddition reaction in the presence of AgBF₄ to provide the chiral [Fe(CO)(Cp)I(thiophosphane- κ^2P,S)] (Fig. 9) in modest yields [53]. The presence of a mixture of diastereoisomers in solution is deduced from the difference in the ³¹P NMR chemical shifts associated with the two possible ring conformations of the chelating ligand.

2.2.2. Penta- and hexacoordinated complexes

Hybrid bidentate ligands have been employed for the development of synthetic models of hydrogenase, and most of these models are chiral-at-metal. One example is the unstable chiral acyliron (II) thiolate [Fe(CO)₃{Ph₂PC₆H₄C(O)- κ^2C,P }(SPh)] (Fig. 10), which was obtained by oxidative addition of phosphane thioesters to [Fe₂(CO)₉] or by carbonylation of the also chiral diiron [{Fe₂(CO)₃{Ph₂PC₆H₄C(O)}₂(SPh)₂] dimer.[71] Structural X-ray elucidation confirms the distorted octahedral geometry of this compound with CO ligands in the *fac* position,

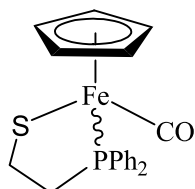


Fig. 8. Schematic representation of [Fe(CO)(Cp)(dpps- κ^2P,S)].

which is present as both enantiomers in the crystal.[72] The substitution of a carbonyl by cyanide in [Fe(CO)₃{Ph₂PC₆H₄C(O)- κ^2C,P }(SPh)] is stereospecific, as confirmed by the ¹³C, and ³¹P NMR experiments to provide the iron (II) chiral [Fe(CN)(CO)₂{Ph₂PC₆H₄C(O)- κ^2C,P }(SPh)] product, with cyanide located *cis* to the phosphane.[71].

Simplest iron carbonyls are easily derivatisable by hybrid phosphanes. For example, [Fe₂(CO)₉] reacted with 2-diphenylphosphino-benzaldehyde (pcho) to give the achiral [Fe(CO)₄(pcho- κ^1P)] with C_{3v} symmetry. Photolysis of this compound produced a mixture of isomeric tricarbonyls [Fe(CO)₃(η^2 -pcho- κ^1P)] (Fig. 11a).[73] When this complex reacts with more pcho, [Fe(CO)₂{(Ph₂PC₆H₄)CH(O)CH(O)(C₆H₄PPh₂)- κ^4O,O',P,P' }] (Fig. 11b) was obtained, which is a chiral iron (II) compound with a tetradentate ligand. The geometry around the iron stereocenter of this complex is octahedral, and it crystallized in a centrosymmetric (P-1) space group. The substitution of one CO by a monodentate ligand L (L = NCMe, PMe₃, py) originated the [Fe(CO)(L){(Ph₂PC₆H₄)CH(O)CH(O)(C₆H₄PPh₂)- κ^4O,O',P,P' }] racemates.[74] The reaction of the above mentioned [Fe(CO)₃(η^2 -pcho- κ^1P)] compound with triphenylphosphane led the chiral-at-metal [Fe(CO)₂(η^2 -pcho- κ^1P)(PPh₃)] complex (Fig. 11c). NMR and crystallographic analyses confirmed that phosphanes are mutually *trans* and the formyl group is π -bonded within a pseudooctahedral geometry, and the presence of this compound as a racemic mixture in the unit cell.[73].

The reaction of [Fe(bda)(CO)₃] with imino-phosphanes, such as Ph₂PC₆H₄CH = NC₆H₄-4-Cl (pchncl) (Fig. 12a), afforded the chiral π -bound imine [Fe(CO)₃(η^2 -pchncl- κ^1P)] compound (Fig. 12b), which was crystallographically isolated as racemic mixture.[75] This compound racemized on the NMR scale time through the achiral N-bonded imine compound depicted in Fig. 12c. The same reaction with methoxy derivate (pchnome) produced the π - and N-bonded [Fe(CO)₃(pchnome)] isomers in a *ca.* 4:1 ratio, respectively.

Derivatization of chiral [Fe(CO)₃(η^2 -pchncl- κ^1P)] provided additional chiral-at-iron compounds. For example, the carbonyl substitution

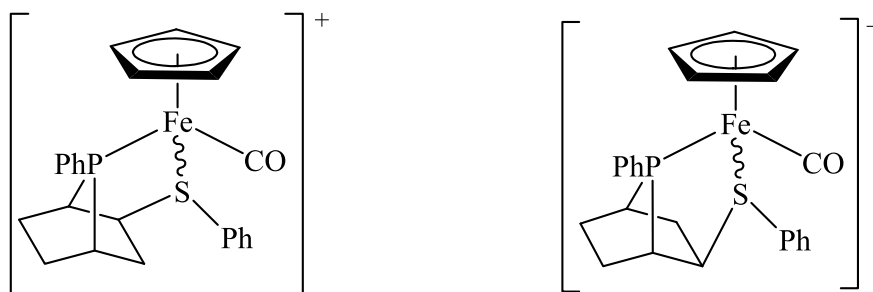


Fig. 9. Schematic representation of the $[\text{Fe}(\text{CO})(\text{Cp})\text{I}(\text{thiophosphane-}\kappa^2\text{P,S})]$ diastereomers.

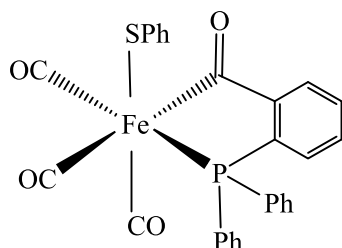


Fig. 10. Scheme of the iron compound formed with a PC ligand.

reaction of $[\text{Fe}(\text{CO})_3(\kappa^1\text{P-}\eta^2\text{-pchncl})]$ by PMe_3 gave the chiral $[\text{Fe}(\text{CO})_2(\text{pchncl-}\kappa^2\text{P,N})(\text{PMe}_3)]$ complex, which crystallized as a racemic mixture of pseudo TB enantiomers with two non-equivalent phosphanes mutually *trans*.

The stoichiometric reaction between $[\text{Fe}(\text{bda})(\text{CO})_3]$ and *pchncl* (1:2) led the chiral diamido complex $[\text{Fe}(\text{CO})_2\{(\text{Ph}_2\text{PC}_6\text{H}_4)\text{CH}(\text{NC}_6\text{H}_4\text{-4-Cl})\text{CH}(\text{NC}_6\text{H}_4\text{-4-Cl})(\text{C}_6\text{H}_4\text{PPh}_2)\text{-}\kappa^4\text{N,N',P,P'}\}]$ (Fig. 13a) by imine-imine coupling, and it crystallized as a racemic mixture. The oxidation of this tetradentate complex with FcBF_4 ($\text{Fc} = [\text{Fe}(\text{C}_5\text{H}_5)_2]^+$) promoted the breaking of the C-C aliphatic bond to lead to the chiral *cis*- $[\text{Fe}(\text{CO})_2(\text{pchncl-}\kappa^2\text{P,N})_2]$ complex (Fig. 13b), with no formation of the *trans* isomer. Reaction with *pcho* gave the octahedral tetradentate chiral $[\text{Fe}(\text{CO})_2\{(\text{Ph}_2\text{PC}_6\text{H}_4)\text{CH}(\text{O})\text{CH}(\text{NC}_6\text{H}_4\text{-4-Cl})(\text{Ph}_2\text{PC}_6\text{H}_4)\text{-}\kappa^4\text{N,O,P,P'}\}]$

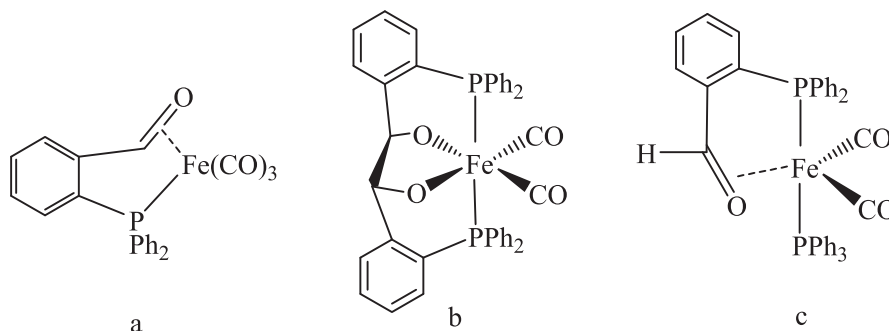


Fig. 11. Scheme of the compounds formed with *pcho* ligand and iron.

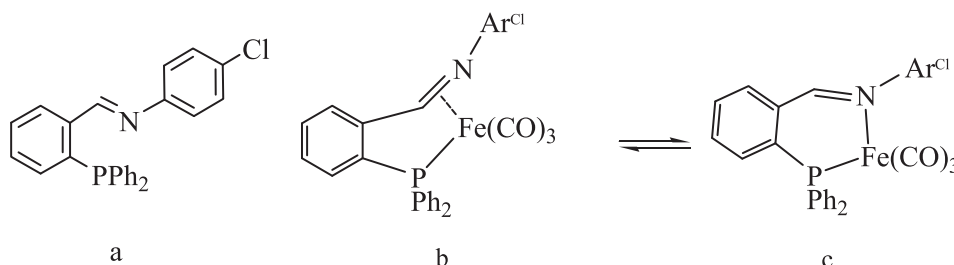


Fig. 12. Representation of *pchncl* ligand and the corresponding tricarbonyl iron iminophosphane isomers.

compound (Fig. 13c), which crystallized in a centrosymmetric (P21c) space group.[73].

Not only are the carbonyl iron precursors used for obtaining chiral iron complexes with phosphanes. The reaction of $[\text{Fe}(\text{PMe}_3)_4]$ with 2-diphenylphosphino)phenol (*dppoH*) led to the chiral hydride $[\text{Fe}(\text{dppo-}\kappa^2\text{O,P})\text{H}(\text{PMe}_3)_3]$ as only one isomer, with the hydride in *trans* position to one PMe_3 (Fig. 14a).[76,77] This compound crystallized in the enantiomorphic P212121 space group, however, no Flack parameter is described and the enantiopurity remains unknown.[76] Reaction of $[\text{Fe}(\text{dppo-}\kappa^2\text{O,P})\text{H}(\text{PMe}_3)_3]$ with CO displaces selectively one of the PMe_3 to give $[\text{Fe}(\text{CO})(\text{dppo-}\kappa^2\text{O,P})\text{H}(\text{PMe}_3)_2]$ as two isomers identified by NMR spectroscopy in two isomeric forms: the chiral “b” and achiral “c” (Fig. 14), being “c” the major isomer.[76] It can be noticed that the reaction of 2-diphenylphosphino)phenols with FeCl_3 gave homoleptic trischelate compounds, as racemic mixtures of high spin Fe(III) in an octahedral geometry. The authors suggest that, for steric reasons, the P atoms of both enantiomers adopt a meridional configuration.

Pentacoordinated chiral derivatives with *dppoH*, such as $[\text{Fe}(\text{dppo-}\kappa^2\text{O,P})\text{I}(\text{PMe}_3)_2]$ and $[\text{Fe}(\text{dppo-}\kappa^2\text{O,P})_2(\text{PMe}_3)]$ (Fig. 15), were prepared from $[\text{FeI}(\text{Me})(\text{PMe}_3)_4]$ and *dppoH* with moderate to high yields. These compounds are fluxional in solution and were obtained as racemic mixtures, also within single crystals.[76].

Pérez-Lourido *et al.* isolated some chiral iron compounds with phosphinothiolate ligands (such as 2-(Ph_2P)-6-(Me_3Si) $\text{C}_6\text{H}_3\text{SH}$, Fig. 16a) by electrochemical oxidation of iron anodes.[78] Concretely, the chiral

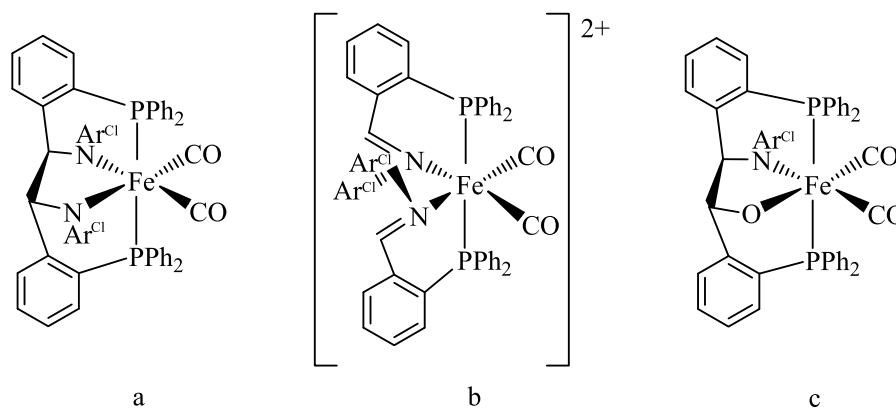


Fig. 13. Structure of compounds formed by iminophosphanes and iron.

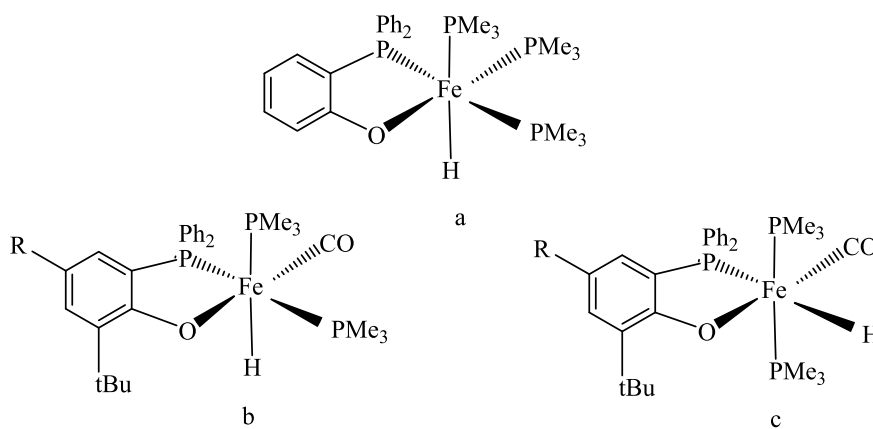


Fig. 14. Schematic representation of compounds of dppe and iron.

mer-[Fe{2-(Ph₂P)-6-(Me₃Si)C₆H₃S- κ^2 P,S }₃] iron (III) complex (Fig. 16b) crystallized as a racemic mixture of isomers, and the chirality was confirmed only by X-ray characterization. The distorted octahedral geometry of the complex, with meridional sulfur and phosphorous atoms, suggests that the bulky trimethylsilyl substituents do not considerably distort the structure of the compound.

Holzhaacker *et al.* reported chiral iron (II) complexes bearing N-(2-pyridinyl)aminophosphane (dipa) ligands.[79] Reaction of two equivalents of dipa with the *cis*-[Fe(CO)₄X₂] (X = Cl, Br) or FeX₂ precursors afforded the low-spin and octahedral chiral *cis*-[Fe(CO)(dipa- κ^2 N,P)₂X] compound (Fig. 17a). IR and NMR data confirm the formation of only one regioisomer. X-ray diffraction structural analysis of the chloride

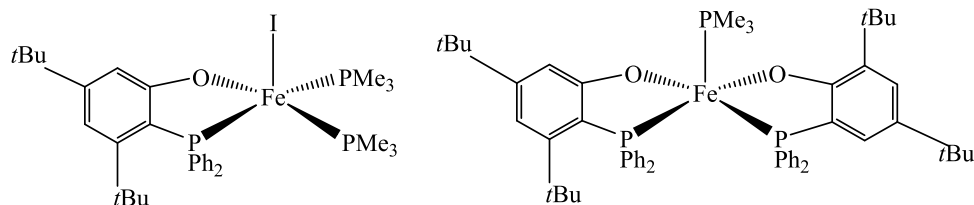


Fig. 15. Schematic representation of pentacoordinate compounds with dppe ligands.

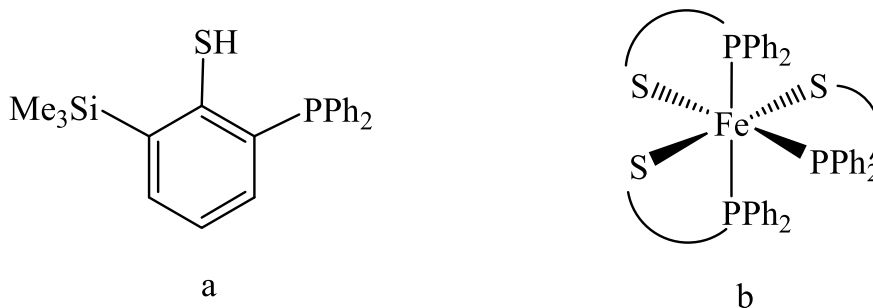


Fig. 16. The phosphinothiol and the complex formed with Fe(III).

complex settles the C₁-symmetry of the compound and the location of the CO *trans* to a pyridine ligand. The addition of one equivalent of dipa to *cis*-[FeBr₂(CO)₄] led selectively to the chiral *cis,cis*-[FeBr₂(CO)₂(dipa-κ²N,P)] (Fig. 17b) stereoisomer, with one Br atom *trans* to the P atom.

The reaction of [FeBr₂(dipa-κ²N,P)] and CO also provided the chiral *cis,cis*-[FeBr₂(CO)₂(dipa-κ²N,P)] compound, which was obtained as a stable and minor isomer mixed with the *cis*-CO,*trans*-Br isomer (Fig. 17c). Both compounds were identified by UV-Vis and IR techniques. The low-spin chiral *cis,cis*-[Fe(NCtBu)₂(dipa-κ²N,P)X₂] (X = Cl, Br) compounds, analogous to Fig. 17b with *t*BuCN *trans* to N, were obtained in high yields by treatment of [Fe(dipa-κ²N,P)X₂] with *t*BuCN. The stereoselectivity of the reaction was confirmed by [¹³C] NMR and IR characterizations.

The addition of 1 or 2 equivalents of dppa to a FeX₂ (X = Cl, Br) suspension in THF led to the high-spin and octahedral iron (II) [Fe(dppa-κ²N,P)₂X₂] compounds.[80] These compounds are unstable in solution and the stereochemistry was suggested as *cis* by reactivity studies in different solvents, SQUID magnetometry, [57]Fe Mössbauer, spectroscopic and DFT studies. The [Fe(dppa-κ²N,P)₂X₂] compounds evolved in methanol through an intermolecular ligand transfer mechanism to the diamagnetic chiral *fac*-[Fe(dppa-κ²N,P)₃]²⁺ product (Fig. 18a), and this mechanism was followed by ³¹P NMR. This complex was also prepared by a reaction between FeX₂ and three equivalents of the aminophosphane in methanol. The X-ray structure of the *fac*-[Fe(dppa-κ²N,P)₃]Br₂ compound crystallized in a non-centrosymmetric space group (Fdd2, Flack parameter of -0.008(4)) and confirms all phosphorous and nitrogen atoms located *cis* to one another, respectively. The reactivity study of the *cis*-[Fe(κ²N,P-dppa)₂X₂] complexes in NCMe shows a different behavior: the substitution of two halide ligands by the nitriles took place to give the diamagnetic and chiral octahedral dicationic *cis*-[Fe(NCMe)₂(dppa-κ²N,P)₂]²⁺ (Fig. 18c) complex as a major isomer, which was crystallized in a centrosymmetric triclinic space group. The minor isomer shows a singlet by ³¹P NMR, and up to four stereoisomers are conceivable by the authors.

2.3. O-P-O phosphanes

Some monophosphanes bearing two additional oxygen atoms can be bonded to the iron atom in a bi- or tridentate form to provide chiral complexes. Deprotonation of Hopoh (Fig. 19a) with one or two equivalents of NaH provided the Na(opoh)(DME)₂[81] and Na₂(opo)(DME)₂ salts,[82] respectively. Treatment of FeCl₂ with two equivalents of Na(opoh)(DME)₂ gave the high-spin C₂-symmetric iron (II) *trans*-[Fe(opoh-κ²O,P)₂(THF)₂] (Fig. 19b) complex in high yield.[81] Its structure elucidation by X-ray diffraction determines the chirality of this structure, in which the phosphorous atoms become stereocenters once coordinated with the iron atom. The configurational other possible stereoisomers was not investigated in the solid state or solution.

3. Iron compounds with diphosphanes

3.1. Pseudo-tetrahedral complexes

The half-sandwich “[Fe(Cp)L(PP)]” (L = monodentate ligand; PP = diphosphane) compounds are pseudo-tetrahedral and should contain diphosphanes with two different phosphorous atoms to be chiral-at-metal. This condition makes this family of compounds scarce. Up to four half-sandwich diastereomers (two pairs of enantiomers) containing diphosphanes (Fig. 20) were obtained with high diastereoselectivities, *via* intramolecular [4 + 2] Diels-Alder cycloaddition reaction (similar to the one described in section 2.2.1) between the substituted phosphole in [Fe(CO)(Cp)(dmpp)I] and a vinylphosphane (dvpv).[53] New stereocenters at the diphosphane ligand were generated because of this cycloaddition-coordination reaction, and it was reproduced by using other vinylphosphanes. For example, in the case of using dvpp and the same iron precursor, three iron diastereomers were obtained.

Brunner *et al.* contributed to the development of cyclopentadienyl chiral-at-iron [Fe(Cp)L(prophos)]PF₆ (L = monophosphane) compounds (Fig. 21) with one enantiomerically pure diphosphane bearing one stereocenter in the ethylene skeleton, such as prophos.[83] These compounds were prepared by a reaction between the [FeCp(NCMe)(prophos)]PF₆, precursor, which is a configurationally labile compound, and an excess of the selected monophosphane. All these compounds crystallized in non-centrosymmetric space groups and the type of the monophosphane influences the enantiopurity of the crystallized compound: a S_{Fe} configuration is present for compounds containing PPh₂ and PPh(OMe)₂, whereas the stereochemistry changes to R_{Fe} when PPh₂(OR) (R = Me, Et, and ⁱPr) ligands are present. Surprisingly, only in this last case, there is an unambiguous correlation between single crystal X-ray and ³¹P{¹H} NMR structural elucidations.

Other half-sandwich iron compounds contain optically pure C₂-diphosphanes, for example, bmppb, with two symmetric C or P stereocenters that have been reported.[84–95] In these cases, the chirality of the compounds is associated with that of the phosphane and there is not any stereogenic iron centre because of the C₂-symmetry of the diphosphane.

3.2. Octahedral homoleptic complexes

Homoleptic octahedral iron compounds containing diphosphane ligands are restricted to achiral phosphanes. Only a few examples of tris (chelate) iron (II) complexes are reported in the literature, namely [Fe(dmpp)₃X₂] (X = Cl or I)[96], [Fe(PP)₃](BF₄)₂ (PP = dmpp, dmpe, depe)[97,98], [Fe(tmdf)₃](FeBr₄)₂[99] and [Fe(dmeoprpe)₃](ClO₄)₂. [100] Among them, the last compound was the only described crystallographically. Homoleptic iron compounds in other oxidation states, such as [Fe(dmpe)₃], are also scarce. All these compounds are stereogenic-*only-at-metal* complexes and were obtained as a racemic mixture of the two helical Λ and Δ enantiomers. Their enantiomeric resolution remains unknown.

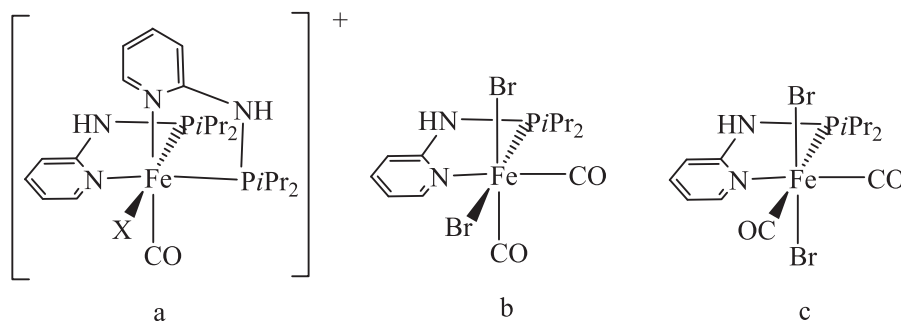


Fig. 17. Schematic representation of the iron isomers with dipa.

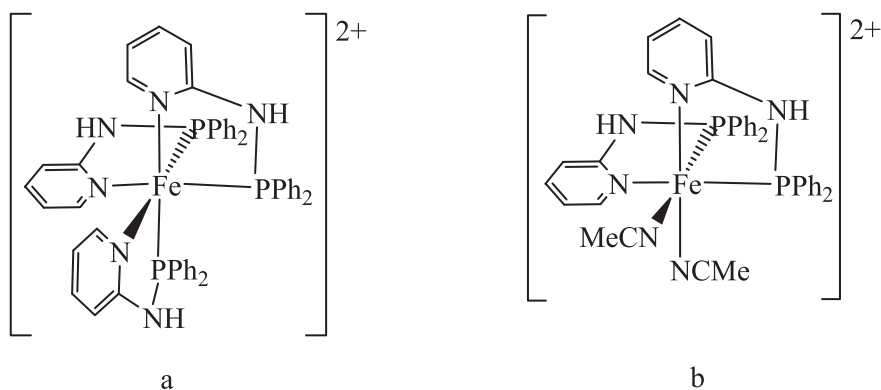


Fig. 18. Schematic representation of the iron isomers with dppa.

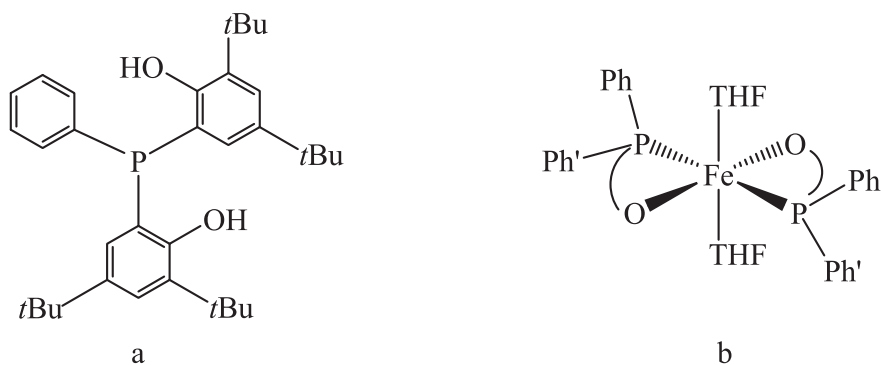


Fig. 19. Schematic representation of the (a) Hopoh ligand and (b) the Fe(II) derived compound.

3.3. Octahedral heteroleptic "[Fe(PP)₂]" complexes

These complexes generally refer to iron(II) [Fe(PP)₂]²⁺ systems, which contain additional ligands (neutral or anionic, and mono- or bidentate) that complete the coordination sphere. The two chelating

diphosphane ligands limit the number of possible stereoisomers to *cis* and *trans* configurations and, when remaining ligands are in *cis* disposition, these complexes result in chiral-at-iron isomers, keeping the Λ and Δ nomenclature of the homoleptic tris(chelate) iron diphosphane compounds. If the phosphane and the remaining ligands are non-chiral,

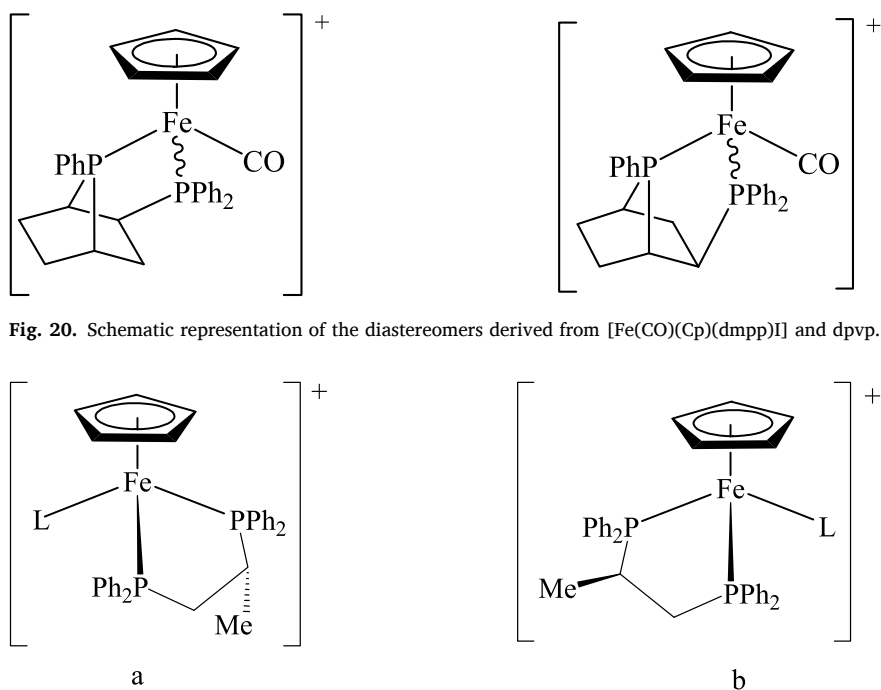


Fig. 20. Schematic representation of the diastereomers derived from [Fe(CO)(Cp)(dmpp)I] and dpvp.

Fig. 21. Schematic representation of (a) (R_{Fe}, R_C)-[Fe(Cp)L(propfos)]⁺ (L = PPh₂(OR), R = Me, Et, *i*Pr) and (b) (S_{Fe}, R_C)-[Fe(Cp)L(propfos)]⁺ (L = PPh₂, PPh(OMe)₂).

the stereogenic-only-at-iron compounds generally provide racemic Λ and Δ -*cis* mixtures. In the case of optically pure phosphanes present, only one iron stereoisomer would be obtained. In general, configurationally stable “*cis*-[Fe(L-L)(PP)₂]” systems (L-L = ligand with two donor atoms) have been isolated, however, the “[FeL₂(PP)₂]” systems (L = monodentate ligand) are commonly fluxional in solution, or *cis* and *trans* isomers can be identified, thus preventing, in both cases, the isolation of pure *cis* (or *trans*) compounds. It is not clear how the nature of the reactants and the reaction conditions can control the *cis/trans* stereospecificity of the formation of the iron compounds, and it is a topic that still is open to discussion.

The separation between Λ and Δ -*cis* isomers is promising for applications in stereospecific transformations and the field of optically active materials. However, the studies reported on the configurational stability of *cis* iron compounds are scarce and are centred on *cis/trans* isomerization reactions. The enantiomeric resolution of “[FeL₂(PP)₂]” and “*cis*-[Fe(L-L)(PP)₂]” compounds has not been explored.

In this section, we classify the octahedral chiral-at-iron heteroleptic diphosphane compounds in two subsections: one with achiral phosphanes and another with chiral phosphanes. Most of the chemistry is included in the first subsection, which is divided into two parts in the function of the nature of the non-phosphane ligands and their mode of coordination. Here, we deal with the factors that could be responsible for the stereoselectivity in the formation of pure *cis* isomers. In the second subsection, the use of chiral phosphanes for the preparation of optically active iron complexes is presented.

3.3.1. Complexes with achiral phosphanes

The isomeric possibilities of the octahedral “*cis*-[FeL₂(PP)₂]” and “*cis*-[Fe(L-L)(PP)₂]” compounds, bearing achiral PP, are related to the identity of the non-phosphane ligands. If L are identical, a racemic mixture of chiral-at-iron compounds is expected to be obtained, whereas four possible optical isomers could be obtained when L are different, as occurs in “*cis*-[FeHL(PP)₂]” compounds. In this section, we report both families of compounds. In addition, we describe the isolation of the non-chiral *trans* isomers, which often appear mixed with *cis* isomers as reaction products.

3.3.1.1. “*cis*-[FeLL'(PP)₂]” (L, L' = monodentate ligands) complexes.

There is no general synthetic approach for the isolation of the “*cis*-[FeL₂(PP)₂]” isomers as pure compounds, and the competition with the formation of *trans* isomer is generally present. In a first attempt to find a synthetic strategy, Tyler *et al.* found that the *cis/trans* stereochemistry of certain [Fe(PP)₂X₂] compounds (PP = R₂PCH₂CH₂PR₂ being R = alkyl chain, aryl, alkyl with terminal hydroxy or methoxy group (Fig. 22); X = halide) can be modulated by the alkyl chain length of the diphosphane, its hydrophilic nature and the solvent used. [101] In general, the water-insoluble phosphanes (such as dmpe, [102] depe and dprpe, [103] dbpe, [104] dppe, [105] dppp and dmeoprpe, [101] and dmbz [106,107]) afford the non-chiral *trans*-[FeCl₂(PP)₂] isomers. However, the solvent can intervene in the stereoselectivity of the reaction. For example, a *cis/trans*-[FeCl₂(dmbz)₂] mixture was isolated if the preparation was carried out in THF instead of ethanol. [108].

The influence of the solvent on the stereoselectivity of the iron conformers could be applicable in the reaction between iron precursors and the water-soluble phosphanes. Whereas the reaction of water-soluble phosphanes bearing long-chain terminal groups, as dhbupe

and dhpepe, with FeCl₂·4H₂O in alcohols provided *trans*-[FeCl₂(PP)₂] products, the stereoselectivity changed to the *cis* iron products when water is used as solvent. [101] These *cis* iron complexes were obtained as a racemic mixtures, based on NMR and X-ray results. Surprisingly, the same reaction with dhrpe in alcohols or water as solvents, indistinctively, afforded *cis*- and *trans*-[FeCl₂(dhrpe)₂] mixtures. Probably, it could be attributed to steric and/or electronic factors of the phosphane substituents.

The fact that phosphorous atoms are part of an aliphatic cycle can condition the more selective formation of *cis*-[FeL₂(PP)₂] isomers. For example, the reaction between FeCl₂ and deprope in THF provided *cis*-[FeCl₂(deprope)₂] (Fig. 23a). [109] This product was identified as a pure *cis* isomer in solution, considering exclusively its ³¹P NMR spectrum. Single crystal X-ray diffraction confirmed its isolation as a racemic mixture. However, the same reaction with the slightly less bulky bpe6 phosphane (Fig. 23b) afforded the *trans* isomer. [110] The similar bpe5 phosphane (Fig. 23b), once mixed with FeCl₂ in THF, gave the *cis*-[Fe(bpe5)₂Cl₂] compound, which was isolated as single crystals and identified as a racemic mixture by X-ray diffraction. [111] The higher steric hindrance of the cyclic phosphane groups for bpe6 than bpe5 (ϕ (C-P-C)^{bpe6} = 100° > ϕ (C-P-C)^{bpe5} = 92° in the corresponding structures) supports the formation of the respective *trans* and *cis* isomers. However, while the steric and electronic characteristics of the phosphane groups seem to control the formation of [FeCl₂(PP)₂] complexes stereoselectively, the preparation of the *cis* isomers is not straightforward and is difficult to rationalize. To illustrate this, the identification of iron isomers in the solid state does not always match with that acquired in the solution. This is the case of the above mentioned *cis*-[Fe(bpe5)₂Cl₂], in which ³¹P{¹H} NMR spectra do not agree with the expected *cis* spin pattern observed in the solid state. [111] Concretely, this compound shows a fluxional behavior at room temperature, and two apparent triplets and a singlet appeared (corresponding to ca. 90/10 ratio) at low temperature (233 K in THF), which were ascribed to the *cis* and *trans*-[Fe(bpe5)₂Cl₂] isomers, respectively. In addition, the electronic and steric factors of the non-phosphane ligands influence drastically the selectivity of the formation of iron conformers. For example, the chloride by CO exchange led *cis*-[Fe(bpe5)₂Cl(CO)]⁺ as a single isomer, identified in solution by four multiplets in its ³¹P{¹H} NMR spectrum and as a racemic mixture in the crystal cell.

While ruthenium complexes containing two diphosphane ligands with large chelate bites tend to form *cis* complexes, there are not so many examples reported for iron analogues. [112,113] The reaction of [Fe(NCMe)₆](BF₄)₂ with a diphosphane with a pendant nitrogen base (depma) formed the compound [Fe(depma)₂(NCMe)₂](BF₄)₂, whose ³¹P NMR spectrum is compatible with an AA'BB' system, and could be associated to a *cis* geometry. [112] Carbon monoxide reacted with this compound to displace only one molecule of NCMe leading *cis*-[Fe(CO)(depma)₂(NCMe)](BF₄)₂, which crystallized as a mixture of 2 enantiomers. The substitution of one depma ligand for a diphosphane with a smaller chelate bite, such as dmpm, formed the *trans*-[Fe(depma)(dmpm)(NCMe)₂](BF₄)₂ isomer.

The development of hydrido iron compounds with diphosphanes, “[FeHL(PP)₂]”, is highly attractive for hydrogen transfer reactions, however, they have not been studied in stereoselective transformations so far. [114,115] The examples of [Fe(H)₂(PP)₂] are limited to dmpe and dppe phosphanes, and their derivatization to monohydrido “[FeHL(PP)₂]” has been deeply studied. As halides, hydrido ligands also



Fig. 22. Schematic representation of some diphosphane compounds.

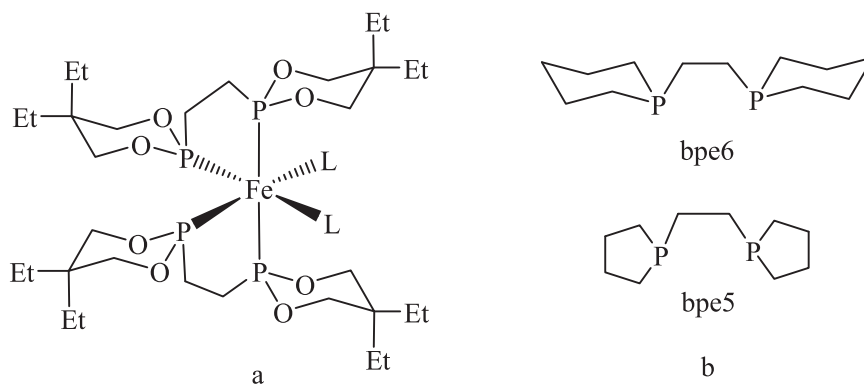


Fig. 23. Schematic representation of: (a) *cis*-[Fe(deprope)₂L₂] (L = Cl, Me), and (b) bpe5 and bpe6.

influence the stability between *cis* and *trans* configurations for “[FeHL(PP)₂]” compounds.

The [Fe(dppe)₂(H)₂] compound was prepared from anhydrous FeCl₂, dppe and NaBH₄, [115–118] or by reaction between *trans*-[FeCl₂(dppe)₂] and an excess of LiAlH₄ in THF. [117] Aresta *et al.* suggested a *cis* configuration in the basis of the two IR hydride bands at 1870 and 1875 cm⁻¹. [117] This configuration, also shown in the structure of the ruthenium analogue, [119] is often assumed until present. However, the hydride IR signal is generally reported as a unique signal, and the identification of two broad signals by ³¹P{¹H} NMR spectrum confirms the fluxionality of [Fe(dppe)₂(H)₂] in solution. [116,120] This compound is photoactive, [120] and it resulted in an efficient pre-catalyst in hydrosilylation of carbonyl compounds under visible light activation. [121].

The [Fe(dmpe)₂(H)₂] analogue is also fluxional at room temperature and displays a spin pattern similar to AA'BB' consistent with a *cis* geometry only at the low-temperature limit in toluene. [115,122] Treatment of [Fe(dmpe)₂(H)₂] with laser flash photolysis gave the reduced [Fe(dmpe)₂] compound, as confirmed *in situ* by NMR. This intermediate promotes the reaction with H₂, arenes, alkenes, alkanes, triethylsilane and HBpin by oxidative addition, to generally provide *cis/trans* mixtures of iron (II) complexes of general formula [FeHL(PP)₂], also identified by ³¹P{¹H} and ¹H NMR. [13,123,124] Only in the case of photochemical pentane activation, the *cis*-pentyl hydrido complex was detected as pure *cis* stereoisomers (Fig. 24), and no *cis/trans* isomerization was described. However, the decomposition registered above -20 °C hampered its isolation. [125,126].

Other *cis*-[FeHL(PP)₂] (L = aryl) compounds were selectively obtained by simple breaking of a sp² C-H bond. For example, the reduction of *trans*-[FeCl₂(dmpe)₂] by NaNp (Np = naphthylenide) affords the *cis*-[Fe(dmpe)₂H(Np)] complex mixed with the [(Fe(dmpe)₂)₂(μ-dmpe)] dimer. [127] The identification of the ABCD pattern by ³¹P{¹H} NMR for *cis*-[Fe(dmpe)₂H(Np)] is consistent with a *cis* structure. The intramolecular sp² C-H oxidative addition to Fe(0) diphosphane complexes was also reported following additional strategies to give selectively the *cis* isomer. The simple refluxing (or photolysis) in toluene of the [Fe(η²-C₂H₄)(dppe)₂] precursor provided the *ortho*-metalated *cis*-[Fe{o-(C₆H₄)PhPC₂H₄PPH₂-κ³C,P,P'}(dppe)H] complex (Fig. 25). [128,129] The *cis* configuration was confirmed by the ABCD spin system, determined by

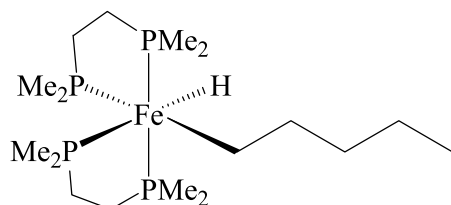


Fig. 24. Schematic representation of the *cis*-[Fe(dmpe)₂H(pentyl)] compound.

experimental and calculated ³¹P{¹H} NMR spectra. [128].

The monohydrido diphosphane iron (II) complexes were combined with hydrazido and amido ligands to afford [Fe(dmpe)₂HL]ⁿ (L = N₂H₄, n = 1+; L = NH₂, n = 0) as purely *cis* isomer or *cis/trans* mixtures. [130,131] The hydrazido *cis*-[Fe(dmpe)₂H(N₂H₄)Cl] compound was isolated by *in situ* crystallization after 2.5 months from a THF solution of *trans*-[FeCl(dmpe)₂H] and hydrazine (Fig. 26). [130] The *cis*-[Fe(dmpe)₂H(N₂H₄)]⁺ complex appears as a racemic mixture of Λ and Δ isomers in the unit cell. The hydrazine binds in an end-on mode to the iron atom, and the bond distances between the Fe and two N atoms are similar to those observed for the *trans* isomer. Regarding amido ferrous compounds, Fox and Bergman treated the *trans*-[FeCl(dmpe)₂H] complex with NaNH₂ in a THF/NH₃ mixture, and the *trans*- and *cis*-[Fe(dmpe)₂H(NH₂)] isomers were obtained in 4:1 ratio. In this case, only the *trans* amido complex could be crystallized. [131].

The incorporation of two alkyl ligands into the [Fe(PP)₂]²⁺ species is limited to methyl and generally leads to *cis/trans*-[FeMe₂(PP)₂] mixtures. Kwok Wong *et al.* synthesized selectively the *cis*-[Fe(dmpm)₂(Me)₂] complex by the addition of dmpm and Me₂Mg to a suspension of [Fe(O₂CMe)₂] in THF at low temperature. [96] Its configuration was determined by the authors from the ¹H and the AA'BB' spin pattern of the ³¹P NMR spectra, and it was noted that the product must be isolated quickly to circumvent isomerization to the *trans* product. In contrast, the alkylation of *trans*-[FeCl₂(PP)₂] (PP = dmpe, depe) using methylolithium or dimethylmagnesium gave *cis*- and *trans*-[FeMe₂(PP)₂] isomeric mixture. [132–134] Both isomers were identified by ³¹P{¹H} NMR spectroscopy and at room temperature, which correspond to two apparent triplets and a singlet, respectively. Recent studies have shown that the UV (350 nm) irradiation of the [Fe(dmpe)₂Me₂] and HBpin mixture affords the hydrido(boryl)iron [Fe(Bpin)(dmpe)₂H] complex, identified by NMR spectroscopy in 1:1 *cis/trans* ratio. [13] The *cis* isomer is fluxional and only at 213 K a multiplet at -13.7 ppm is detected by ¹H NMR and ³¹P{¹H} NMR shows four signals associated with an ABCD spin system. The *trans*-[Fe(Bpin)(dmpe)₂H] isomer was isolated by evaporation of the *cis/trans* solution mixture, and identified by solid-state NMR, IR and X-ray diffraction. Nevertheless, subsequent redissolution of the *trans* isomer promoted the isomerization with concomitant production of the equimolar *cis/trans*

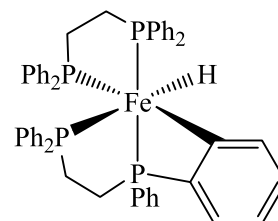


Fig. 25. Schematic representation of [Fe{o-(C₆H₄)PhPC₂H₄PPH₂-κ³C,P,P'}(dppe)H].

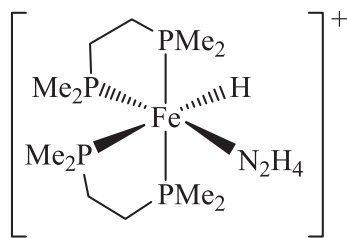


Fig. 26. Schematic representation of one *cis*-[Fe(dmpe)₂H(N₂H₄)]⁺ isomer.

mixture.

The [Fe(dmpe)₂Me₂] analogue was obtained by reaction between [Fe(acac)₃], dppe and AlMe₂(OEt) (or AlMe₃). [125] The authors did not describe its recrystallization or NMR spectra and did not assign any stereochemistry. Slight warming of [Fe(dmpe)₂Me₂] in toluene provided the *ortho*-metalated iron (II) isomer, *cis*-[Fe{o-(C₆H₄)PhPC₂H₄PPh₂-κ³C, P, P'}(dmpe)Me], analogous to the hydrido compound (*vide supra*, Fig. 25) and, while authors have isolated orange crystals, no structure was determined. [125].

The reaction of *trans*-[FeCl₂(dmbz)₂] with two equivalents of methylolithium afforded the dimethyl complex [Fe(dmbz)₂(Me)₂], which was isolated as a *cis/trans* mixture. The monitoring of the reaction by ³¹P NMR in d₈-THF showed that *cis*-[Fe(dmbz)₂(Me)₂] was formed initially, but this isomer underwent partial isomerization as the solution was concentrated and, at equilibrium, the *trans:cis* ratio was ca. 1:4. [108].

Fang *et al.* described the preparation of *cis*-[Fe(deprope)₂(Me)₂] (Fig. 23, X = Me) by reaction of *cis*-[FeCl₂(deprope)₂] and Mg(Me)₂ in THF. [109] The *cis* configuration is confirmed by ³¹P NMR, with the detection of two triplets, and the J_{PH} value registered by ¹H NMR. This compound is configurationally stable in solution and for days, a behavior that contrasts with that described for similar *cis*-[Fe(Me)₂(PP)₂] (PP = dmpm, dmpe, depe, dmbz) compounds described above. The *cis* structure of the octahedral *cis*-[Fe(deprope)₂(Me)₂] complex is settled by X-ray analysis and crystallized as a racemic mixture in the single crystal analyzed.

3.3.1.2. “[Fe(L-L)(PP)₂]” (L-L = ligand with two donor atoms) complexes. Several ligands bearing H, C, O, S or halogen donor atoms with different denticities and hapticities provide chiral-at-iron bisphosphane compounds. Regarding alkylated iron compounds, the [Fe(dmpe)₂(o-xylene-κ²C, C’)] (Fig. 27) compound is, as far as we know, the only example of a [Fe(PP)₂]²⁺ system chelated to a κ²-dialkyl ligand, which is described as a racemic mixture of compounds within a centrosymmetric space group. [135].

Hills *et al.* reported that the fluxional hydrido dihydrogen *trans*-[Fe(dmpe)₂H(η²-H₂)]⁺ iron (II) complex provided chiral *cis* iron compounds after reaction with cyclopropenes and acetylenes. [136] Reaction with 3,3-dimethylcyclopropene led the [Fe{(HH₂C)C = CMe₂-κ²C, H}(dmpe)₂]⁺ complex (Fig. 28a), which crystallized in a centrosymmetric space group. This compound depicts an agostic interaction involving the iron atom and the hydrogen of the dimethylallene, and it was identified by ¹H NMR. Analogous reaction with phenylacetylene (HC≡CPh) gave *cis*-[Fe{(Ph(H)C)C-C≡CPh-κ³C, C’, C’’}(dmpe)₂]⁺ (Fig. 28b) as a

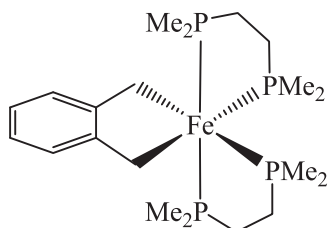


Fig. 27. Schematic representation of [Fe(dmpe)₂(o-xylene-κ²C, C’)].

racemic mixture. [136,137] This enynyl iron complex was first described by Field *et al.*, and it was isolated through a reaction between *trans*-[FeCl₂(dmpe)₂] and an excess of phenylacetylene. [138] Leigh expanded the reactivity of alkynes to the analogous *trans*-[Fe(depe)₂H(η²-H₂)]. This precursor reacted with an excess of propyne (HC≡CMe) to give the κ³-butenylnyl [Fe{(Me(H)C)C-C≡CMe-κ³C, C’, C’’}(depe)₂]⁺ complex, identified by X-ray diffraction. [137] This structure crystallized in an enantiomorphic P212121 space group, but the absolute structure configuration was not given. The ³¹P{¹H} NMR patterns for both depe and dmpe enynyl compounds correspond to an ABCD spin system, which confirms their asymmetry.

The κ³ connectivity between a family of [R(H)C = C-C≡CR]⁻ butenylnes (R = Me, ^tBu, Ph, 4-(HC≡C)Ph, 3,5-(HC≡C)₂Ph) and [Fe(dmpe)₂]²⁺ was reported by Field *et al.* [139] The resulting [Fe{R(H)C = C-C≡CR-κ³C, C’, C’’}(dmpe)₂]⁺ compounds were synthesized by protonation and intramolecular C-C coupling of the *trans*-bis(acetylide) iron (II) complexes, analogous structurally to the compound represented in Fig. 28b. The structures of these iron compounds were elucidated only by NMR in solution. Four distinct phosphorous resonances were detected by ³¹P{¹H} NMR, which confirms the unsymmetrically substituted octahedral *cis* complex containing a FeP₄ ligand set. The same strategy was applied for the preparation of symmetrically and unsymmetrically 1,4-disubstituted κ³-butenylnyl complexes, to lead to a mixture of two regioisomers, namely [Fe{R(H)C = C-C≡CR’-κ³C, C’, C’’}(dmpe)₂]⁺ and [Fe{R’(H)C = C-C≡CR-κ³C, C’, C’’}(dmpe)₂]⁺ (R = aliphatic or aromatic substituent (Fig. 29)). [140] The configurational stability of all isomers was confirmed by NMR at 300 K, and four crystallographic structures confirmed their isolation as racemic mixtures of distorted octahedral geometries. These κ²- and κ³-enynyl-iron(II) complexes are conformationally stable at room temperature, however, their chiral-at-metal identity was not identified.

Other bidentate and polyhapto oxygen donor ligands can complete the “[Fe(PP)₂]” unit to lead *cis* octahedral iron(II) products. Field *et al.* prepared the κ²-acetato-iron (II) [Fe(dmpe)₂(O₂CCH₃-κ²O, O’)]⁺ racemate by CO₂ insertion (at high pressure conditions) into the Fe-Me bond in [Fe(dmpe)₂(Me)₂], or by reaction of iron (II) acetate and two equivalents of dmpe. [133] These authors assigned its *cis* configuration by the identification of two apparent triplets by ³¹P{¹H} NMR. In the same work, the synthesis of the [Fe(depe)₂(O₂CCH₃-κ²O, O’)]⁺ analogue implies the reaction between sodium acetate and *trans*-[FeCl₂(depe)₂]. This acetato-iron (II) was obtained as a racemate and shows a distorted octahedral geometry depicted in its X-ray structure. The pair of pseudo-triplets detected by ³¹P{¹H} NMR, and the two IR bands associated with the asymmetric and symmetric stretching vibrations of the acetato complex, [Fe(dmpe)₂(O₂CO-κ²O, O’)], seems to be obtained by the addition of K₂CO₃ to a methanol solution of the *trans*-[FeCl₂(dmpe)₂] complex. [133] This carbonato-iron (II) complex crystallized as a racemic mixture in a distorted octahedral geometry, with a considerable disorder for dmpe ligands.

Carbon dioxide insertion into the Fe-H bond was reported by Leigh *et al.* [141,142] The *cis*-[Fe(dmpe)₂(O₂CH-κ²O, O’)]BPh₄ compound was prepared by CO₂ reaction with *trans*-[Fe(dmpe)₂H(η²-H₂)]BPh₄ in THF. ³¹P{¹H} NMR measurements provided two triplets (at -67.3 and -78.5 ppm) that were interpreted as an AA’BB’ pattern, in agreement with a *cis* configuration of the product. It was obtained as a single iron species based on the Mössbauer spectrum in the solid state. However, the authors described a small triplet at -78.4 ppm (²J_{PP} 35.4 Hz) by NMR, which suggests the presence of another iron *cisoid* form, conceivably with monodentate formate.

Other insertion reactions into the Fe-H bond were reported. Leigh *et al.* prepared the [Fe{CHCHC(OMe)O-κ²C, O}(dmpe)₂]BPh₄ (Fig. 30a) compound by reaction of methyl propiolate with a *trans*-[FeCl₂(dmpe)₂]/NaBH₄ mixture, or by direct propiolate reaction with *trans*-[Fe(dmpe)₂H(η²-H₂)]BPh₄. [141,143] In both cases, the reaction is explained as insertion of acetylene into the iron-hydrido bond of the

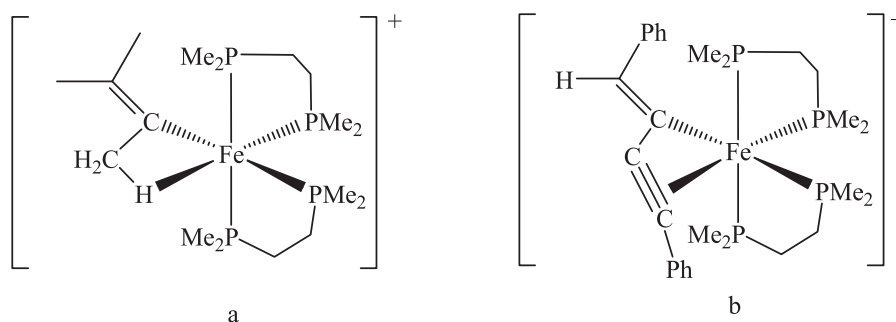


Fig. 28. Schematic representation of: (a) $\text{Fe}\{(\text{HH}_2\text{C})\text{C}=\text{CMe}_2\text{-}\kappa^2\text{C,H}\}(\text{dmpe})_2\}^+$ and (b) $\text{cis-}[\text{Fe}\{(\text{Ph}\{\text{H}\}\text{C})\text{C}\equiv\text{CPh-}\kappa^3\text{C,C',C''}\}(\text{dmpe})_2\}^+$.

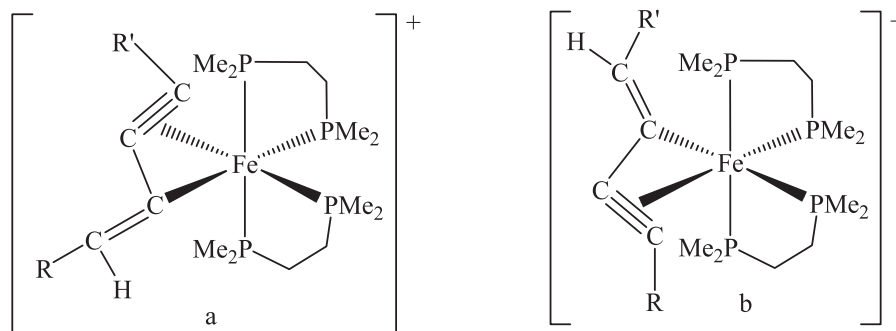


Fig. 29. Schematic representation of the regioisomers: (a) $[\text{Fe}\{\text{R}(\text{H})\text{C}=\text{C}\text{-C}\equiv\text{CR}'\text{-}\kappa^3\text{C,C',C''}\}(\text{dmpe})_2\}^+$ and (b) $[\text{Fe}\{\text{R}'(\text{H})\text{C}=\text{C}\text{-C}\equiv\text{CR}\text{-}\kappa^3\text{C,C',C''}\}(\text{dmpe})_2\}^+$ (R = aliphatic or aromatic substituent).

$\text{trans-}[\text{Fe}(\text{dmpe})_2(\text{H})(\eta^2\text{-H}_2)]^+$ complex, which can be obtained *in situ*. Whereas $[\text{Fe}\{\text{CHCHC}(\text{OMe})\text{O-}\kappa^2\text{C,O}\}(\text{dmpe})_2]\text{BPh}_4$ was not characterized crystallographically, its *cis* conformation was confirmed by the appearance of an ABCD spin system in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

A few years later, Almeida *et al.* [144] obtained the analogous vinyl $[\text{Fe}\{\text{CHCHC}(\text{OMe})\text{O-}\kappa^2\text{C,O}\}(\text{dppe})_2]\text{BF}_4$ compound after a reaction between methyl propiolate, TlBF_4 and a THF solution of *trans-}[\text{FeCl}(\text{dppe})_2\text{H}] under sunlight/Ar. For the resulting iron vinyl compound, the authors described a complex ABCD spin system by $^{31}\text{P}\{^1\text{H}\}$ NMR, though no spectral description was detailed. Its X-ray structural analysis shows that the ligand arrangement around the iron conforms to a distorted octahedral, with the two dppe ligands pushing each other, and forcing the C-Fe-O angle of the five membered metallacycle to a value of $80.0(6)^\circ$. The Fe-X (X = O, C) distances agree with a bonded ester and C (α) vinyl groups, respectively, and with a hybrid structure between the two mesomeric forms of the planar chelating vinyl ligand skeleton (Fig. 30b). This compound crystallized as a racemic mixture.*

Ferralactones were prepared by Jurd *et al.* The $[\text{Fe}\{\text{OC}(\text{=O})\text{CHCH-}\kappa^2\text{C,O}\}(\text{depe})_2]$ (Fig. 31a) was obtained as the only product by reaction between *trans-}[\text{FeH}(\text{C}\equiv\text{CH})(\text{depe})_2] and CO_2 under room conditions. [145] The same year, Adamson *et al.* prepared the same compound by reductive coupling of the $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\text{depe})_2]$ with CO_2 in the presence of ethylene. [146] At low temperature, an insertion of CO_2 into the β -carbon of the acetylide afforded the ferralactone depicted in Fig. 31b.*

Both compounds correspond to an ABCD pattern by ^{31}P NMR, in agreement with the octahedral geometry elucidated by X-ray crystallography, and crystallized as racemic mixtures. The reaction of CO_2 with the functionalized *trans-}[\text{FeH}(\text{C}\equiv\text{CR})(\text{depe})_2] (R = Ph, COOEt) led to the corresponding ferralactones shown in Fig. 31a. Both compounds are octahedral and were obtained as racemic mixtures, as confirmed by NMR and X-ray results. A family of analogous substituted and non-substituted ferralactone compounds with dmpe were also reported. [147].*

Carbon disulphide insertion into the iron-hydrogen bond of “[FeH(PP) $_2$] $^+$ ” species afforded bis(thiolated) *cis*-racemates. Thus, the reaction of *trans-}[\text{FeCl}(\text{dppe})_2\text{H}] with CS_2 and TlBF_4 led to the dithioformate $[\text{Fe}(\text{dppe})_2(\text{S}_2\text{CH-}\kappa^2\text{S,S'})]\text{BF}_4$ complex. [144] A pair of triplets were detected by $^{31}\text{P}\{^1\text{H}\}$ NMR, confirming the *cis* stereochemical arrangement of the diphosphanes. A complex multiplet at 9.52 ppm is assigned as the X part of the AA'BB'X spin system of the ^1H NMR spectrum. The $[\text{Fe}(\text{dmpe})_2(\text{S}_2\text{CH-}\kappa^2\text{S,S'})]\text{BPh}_4$ analogue was synthesized by reaction of CS_2 with the *trans-}[\text{FeCl}_2(\text{dmpe})_2]/\text{NaBH}_4 mixture, or by direct reaction with *trans-}[\text{Fe}(\text{dmpe})_2\text{H}(\eta^2\text{-H}_2)]\text{BPh}_4. [141,142] This compound was identified by IR and NMR techniques, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two triplets, characteristic of an AA'BB' spin system, which agrees with the *cis* conformation of the resulting racemate.***

The $[\text{Fe}(\text{depe})_2(\text{S}_2\text{CR-}\kappa^2\text{S,S'})]^n+$ (R = PEt_3 , n = 2; R = H, n = 1) isomers were identified as racemic mixture in their crystal structures.

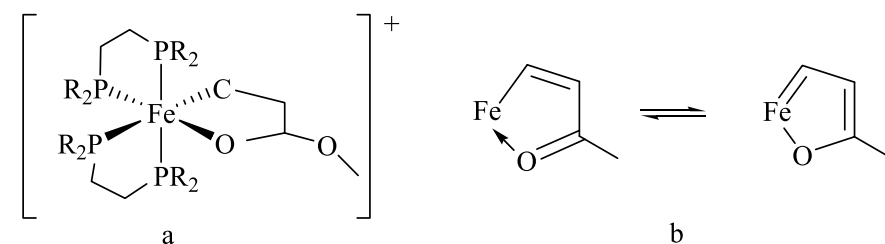


Fig. 30. Schematic representation of (a) $[\text{Fe}\{\text{CHCHC}(\text{OMe})\text{O-}\kappa^2\text{C,O}\}(\text{PP})_2\}^+$ and (b) the isomeric forms of its metallacycle. In the figure R = Me, Ph.

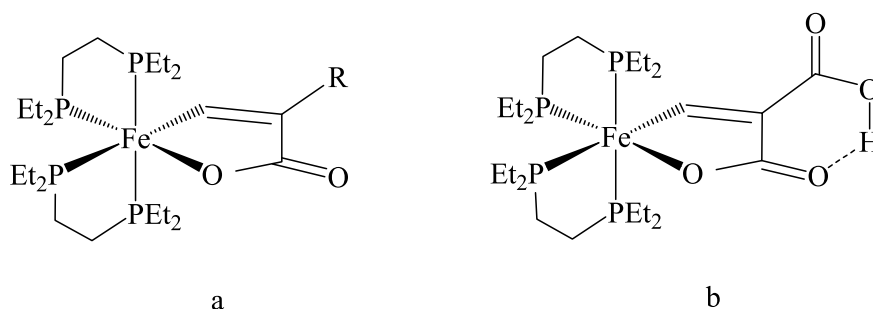


Fig. 31. Schematic representation of (a) $[\text{Fe}\{\text{OC}(=\text{O})\text{CRCH-}\kappa^2\text{C,O}\}(\text{depe})_2]$ ($\text{R} = \text{H, Ph, COOEt}$) and (b) $[\text{Fe}\{\text{OC}(=\text{O})\text{C}(\text{C}(=\text{O}))\text{CH-}\kappa^2\text{C,O}\}(\text{depe})_2]$.

The synthesis of the triethylphosphane-carbon compound was done by mixing $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, depe, and Et_3PCS_2 , in the first reaction step, followed by NaBPh_4 addition. The $[\text{Fe}(\text{depe})_2(\text{S}_2\text{CH-}\kappa^2\text{S,S}')](\text{BPh}_4)$ compound was obtained by hydride attack at the triethylphosphane-carbon disulfide iron precursor, with subsequent loss of PEt_3 . [148] The octahedral geometries and the *cis* stereochemical configuration of both complexes was confirmed by X-ray structural characterization of the centrosymmetric single crystals.

Few iron (II) complexes with diphosphane ligands and chelating thiolato-alkenyl ligands were obtained as racemates by photochemical C-S activations, and structurally characterized as *cis* isomers. [149,150] Photolysis of $[\text{Fe}(\text{dmpe})_2(\text{H})_2]$ and 2-methylthiophene provided H_2 and the C-S insertion product, $[\text{Fe}(\text{dmpe})_2\{\text{SCR}(\text{CH})_2\text{CH-}\kappa^2\text{C,S}\}]$ ($\text{R} = \text{H, Me}$) (Fig. 32a), which was identified by $^{31}\text{P}\{^1\text{H}\}$ NMR and X-ray diffraction (only when $\text{R} = \text{Me}$). [149] The X-ray structure of $[\text{Fe}(\text{dmpe})_2\{\text{SCMe}(\text{CH})_2\text{CH-}\kappa^2\text{C,S}\}]$ shows its octahedral geometry and confirms the formation of a 6-member thiaferracycle. This compound crystallized in an enantiomorphic group, but no information about its enantiopurity is reported. The above mentioned photoreaction also provided the *trans*- $[\text{Fe}(\text{dmpe})_2\text{H}\{\text{C}(\text{CH})_2\text{CR}\}\text{S-}\kappa^1\text{C}\}]$ (Fig. 32b) as a product of the C-H insertion. Photolysis of *cis*- $[\text{Fe}(\text{dmpe})_2(\text{H})_2]$ with 3-methylthiophene promoted the 1–2 and 1–5 insertion reactions, but the $[\text{Fe}(\text{dmpe})_2(\text{SCHCMeCHCH-}\kappa^2\text{C,S})]$ 1–5 insertion product was obtained regioselectively as the major C-S insertion isomer, and identified by $^{31}\text{P}\{^1\text{H}\}$ NMR. Other *cis*- and *trans*- $[\text{Fe}(\text{dmpe})_2\text{H}(\text{SC}_5\text{H}_4\text{-}\kappa^1\text{S})]$ isomers were also identified by NMR spectroscopy as products of the C-H cleavage of the thiophene under reaction conditions.

The regioselective C-S bond cleavage is also observed in the synthesis of the $[\text{Fe}(\text{depe})_2(\text{C}_8\text{H}_6\text{S-}\kappa^2\text{C,S})]$ (Fig. 33a) compound, after oxidative addition of the benzo[*b*]thiophene to the $[\text{Fe}(\text{depe})_2\text{N}_2]$ precursor. [150] This compound is obtained mixed with *trans*- $[\text{Fe}(\text{depe})_2\text{H}(\text{C}_8\text{H}_5\text{S-}\kappa^1\text{C})]$ isomer (Fig. 33b). The *cis* configuration was confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR (ABCD spin system) and by X-ray diffraction. The crystallographic analysis confirms the existence of the racemic mixture, and the structure of the compound displays an octahedral geometry with an iron atom bonded to the thiaferracycle. The reaction of $[\text{Fe}(\text{depe})_2\text{N}_2]$ with thiophene and substituted thiophenes afforded similar *cis/trans* mixtures,

which were identified by $^{31}\text{P}\{^1\text{H}\}$ NMR.

The $[\text{Fe}(\text{dmpe})_2\{\text{SCH}_2\text{N}(\text{Et})\text{C}(\text{O})\text{O-}\kappa^2\text{O,S}\}]$ compound is another example of a chiral S,O-bidentate ferracycle isolated as a racemic mixture in solution and its crystalline form. This compound was obtained by carbon dioxide addition to the *trans*- $[\text{Fe}(\text{dmpe})_2(\text{H})_2(\text{SC}(\text{H})\text{N}(\text{Et-}\kappa^1\text{S}))]$ followed by a rearrangement reaction to the ferracycle above mentioned. [151].

The formation of chiral “ $[\text{Fe}(\text{PP})_2]$ ” compounds bridged with specific metal anions forces the *cis* configurations of the iron compounds. The reaction between FeBr_2 and dmbz provided *cis*- $[(\text{dmbz})_2\text{Fe}(\mu\text{-Br})_2\text{FeBr}_2]$ mixed with *trans*- $[\text{FeBr}_2(\text{dmbz})_2]$. [152] The analogous *cis*- $[(\text{dmbz})_2\text{Fe}(\mu\text{-Br})_2\text{ZnBr}_2]$ product was obtained by reaction between FeBr_2 , dmbz and ZnBr_2 . Both *cis* compounds interact with two bromine atoms of the $[\text{FeBr}_4]^{2-}$ or $[\text{ZnBr}_4]^{2-}$, respectively, and they were obtained as racemic mixtures in the solution and the crystallographic cell.

Other counterions act as a bidentate ligand and stabilize the *cis* conformation of the “ $[\text{Fe}(\text{PP})_2]$ ” unit. The reaction of $[\text{FeSO}_4] \cdot 7\text{H}_2\text{O}$ with depe, dhbupe, dhpepe [101] or dmeoprpe [100] in alcohol or water provided the $[\text{Fe}(\text{PP})_2(\text{SO}_4\text{-}\kappa^2\text{O,O}')]$ compounds, in which the sulfate is bound to the iron atom in a bidentate form and establishes the *cis* configuration of the compounds. The configuration was evidenced by the detection of two triplets in the ^{31}P NMR spectra and proposed, for some cases, by the identification of IR bands of the sulfate. The structure of the *cis*- $[\text{Fe}(\text{dhbupe})_2(\text{SO}_4\text{-}\kappa^2\text{O,O}')]$ compound was characterized by single crystal X-ray diffraction and evidences its isolation as a racemate. Interestingly, some monodentate iron-counterion interactions also provided *cis* configurations. In the case of the mauve-grey solid *cis*- $[\text{Fe}(\text{BF}_4)_2(\text{dmbz})_2]$, the authors assumed the *cis* configuration considering the four different resonances of the methyl hydrogens in the ^1H spectrum, and that the anions are weakly bound to iron in a monodentate fashion. [108] The same authors claim the same configuration for the bis (triflate) complex, *cis*- $[\text{Fe}(\text{CF}_3\text{SO}_3)_2(\text{dmbz})_2]$, but no identification nor experimental details were reported.

3.3.2. Complexes with chiral phosphanes

In a pioneering work, Nell *et al.* prepared non-resolved secondary chiral phosphanes for the synthesis of the chiral-at-metal *cis*-

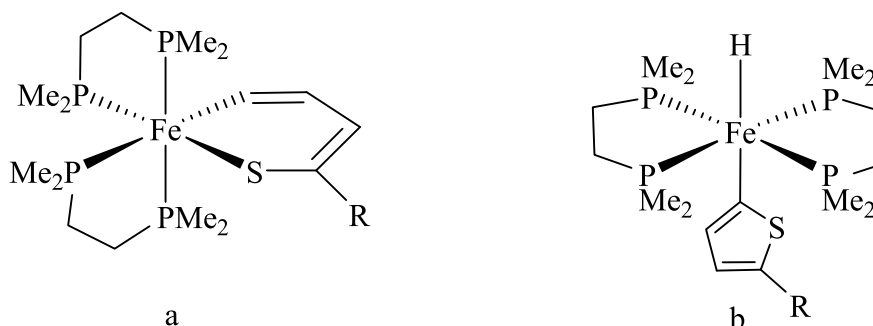


Fig. 32. Schematic representation of: (a) $[\text{Fe}(\text{dmpe})_2\{\text{SCR}(\text{CH})_2\text{CH-}\kappa^2\text{C,S}\}]$ ($\text{R} = \text{H, Me}$) and (b) *trans*- $[\text{Fe}(\text{dmpe})_2\text{H}\{\text{C}(\text{CH})_2\text{CR}\}\text{S-}\kappa^1\text{C}\}]$.

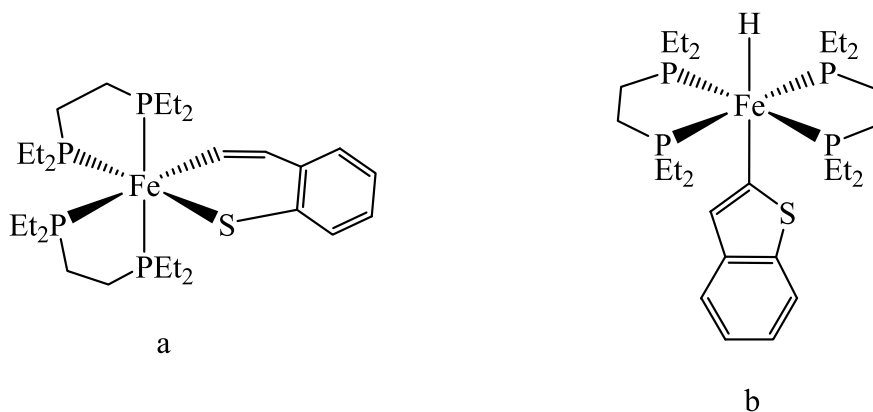


Fig. 33. Schematic representation of: (a) $[\text{Fe}(\text{depe})_2(\text{C}_8\text{H}_6\text{S}-\kappa^2\text{C},\text{S})]$ and (b) $\text{trans}-[\text{Fe}(\text{depe})_2\text{H}(\text{C}_8\text{H}_5\text{S}-\kappa^1\text{C})]$.

$[\text{FeCl}_2(\text{PP})_2]$ (PP = meoprpe, meoprpp, mppe, mppp) compounds, using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as the metallic precursor.[153] Reddish-purple products were obtained and, based on previous reports, the authors associated this color with the selective formation of *cis* isomers. Since each phosphane contains a mixture of three stereoisomers, it was expected that a mixture of up to seven diastereomeric pairs of *cis*- $[\text{FeCl}_2(\text{PP})_2]$ enantiomers would be obtained (Fig. 34a). The NMR spectra confirm this and exhibit multiple peaks that cannot be structurally interpreted. Among these complexes, only the (Λ) -*cis*- $[\text{Fe}\{\{(S,S)\text{-mppp}\}(R,R)\text{-mppp}\}\text{Cl}_2]$ compound crystallized in the enantiomorphic space group P21, but its enantiopurity remains unknown since no absolute configuration was given for the crystal. The stereoisomer depicted in Fig. 34b shows its Λ conformation, in which the phosphorus stereocenters are *R,R* and *S,S*.

Only a few additional enantiopure chiral-at-iron octahedral compounds were identified and isolated by the use of optically pure diphosphanes.[154–156] We obtained the chiral $[\text{FeH}(\eta^2\text{-H}_2)(\text{PP})_2]^+$ (PP = (*R,R*)-, (*S,S*)-Me-DuPhos) (Fig. 35b),[154] as the first iron (II) complexes bearing C_2 -enantiopure diphosphanes (Fig. 35a). These complexes were obtained by hydrogen activation by $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ in the presence of the corresponding phosphane in solution. The compounds are fluxional at room temperature, and NMR experiments at low temperature confirmed the existence of the *trans* isomers, whose chirality is associated with the ligands. Whereas DFT calculations pointed out the highest stabilization energy of the *trans* isomer concerning the Λ - and Δ -*cis* diastereoisomers, the chiral-at-metal Λ -*cis*- $[\text{FeH}(\eta^2\text{-H}_2)\{\{(R,R)\text{-Me-DuPhos}\}_2\}\text{BF}_4]$ isomer was isolated in the solid state, and identified as enantiomerically pure by single crystal X-ray analyses. The dihydrogen ligand was replaced by CO or NCMe to form a conformationally rigid *cis/trans*- $[\text{FeHL}(\text{PP})_2]\text{BF}_4$ (L = CO, NCMe) mixture,

being the *cis* isomers the most abundant in solution, as confirmed by NMR and IR characterizations.

Looking for the selective isolation of *cis* monohydride derivatives, the reaction of the hydrido dihydrogen Me-DuPhos iron precursors with ethers and halides was studied by NMR.[155] Metathesis between dihydrogen and poorly donor ethers (THF or Et_2O) is viable even in mild conditions. Although pure *cis* isomers were identified in some cases, no compound was isolated because of their instability. Again, the solvent plays a role in the stereoselectivity of the substitution reaction. Thus, *cis/trans*- $[\text{Fe}(\text{ether})\text{H}\{(R,R)\text{-Me-DuPhos}\}_2]^+$ mixture was identified in the presence of a small amount of ethers in CD_2Cl_2 , whereas the *cis* isomer was identified as a unique isomer in pure THF- d_8 . The dihydrogen exchange with iodide or chloride afforded the *cis*- and *trans*-substituted isomers, and only the chloride compound isomerized to the *trans* product.

Rennie *et al.* isolated the octahedral iron chiral Δ -*cis*- $[\text{FeCl}_2\{(R,R)\text{-bnpe}\}_2]$ compound as a pure enantiomer in the crystal cell.[156] This compound has been prepared from $\text{FeCl}_2 \cdot 1.5\text{THF}$ and (*R,R*)-bnpe precursors, and the $^{31}\text{P}\{^1\text{H}\}$ NMR identification of a singlet is characteristic of the fluxional behavior in solution.

3.4. Pentacoordinate “[FeL(PP)₂]” complexes

The “*cis*- $[\text{Fe}(\text{PP})_2\text{L}]$ ” species described in this section were considered as pentacoordinated since the L ligands, such as dinitrogen, halides, CO and carbenes, among others, were treated as monodentate or monohapto. While in solution, the “ $[\text{Fe}(\text{PP})_2\text{L}]$ ” species are commonly fluxional, in the solid state the pentacoordinated compounds can adopt geometries between TB and SP. Their distortion from TB geometry can

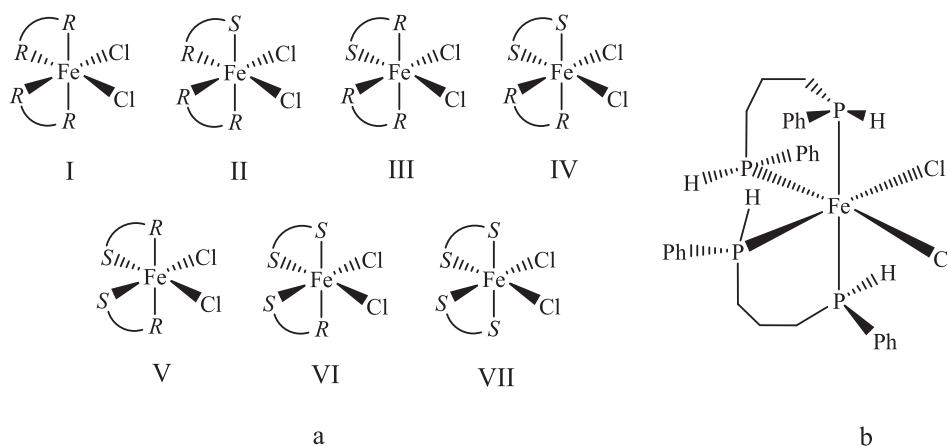


Fig. 34. Schematic representation of (a) the seven Λ diastereoisomers of *cis*- $[\text{FeCl}_2(\text{PP})_2]$ (PP = meoprpe, meoprpp, mppe, mppp); there are another seven Δ stereoisomers and (b) Λ -*cis*- $[\text{FeCl}_2\{(S,S)\text{-mppp}\}(R,R)\text{-mppp}\}$, this enantiomer corresponds to IV in (a). *R* and *S* refer to the configuration of each P stereocenter.

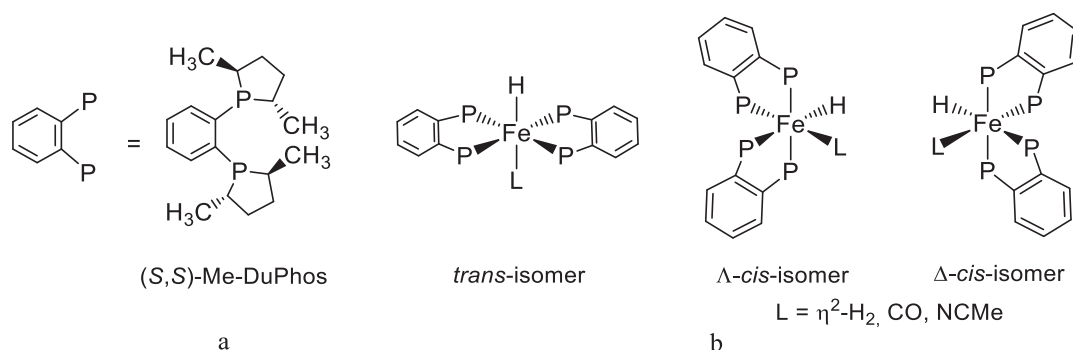


Fig. 35. Schematic representation of (a) (S,S) -Me-DuPhos and (b) stereoisomers of $[\text{FeHL}((S,S)\text{-Me-DuPhos})_2]^+$ ($L = \eta^2\text{-H}_2, \text{CO}, \text{NCMe}$). The (R,R) -Me-DuPhos forms analogous iron isomers.

be determined by the structural parameter τ , reported by Addison *et al.* [157] This intermediate TB/SP geometry makes the iron atom stereogenic, and it can be described by the helix-like configuration of the two bidentate phosphanes. In general, the iron (0) and iron(I) five-coordinated complexes with two diphosphanes show approximately TB structures in the solid state, in which L lies in the equatorial plane. This contrasts with the iron (II) complexes, which are close to SP structures with L in the axial position.

3.4.1. “[FeL(PP)₂]” ($L = \text{monodentate ligand}$) complexes

Several pentacoordinated iron complexes with an approximately TB geometry and one halogen or carbene ligands in the equatorial plane were reported. All of them are neutral, and paramagnetic, and were obtained as racemic mixtures. Bedford *et al.* prepared iron (I) $[\text{Fe}(\text{PP})_2\text{L}]$ ($\text{PP} = \text{dppe}, \text{dpbz}$; $L = \text{Cl}, \text{Br}, \text{phenyl}, 4\text{-tolyl}$), (Fig. 36) as air-sensitive and low spin Fe(I) pentacoordinate complexes, which resulted active catalysts in the Negishi cross-coupling reaction of arylzinc reagents with benzyl, pyridyl or alkyl halides. [158–160] The $[\text{Fe}(\text{dpbz})_2\text{X}]$ ($X = \text{Cl}, \text{Br}$) complexes were obtained by reduction of the iron (II) $[\text{Fe}(\text{dpbz})_2\text{X}_2]$ precursor [161] with an excess of BnMgX . In contrast, the organometallic $[\text{Fe}(\text{dpbz})_2(4\text{-tolyl})]$ complex was obtained by reaction between $[\text{Fe}(\text{dpbz})_2\text{X}_2]$ and $(4\text{-tolyl})\text{MgBr}$ (2 eq) or $(4\text{-tolyl})_2\text{Zn}$ (1 eq). [158] The $[\text{Fe}(\text{dppe})_2\text{X}]$ ($X = \text{Cl}, \text{Br}$) complexes were prepared by the same authors by reaction of a $[\text{Fe}(\text{dppe})_2\text{X}_2]:\text{dppe}$ (1:1) mixture with BnMgX . [159] Single crystal X-ray identification of these compounds confirmed the slightly distorted TB structure with the halide or 4-tolyl ligand in the equatorial plane. [158] In contrast, the $[\text{Fe}(\text{dppe})_2\text{Y}]$ ($Y = \text{phenyl}, 4\text{-tolyl}$), analogues show intermediate SP/TB structures and were synthesized by reaction of the $[\text{Fe}(\text{dppe})_2\text{Cl}]$ precursor with YMgX ($Y = \text{phenyl}, X = \text{Br}$; $Y = 4\text{-tolyl}, X = \text{Cl}$, respectively). [160] The iron (I) dpbz and dppe complexes appear as racemic mixtures in the solid state. In a different synthetic procedure, Boncella *et al.* reported a paramagnetic iron (I) $[\text{FeCl}(\text{dppene})_2]$ compound, which was obtained quantitatively by reaction of $[\text{FeCl}(\text{py})_2\text{R}]$ ($R = \text{Ph}_2\text{C}(\text{TMS})$) and two equivalents of dppene . [162] The solid-state structure of $[\text{FeCl}(\text{dppene})_2]$ contains a racemic mixture of the compounds with a distorted TB geometry.

Another family of pentacoordinated iron (II) compounds are the paramagnetic $[\text{Fe}(\text{PP})_2\text{X}]^+$ ($X = \text{halogen}$) complexes. The

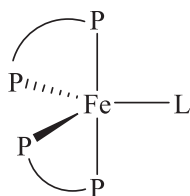


Fig. 36. Schematic representation of $[\text{Fe}(\text{PP})_2\text{L}]$ ($\text{PP} = \text{dppe}, \text{dpbz}$; $L = \text{Cl}, \text{Br}, \text{phenyl}, 4\text{-tolyl}$).

pentacoordinated $[\text{Fe}(\text{depe})_2\text{X}]\text{BPh}_4$ ($X = \text{Cl}, \text{Br}$) was obtained by the addition of NaBPh_4 to a methanolic mixture of $[\text{Fe}(\text{depe})_2\text{X}_2]$. [163] The single crystal X-ray diffraction confirms the presence of chiral complexes in the solid state with intermediate SP/TB geometries for both structures, being closer to SP (τ values of *ca.* 0.42). Whereas the bromo complex crystallized as a racemic mixture, the chloro complex crystallized in an enantiomorphic space group (P212121). The Flack parameter of this structure (0.008 (15)) confirmed the enantiopurity of the complex, however, no mention of this spontaneous resolution was reported.

The $[\text{Fe}(\text{dmeoprpe})_2\text{Cl}]\text{BPh}_4$ complex was prepared in an analogous procedure from NaBPh_4 and $[\text{Fe}(\text{dmeoprpe})_2\text{Cl}_2]$. [164] Its five-coordinate structure shows a TB distortion from the SP geometry ($\tau = 0.13$). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature shows no signal, whereas in the spectrum at low temperature (193 K) a singlet is reported. Paramagnetic behavior is discarded since the ^1H NMR is detectable at room temperature. Thus, the lack of signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum can be assigned to a fluxional mechanism.

Up to this date, iron (0) diphosphane complexes have attracted much attention for their ability to reduce dinitrogen to NH_3 and N_2H_4 . [165] Some “[Fe(N₂)(PP)₂]” systems were proposed as intermediates in such transformations and possibly resulted in chiral-at-metal compounds, however, not all were structurally identified, neither in solution nor in the solid state.

The structure of the pentacoordinated $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$ was not identified by X-ray diffraction techniques. Only Yelle *et al.* determined the TB structure of one of the two possible $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$ enantiomers by computational methods (DFT), with the dinitrogen ligand placed in an end-on mode. [166] The identification of this compound in solution is unclear. The first $^{31}\text{P}\{^1\text{H}\}$ NMR identification of $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$ reported by Leigh *et al.* showed an A_2B_2 spin system. [167] In contrast, in a following paper, a unique resonance was reported for this compound at room temperature and at 223 K. [168] Ashley *et al.* described a wide singlet (fwhm = 6 Hz) for $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$, characteristic of a fluxional behavior. [169].

The structure of analogous $[\text{Fe}(\text{depe})_2(\text{N}_2)]$ was confirmed twice by X-ray crystallography by two independent research groups. The compound crystallized in an orthorhombic Pna21 space group, and it is present as a racemic mixture in the unit cell. The overall structure of $[\text{Fe}(\text{depe})_2(\text{N}_2)]$ is regarded as distorted TB, where the dinitrogen ligand bonds in an end-on fashion to the iron atom and lies in the equatorial plane. [170,171] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Fe}(\text{depe})_2(\text{N}_2)]$ showed a sharp signal at room temperature, which did not show a significant broadening till 218 K, indicating that the compound is fluxional in solution.

Tondreau *et al.* synthesized the iron (0) $[\text{Fe}(\text{dppene})_2(\text{N}_2)]$ complex by reducing the $[\text{FeCl}_2(\text{dppene})_2]$ precursor with two equivalents of sodium under a nitrogen atmosphere, and in the presence of naphthalene as a catalyst. [162] This compound was difficult to isolate

because of its easy decomposition. Fortunately, the structure of $[\text{Fe}(\text{dppene})_2(\text{N}_2)]$ was determined by X-ray diffraction. The compound shows a more distorted TB geometry than $[\text{FeCl}(\text{dppene})_2]$, and it crystallized as a racemic mixture.

Gilbertson *et al.* described the preparation of $[\text{Fe}(\text{dmeoprpe})_2(\text{N}_2)]$ by reductive deprotonation of *trans*- $[\text{Fe}(\text{dmeoprpe})_2\text{H}(\text{N}_2)]^+$. [172] The addition of an excess of TfOH revealed the presence of ammonia and a small quantity of $[\text{N}_2\text{H}_5]^+$. A singlet at δ 79.8 ppm was registered by $^{31}\text{P}\{^1\text{H}\}$ NMR and this multiplicity remained unchanged even lowering the temperature to 193 K, confirming its fluxional behavior in solution. Although the structure was not determined in the solid state, it was proposed isostructural to the previously described dmpe and depe analogues.

In the search of models of the elusive diazenide $[\text{Fe}(\text{NNH})(\text{PP})]^+$ intermediates, postulated in the fixation of N_2 by $[\text{Fe}(\text{PP})_2(\text{N}_2)]$ species, Ashley *et al.* prepared the cationic $\text{Fe}(\text{O})$ silyldiazenido complexes depicted in Fig. 37. [173] Both complexes were isolated by a two-step addition of Me_3SiCl and $\text{K}[\text{BAR}_4^F]$ ($\text{Ar}_4^F = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) to a 1,2-difluorobenzene solution of the $[\text{Fe}(\text{N}_2)(\text{PP})_2]$ ($\text{PP} = \text{dmpe, depe}$) compounds. Their NMR identification shows a singlet in the phosphorous spectra, which evidences the fluxionality of both complexes. Both iron silyldiazenido compounds are isostructural, crystallized as racemic mixtures, and reveal a distorted TB geometry around the Fe centre.

Geri *et al.* showed that the interaction of the $[\text{Fe}(\text{depe})_2(\text{N}_2)]$ fragment with exogenous Lewis acids promotes N_2 “push–pull” activation and provides structural and electronic changes centred in the $\text{Fe}(\text{O})\text{--N}_2$ bond. [174] Among the compounds synthesized, these authors characterized the $[\text{Fe}(\text{depe})_2\{\text{NNB}(\text{C}_6\text{F}_5)_3\}]$ (Fig. 38a) and $[\text{Fe}(\text{depe})_2\{\text{NN}(\text{BH}(3,5\text{-Pr}^i\text{pz}_2)_3)\}]^+$ ($\text{pz} = \text{pyrazolyl}$) compounds in solution and the solid state. Both mono- and dimetallic compounds are chiral and appear as racemic mixtures in the solid state with distorted TB iron structures. The $^{31}\text{P}\{^1\text{H}\}$ NMR identification of the monometallic compound shows a singlet, characteristic of its fluxional behavior, whereas the dimetallic compound depicts two signals (80.34 and 80.11 ppm) with no reported multiplicity. The protonation of $[\text{Fe}(\text{depe})_2\{\text{NNB}(\text{C}_6\text{F}_5)_3\}]$ provided $[\text{Fe}(\text{depe})_2\{\text{NN}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3\}]^+$ (Fig. 38b), and its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum registered at low temperature (-45°C) shows five resonances, from which only three were assigned to the reaction product by the authors. These three signals would be ascribed to an A_2BC spin system, and the two additional signals would be associated with a non-identified secondary product. The elucidated structure of $[\text{Fe}(\text{depe})_2\{\text{NN}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3\}]^+$ confirms its intermediate SP/TB geometry, and this compound crystallises as a racemic mixture.

Regarding pentacoordinated carbonyl iron complexes, few $[\text{Fe}(\text{CO})(\text{PP})_2]$ compounds are reported in the literature and, among them, only one was structurally identified. This is the case of the $[\text{Fe}(\text{CO})(\text{depe})_2]$ compound, which was obtained by N_2/CO ligand exchange from $[\text{Fe}(\text{depe})_2(\text{N}_2)]$, and was identified crystallographically, showing a distorted TB geometry. [171,175] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this complex shows a sharp singlet only at low temperature (218 K), suggesting a fluxional behavior in solution. The similar $[\text{Fe}(\text{CO})(\text{PP})_2]$ ($\text{PP} = \text{dmpe, [123,127] dppe [128]}$) compounds show the same behavior in solution.

3.4.2. “[$\text{FeL}(\text{PP})_2$]” ($L = \eta^2(\text{C},\text{O})$ and $\eta^2(\text{C},\text{C})$ ligands) complexes

A dihapto ligand coordinated to the “[$\text{Fe}(\text{PP})_2$]” unit could be

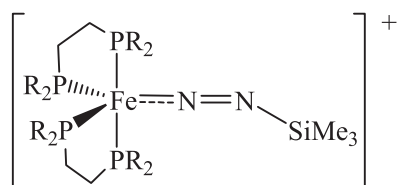


Fig. 37. Schematic representation of $[\text{Fe}\{\text{NN}(\text{SiMe}_3)\}(\text{PP})_2]^+$ ($\text{R} = \text{Me, Et}$).

structurally considered equivalent to a pentacoordinate iron compound. However, among dihapto iron compounds with diphosphanes, only a few dihapto ligands can complete the “[$\text{Fe}(\text{PP})_2$]” unit to lead *cis* iron(II) products.

Komiya *et al.* prepared $[\text{Fe}(\text{depe})_2(\eta^2\text{-(O}_2\text{C)})]^+$ by bubbling CO_2 to a THF solution of $[\text{Fe}(\text{depe})_2(\text{N}_2)]$. [176] The *cis*- $[\text{Fe}(\text{depe})_2(\eta^2\text{-(O}_2\text{C)})]^+$ compound crystallized as a distorted TB structure, and its CO_2 ligand lies on the equatorial plane in a η^2 -fashion. The ABMX spin system was identified in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and the two IR signals associated with two different $\text{C}=\text{O}$ vibrations confirm the asymmetry of this compound. Whereas the compound crystallized in a non-centrosymmetric Cc space group, there is no information about its enantiopurity. Recently, Fernández, Campos *et al.* prepared the $[\text{Fe}(\text{depe})_2\{\eta^2(\text{C},\text{O})\text{-(OCOB}(\text{C}_6\text{F}_5)_3)\}]$ compound by reaction of $[\text{Fe}(\text{depe})_2(\eta^2\text{-(O}_2\text{C)})]^+$ with $\text{B}(\text{C}_6\text{F}_5)_3$. [177] Its $^{31}\text{P}\{^1\text{H}\}$ NMR characterization at -30°C in benzene- d_6 shows a set of 3 signals with relative intensities of 1:1:2 associated to the no-equivalence of the P nuclei. This compound crystallized by spontaneous resolution at low temperature in the Cc space group, with a Flack parameter of 0.009(6).

Baker and Field identified by NMR the iron(0)–ethylene complex $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\text{depe})_2]$ mixed with *cis*- $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)\text{H}(\text{depe})_2]^+$ in a 10:90 ratio, after *in situ* irradiation of $[\text{Fe}(\text{depe})_2(\text{H}_2)]$ in ethylene (5 % mol) dissolved in pentane at low temperature. [178] The hydride product isomerized completely to the $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\text{depe})_2]$ after warming until room temperature, and its $^{31}\text{P}\{^1\text{H}\}$ NMR characterization shows two apparent triplets, characteristic of a *cis* configuration of the phosphanes. More recently, Bernskoetter *et al.* prepared $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\text{depe})_2]$ by reaction between *trans*- $[\text{FeCl}_2(\text{depe})_2]$, KC_8 and ethylene, and it crystallized in a centrosymmetric orthorhombic space group, and its geometry is TB. [146].

Bennett *et al.* prepared $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\text{pdmp})_2]$ by a sodium–amalgam reduction of *trans*- $[\text{FeCl}_2(\text{pdmp})_2]$ under ethylene. [108] The $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\text{pdmp})_2]$ compound crystallized in a centrosymmetric space group, and whereas its geometry was described as TB, with the ethylene ligand in the equatorial plane, it was also proposed as a pseudooctahedron, with the ethylene occupying one edge. The analysis of the Fe–C (ethylene) distances shows that these are significantly shorter than those reported for analogous TB iron(0) complexes, which indicates a ferracyclopropane character of the $\text{Fe-C}_2\text{H}_4$ unit due to the strong back-donation induced by the strong- σ donor and poor π -acceptor abilities of the $\text{Fe}(\text{pdmp})_2$ fragment. Both proposed structures agree with the two triplets found in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum registered at 20°C .

3.5. Heteroleptic “[$\text{Fe}(\text{PP})$]” complexes

In general, the iron “[$\text{Fe}(\text{PP})$]” fragment with only one diphosphane is mostly involved in cyclopentadienyl iron complexes and dimetallic models of hydrogenase, multimetallic compounds and metal clusters with different coordination spheres. Among them, the chiral-at-metal compounds involving single iron species were mainly obtained as racemic mixtures. The stereogenicity at the iron of these monometallic “[$\text{Fe}(\text{PP})$]” species is supported by the different nature of the non-phosphane ligands, their denticity/hapticity and the geometry and coordination number of the compounds. Diphosphanes with ethylene bridge appear in hexa- and pentacoordinated iron environments, with additional S-donor, carbonyl, diene, allene and carbene ligands. The replacement of the ethylene by other $\text{-(CH}_2)_n\text{-}$ ($n = 1, n \geq 3$) bridges has not provided any chiral “[$\text{Fe}(\text{PP})$]” heteroleptic compounds, and few examples of iron complexes bearing diphosphanes with *o*-phenylene skeleton can be found. In this section, we illustrate the structural features and preparations of these compounds.

Among the “[$\text{Fe}(\text{PP})$]” complexes with ethylene diphosphanes, various octahedral iron compounds with sulphur ligands can be found. Concretely, Markó *et al.* reported the structure of the iron complex comprising two phenyl thiolates, and the authors recognized the two *cis*, *cis*- $[\text{Fe}(\text{CO})_2(\text{dppe})(\text{SPh})_2]$ enantiomers within the cell unit of the

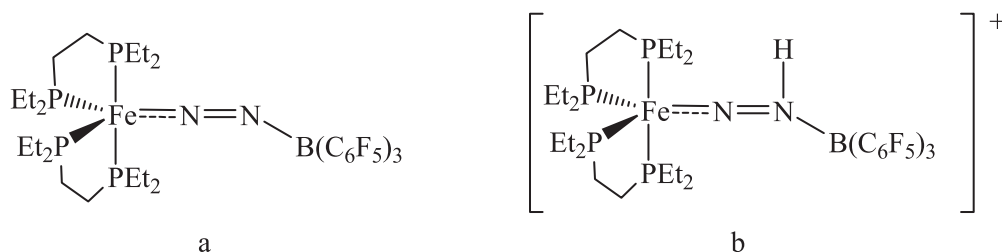


Fig. 38. Schematic representation of (a) $[\text{Fe}(\text{depe})_2\{\text{NNB}(\text{C}_6\text{F}_5)_3\}]$ and (b) $[\text{Fe}(\text{depe})_2\{\text{NN}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3\}]^+$.

centrosymmetric crystal.[179] These authors also isolated analogous compounds bearing additional SR (R = *s*-Bu, *p*-C₆H₄(Me), *p*-C₆H₄(OMe), *p*-C₆H₄{NHC(O)Me}) ligands. All these compounds were prepared by a slow reaction between FeSO₄·7H₂O, dppe, RSH and NaOMe in methanol.

Bidentate S-donor ligands can also afford Δ- and Λ-octahedral enantiomers. Bhattacharyya *et al.* found that the iron (II) and (III) $[\text{Fe}(\text{dedtc})_2(\text{dppe})]^n$ (*n* = 0 and + 1, respectively) compounds (Fig. 39) crystallized in the same P-1 centrosymmetric space group.[180] Two different methods of preparation were drawn for the reduced species: (i) from FeCl₂·4H₂O, Na(dedtc)·H₂O and dppe, (ii) from FeCl₃·6H₂O, ascorbic acid, Na(dedtc)·H₂O and dppe. A similar bidentate $[\text{Fe}(\text{etxant})_2(\text{dppe})]$ compound was also prepared following the same methodology, but no crystal was isolated. The octahedral iron (III) $[\text{Fe}(\text{dedtc})_2(\text{dppe})]\text{FeCl}_4$ compound was obtained from FeCl₃·6H₂O, NH₂OH·HCl, Na(dedtc)·H₂O and dppe precursors, and crystallized in a centrosymmetric space group. A structurally similar compound, $[\text{Fe}(\text{dmdtc})_2(\text{dppe})]\text{BF}_4$, was prepared by Boyd *et al.* and appeared as a racemic mixture in the crystallographic cell.[181] This compound was prepared in a reductive elimination reaction from $[\text{Fe}(\text{dmdtc})_3]\text{BF}_4$ and dppe.[182].

Tridentate S-donor ligands also provide “[Fe(PP)]” chiral heteroleptic compounds, such as *fac*- $[\text{Fe}(\text{CO})(\text{dppe})(\text{mps})]$ (Fig. 40).[183] This compound was prepared in moderated yield by mixing the $[\text{Fe}(\text{CO})_2(\text{mps})]_2$ dimer and two equivalents of dppe, and crystallized as a racemic mixture within a centrosymmetric space group. Surprisingly, among the possible diastereoisomers, only the conformation depicted in Fig. 40 appears in the solid state and solution.

The $[\text{Fe}(\text{dppe})(\text{edabt})]$ compound shows asymmetry because of the *cis*-α configuration of the iron complex (Fig. 41).[184] This conformer was obtained selectively both in the solid state and solution and was prepared from FeCl₂·4H₂O, dppe and a solution of H₂(edabt) previously treated with a methanolic solution of LiOMe, in THF.

Another special case of chirality is found in *mer*- $[\text{Fe}(\text{dmpe})(\text{mabt})(\text{PMe}_3)]^+$, in which the metal stereocenter is induced by the asymmetry of the mabt ligand and the disposition of the diphosphane (Fig. 42).[185] This compound was obtained in high yields by phosphane substitution between the $[\text{Fe}(\text{mabt})(\text{PMe}_3)_3](\text{OTf})$ precursor and dmpe, and subsequent crystallization. The two enantiomers were found as a

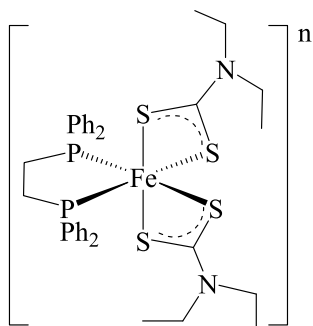


Fig. 39. Schematic representation of $[\text{Fe}(\text{dedtc})_2(\text{dppe})]^n$ (*n* = 0, 1 +).

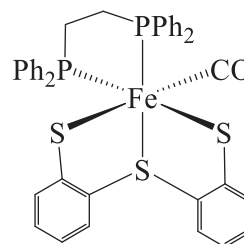


Fig. 40. Schematic representation of *fac*- $[\text{Fe}(\text{CO})(\text{dppe})(\text{mps})]$.

racemic mixture in the crystal for each of the two coordinated isomers identified because of the disorder of the dmpe and PMe₃ ligands.

Carbene “[Fe(PP)]” chiral compounds involving chelating carbenes were also described, and some pseudooctahedral geometries were found. Frühauf *et al.* isolated the single crystal of $[\text{Fe}\{\text{bicyclo}(2.2.1)\text{-}\kappa^3\text{C},\text{N},\text{O}\}(\text{CO})(\text{dppe})]$ (Fig. 43a) as two non-interconverting isomers.[186] The asymmetry of this compound exclusively originated from the asymmetry of the bicyclo. Other similar compounds with monophosphanes were reported in this work. The $[\text{Fe}(\text{CNpTol})(\text{CO})(\text{dppe})]\{\text{NpTol} = \text{C}(\text{NpTol})\text{C} = \text{NpTol-}\kappa^2\text{C},\text{C}'\}$ compound is another example (Fig. 43b)[187], which shares structural similarities with the *cis*- $[\text{Fe}(\text{CNPh})_2(\text{dppe})]\{\text{NPh} = \text{C}(\text{Me})\text{C} = \text{NPh-}\kappa^2\text{C},\text{C}'\}$ compound.[188] The synthetic procedures involve various reaction steps and start from

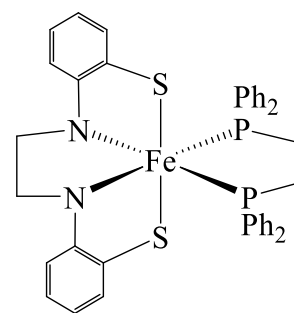


Fig. 41. Schematic representation of *cis*-α- $[\text{Fe}(\text{dppe})(\text{edabt})]$.

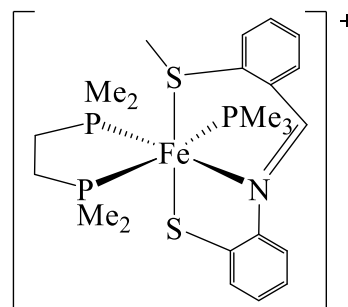


Fig. 42. Schematic representation of a chosen *mer*- $[\text{Fe}(\text{dmpe})(\text{mabt})(\text{PMe}_3)]^+$ isomer.

different precursors, namely $[\text{Fe}(\text{CNpTol})_4(\text{dppe})](\text{ClO}_4)_2$ or $[\text{Fe}(\text{CNPh})_3(\text{dppe})]$, respectively.

The TB geometry of the pentacoordinated carbene $[\text{Fe}\{\text{C}(\text{O})\text{CH}_2\text{-CH}=\text{CH}_2\}(\text{CO})(\text{NO})(\text{dppe})]$ (Fig. 44a) was described by Nakanishi *et al.* [189] NMR identification and no temperature-dependent spectral changes confirmed its structure, whereas no description about its chirality was reported. This compound was obtained by mixing $[\text{Fe}(\eta^1\text{-acyl})(\text{CO})_2(\text{NO})]$ and dppe. Hermes and Girolami determined the X-ray structure of the pentacoordinated $[\text{FeBr}(\text{CO})(\eta^2(\text{C},\text{O})\text{-CO}\{2,4,6\text{-C}_6\text{H}_2\text{Me}_3\})(\text{dippe})]$ (Fig. 44b) complex, that was described as six-coordinated with a distorted octahedral coordination geometry and as a five-coordinate TB structure. [190] This asymmetric compound was isolated in crystalline form and low yields from carbonylation of the $[\text{FeBr}(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)(\text{dippe})]$ carbene compound with 3 atm of carbon monoxide.

Diene and allene ligands are found in octahedral “[Fe(PP)]” complexes. These complexes led chiral structures in the solid state, whereas fluxional behavior can be present in solution. [191] Thus, the $[\text{Fe}(\text{depe})(\eta^3\text{-pentadienyl})_2]$ (Fig. 45) compound appears in solution as an equilibrium mixture of two isomers, *syn* and *anti*, and its X-ray structure confirms iron as a stereocenter. While this compound crystallized as $[\text{Fe}(\text{depe})(\text{syn-}\eta^3\text{-pentadienyl})_2]$, NMR identifications showed that in solution (20 °C) it exists in equilibrium with $[\text{Fe}(\text{depe})(\text{anti-}\eta^3\text{-pentadienyl})(\text{syn-}\eta^3\text{-pentadienyl})]$ as minor isomer. This compound was obtained by treatment of $[\text{FeCl}_2(\text{depe})]$ with potassium pentadienide, and obtained in moderate yields.

Other diene and allene “[Fe(PP)]” compounds with auxiliary carbonyl ligands also provided asymmetric structures that crystallized in centrosymmetric space groups, and in which the asymmetry in the iron atom is found because of the disposition of the unsaturated ligand. This is the case of $[\text{Fe}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{CO})_2(\text{dfep})]$, which was obtained by photolysis of $[\text{Fe}(\text{CO})_3(\text{dfep})]$ in Et_2O . [192] Regarding iron diphosphane/allene iron complexes, the reaction of tetracarbonyl iron precursor (Fig. 46a) with dppe in the presence of trimethylamine *N*-oxide, as a decarbonylating agent, led to a yellow (Fig. 46b) and red (Fig. 46c) compounds. [193] After several hours in solution, the yellow compound converted into red by a carbonyl ligand substitution by the second P atom to the iron. This red compound crystallized in an enantiomorphic P212121 space group, though no description of the enantiopurity of the compound was reported.

Other carbonyl ligands provided chiral at iron compounds in the crystal structure, such as *cis*- $[\text{Fe}(\text{CO})_2(\text{dppe})(\text{H})\{\text{Si}(\text{CH}_3)_3\}]$ (Fig. 47), which appears as a mixture of enantiomers. [194] This compound was prepared under UV-Vis irradiation of $[\text{Fe}(\text{CO})_3(\text{dppe})]$ with HSiMe_3 .

4. Iron compounds with polydentate phosphanes

The study of iron complexes with polyphosphanes began in the '70 s

[195–201] and has been revised on several occasions. [10,202] For a better classification of these ligands, we distinguish between linear, cyclic and tripodal phosphanes. [203].

4.1. Linear ligands

In general, linear polyphosphanes have a flexible skeleton, which allows a variety of coordination modes depending on the substituents on the P atoms and the chain length between them. [8] These ligands generally coordinate to iron when P atoms are connected by two bridging C atoms. In contrast, longer carbon chains, or even polyphosphanes with only methylene bridges coordinate to multiple Fe atoms. For example, triphosphanes with methylene linkages between P atoms are usually bidentate ligands, which form four- or six-member metallacycles leaving a free phosphane. When triphosphanes are tridentate, they act as bridging ligands between two metal atoms. [204,205] Several examples of dinuclear and trinuclear iron compounds are reported, with phosphane as a bridging ligand and without chirality (Fig. 48). [206] This type of multinuclear polyphosphane complexes is out of the scope of this manuscript.

4.1.1. Triphosphanes

The first iron compound with the tridentate linear triphosphane PhP(CH₂CH₂PPh₂)₂ (triphos) was the dinuclear $[\{\text{Fe}(\text{triphos})\}_2(\mu\text{-SH})_3]^+$ complex (Fig. 49), and it was obtained by reaction of triphos with Fe(BF₄)₂·4H₂O in the presence of SH₂. [198] Each Fe atom is bonded to three P atoms of a triphos and three S atoms of the three bridging SH groups, with triphos in *fac* configuration in a distorted octahedral environment for each metal. This compound would be chiral if both ligands were not symmetrically concerning to the plane of symmetry defined by the three S atoms.

Triphos also shows other binding modes to iron. The reaction of anhydrous FeX₂ (X = Cl, Br) with the same ligand led to the formation of the *trans*- $[\text{Fe}(\text{triphos-}\kappa^2)_2\text{X}_2]$, in which triphos acts as bidentate, leaving one terminal P atom uncoordinated. [199,207] The octahedral environment for the Fe atom is depicted in Fig. 50, with the two Cl atoms in *trans* and the two central P atoms also in *trans*. In this complex, the two central P atoms are stereogenic and have different configurations resulting in a compound in the *meso* form. The bidentate coordination for triphos was proposed in 1980 to explain the synthesis and reactivity of the hydride $[\text{Fe}(\text{Cp})\text{H}(\text{triphos-}\kappa^2)]$ complex. [208].

Surprisingly, the reduction of $[\text{FeBr}_2(\text{triphos})]$ with Na originated the chiral-at-metal *mer*- $[\text{Fe}(\text{triphos-}\kappa^2)(\text{triphos-}\kappa^3)]$ compound, with a TB structure and with a bidentate and a tridentate triphos ligands, the latter in *mer* configuration (Fig. 51a). [207,209] Additionally, the configuration of two 5 member rings of tridentate triphos breaks the plane of symmetry of *mer* disposition, thus contributing to the asymmetry of *mer*- $[\text{Fe}(\text{triphos-}\kappa^2)(\text{triphos-}\kappa^3)]$. Both enantiomers appear in

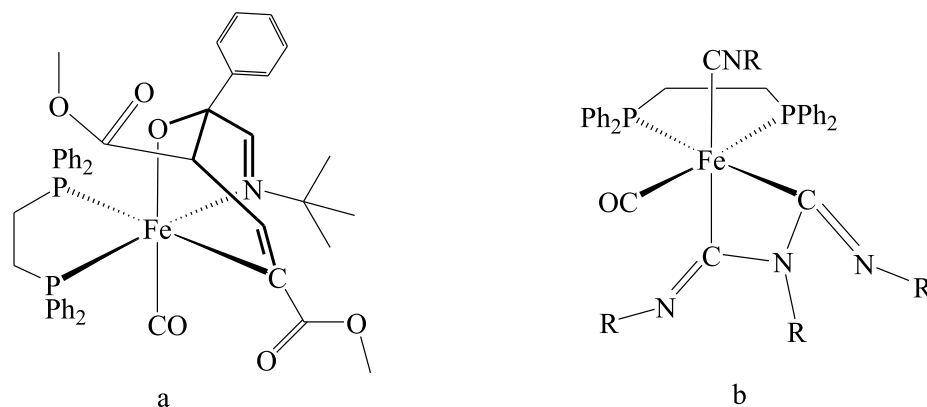


Fig. 43. Schematic representation of (a) $[\text{Fe}(\text{bicycle}(2.2.1)\text{-}\kappa^3\text{C,N,O})(\text{CO})(\text{dppe})]$ and (b) $[\text{Fe}(\text{CNpTol})(\text{CO})(\text{dppe})\{\text{CNpTol} = \text{C}(\text{NpTol})\text{C} = \text{NpTol-}\kappa^2\text{C,C}'\}]$ ($\text{R} = p\text{Tol}$).

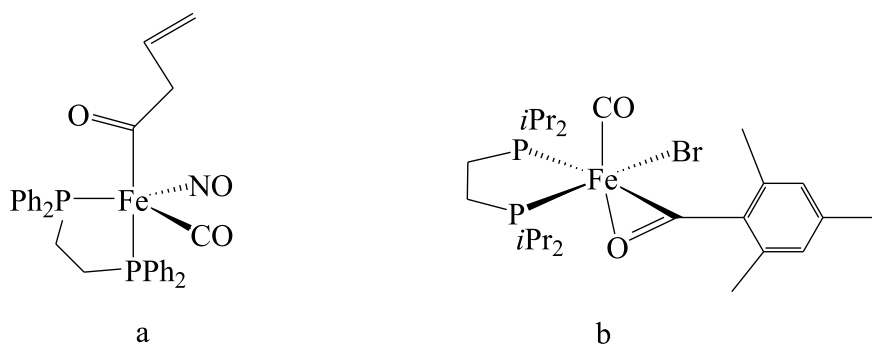


Fig. 44. Schematic representation of (a) $[Fe\{C(O)CH_2=CHCH_2\}(CO)(NO)(dppe)]$ and (b) $[FeBr(\eta^2(C,O)-CO\{2,4,6-C_6H_2Me_3\})(CO)(dippe)]$.

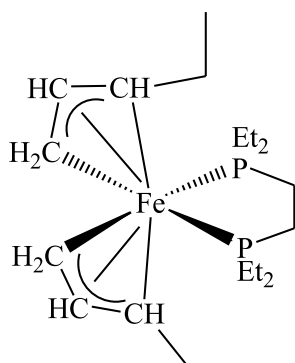


Fig. 45. Schematic representation of $[Fe(depe)(syn-\eta^3\text{-pentadienyl})_2]$.

the crystal structure, and the ^{31}P NMR for this compound confirmed the five Fe-coordinated phosphorus environments with a free phosphane. Interestingly, the *mer* configuration of triphosphane changes to *fac* in the compound *fac*- $[Fe(bpy)(triphos)]$ (Fig. 51b), which was obtained when the reduction of $[FeBr_2(triphos)]$ was carried out in the presence of bpy. [207] This compound shows a chiral SP structure with a terminal P atom in axial position, and appears as a mixture of both enantiomers in the crystallographic cell.

The compound $[FeBr_2(triphos)]$ also reacted with other ligands to form hexacoordinated compounds, however, the *mer* configuration of the phosphane hinders the formation of chiral compounds. [210] The flexibility of triphos can be verified in the formation of a mixture of two, *fac*- and *mer*- $[Fe(NCMe)_3(triphos)]^{2+}$ isomers, obtained by reaction of triphos with $[Fe(NCMe)_6](BF_4)_2$, but neither of them is chiral. [211].

A different behavior is observed with dpppp. This phosphane reacted with $FeCl_2$ in a CO atmosphere to give $[Fe(CO)Cl_2(dpppp)]$, with the phosphane in *mer* and the Cl in *cis* positions (Fig. 52a). [212] This was the first compound of this phosphane with a *mer* configuration, and isomerized to a *fac* configuration at room temperature and with ambient light, with CO *trans* to a terminal P atom (Fig. 52b). The *fac*

configuration is chiral, and its crystal structure contains both enantiomers. A third species was detected in the solution when the process was conducted at 0 °C. Several configurational isomers can be postulated for these species, and among them, the *fac* isomer, with the CO ligand *trans* to P central atom, was proposed as the most plausible isomer based on the ^{31}P NMR spectrum. [212].

If in the dppp we change the phenyl groups of the P terminals for isopropyl groups we obtain the phosphane dippp that reacts with FeX_2 (X = Cl, Br) in THF forming *fac*- $[Fe(dippp)X_2]$ compounds, whose geometry is distorted TB. The pentacoordinate compounds are chiral due to the configuration of the carbon skeleton of phosphane that links the P atoms, and the complex $[FeBr_2(dippp)]$ (Fig. 53a) crystallized as only one enantiomer in the P212121 group. [213].

The rigidity of a chosen polyphosphane could favour the formation of chiral iron compounds. The reaction of dppadp (Fig. 54a) with $FeCl_2$ provided the $[FeCl_2(dppadp)]$ pentacoordinated compound. It shows a distorted TB structure, with the phosphane in the *mer* configuration (Fig. 54b). This compound is chiral because of the disposition of the naphthalene groups, whereas the crystal lattice contains the racemic mixture of enantiomers. [214].

4.1.2. Phosphanes with more than 3P atoms

Linear phosphanes with 4 or more P atoms in the chain, such as tetraphos, have at least two stereogenic P central atoms. Both stereocenters should be stable in the complex formation since the thermal barrier for the inversion of stereogenic P atoms is ca. 125 kJ mol⁻¹. [9] This implies that isomerization reactions cannot be discarded under

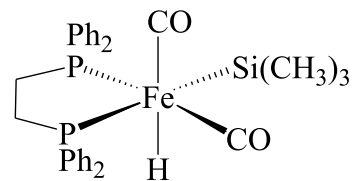


Fig. 47. Schematic representation of *cis*- $[Fe(CO)_2(dppe)(H)\{Si(CH_3)_3\}]$.

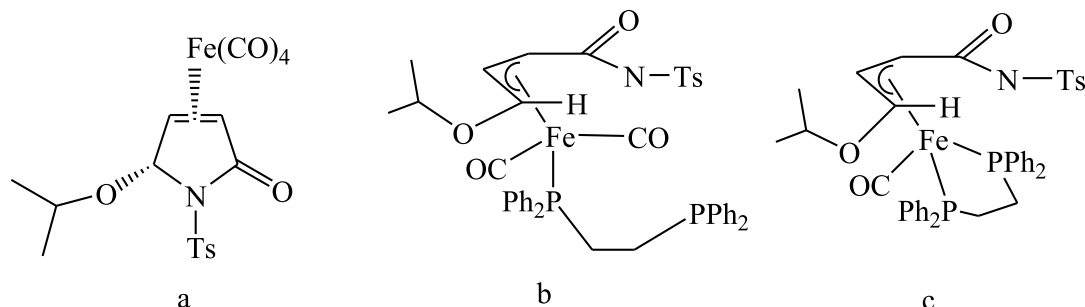


Fig. 46. Schematic representation of selected iron carbonyl complexes.

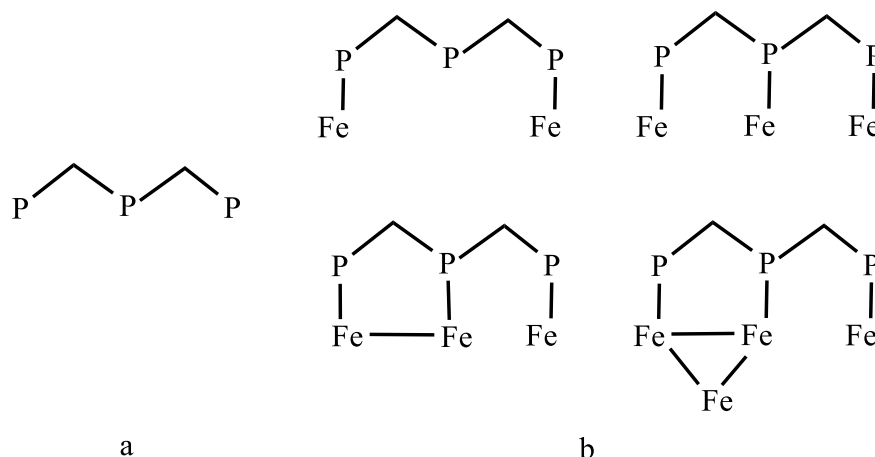


Fig. 48. Schematic representation of (a) a triphosphane with methylene bridges and (b) its coordination modes to multiple iron atoms.

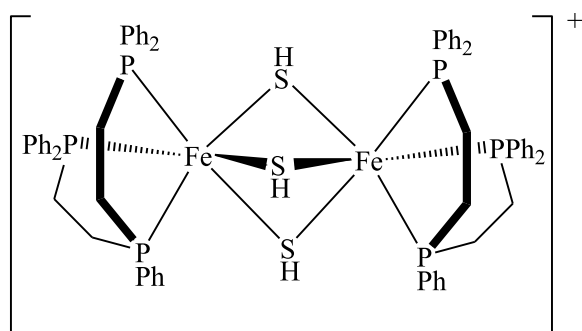


Fig. 49. Schematic representation of $[\{\text{Fe}(\text{triphos})\}_2(\mu\text{-SH})_3]^+$.

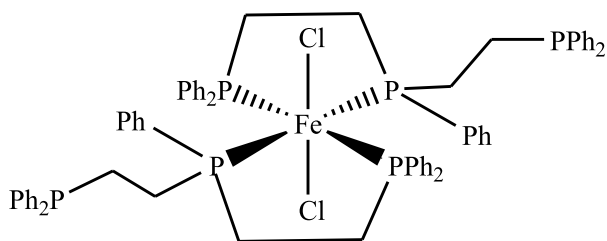


Fig. 50. Schematic representation of $\text{trans-}[\text{Fe}(\text{triphos-}\kappa^2)_2\text{Cl}_2]$.

specific experimental conditions.[215] Tetraphos appears as a mixture of two diastereoisomers, namely, as the *meso* (*S,R*) and racemic *rac* (*S,S*; *R,R*) forms (Fig. 55a).[216,217] Tetraphos can adopt different dispositions in octahedral complexes: *cis-α*, *cis-β* and *trans* for the *rac* form, and only *cis-β* and *trans* for the *meso* form (Fig. 55b).[218] The compounds

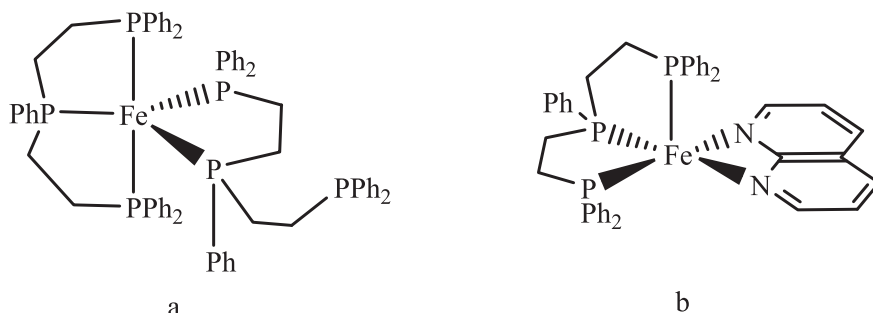


Fig. 51. Schematic representation of selected (a) $\text{mer-}[\text{Fe}(\text{triphos-}\kappa^2)(\text{triphos-}\kappa^3)]$ and (b) $\text{fac-}[\text{Fe}(\text{bpy})(\text{triphos})]$ enantiomers.

with *trans* disposition are not chiral, whereas the *cis* dispositions are chiral and include Δ and Λ enantiomers.

In NCME, $[\text{Fe}(\text{NCMe})_6](\text{BF}_4)_2$ reacts with *rac*-tetraphos gave selectively the *cis-α*- $[\text{Fe}(\text{NCMe})_2(\text{rac-tetraphos})]^{2+}$ octahedral complex, as a mixture of enantiomers (Fig. 56a shows the Λ enantiomer).[218] The structure is chiral at the metal centre, and the two enantiomers appear in the crystal cell. In contrast, the reaction with *meso*-tetraphos provided the achiral *trans-β*- $[\text{Fe}(\text{NCMe})_2(\text{meso-tetraphos})]^{2+}$ octahedral complex (Fig. 56b), instead of the chiral *cis-β* complex.[216,219]

Pentacoordinate compounds with tetraphos (in the *meso* form) can be obtained with *cis-β* configurations, as described by the reaction between tetraphos and FeBr_2 to give the $[\text{FeBr}(\text{meso-tetraphos})]^+$ complex (Fig. 57).[220] It depicts a TB structure, and the Br atom is located in the equatorial position. This iron compound is chiral and the two enantiomers are present in the crystal structure.

Tetraphosm is a similar phosphane with a methylene group as a

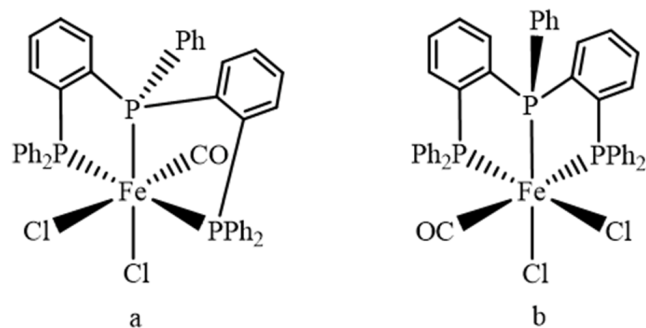


Fig. 52. Schematic representations of the (a) *mer* and (b) *fac* configurations of $[\text{Fe}(\text{CO})\text{Cl}_2(\text{dpppp})]$.

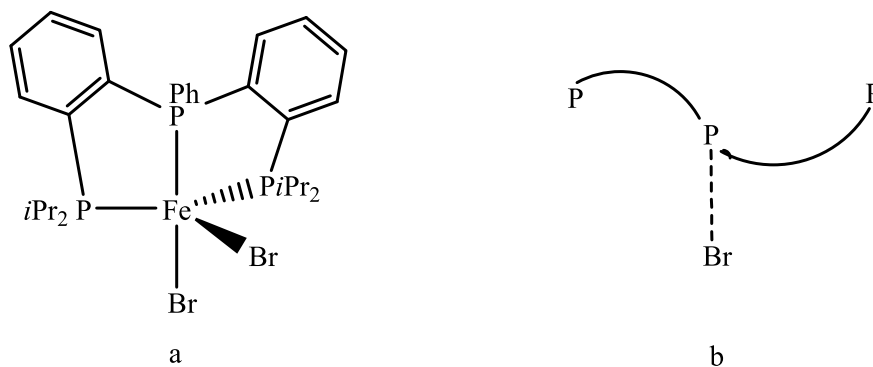


Fig. 53. Schematic representation of (a) $[\text{FeBr}_2(\text{dipp})]$ and (b) simplified version through the Fe-P central bond.

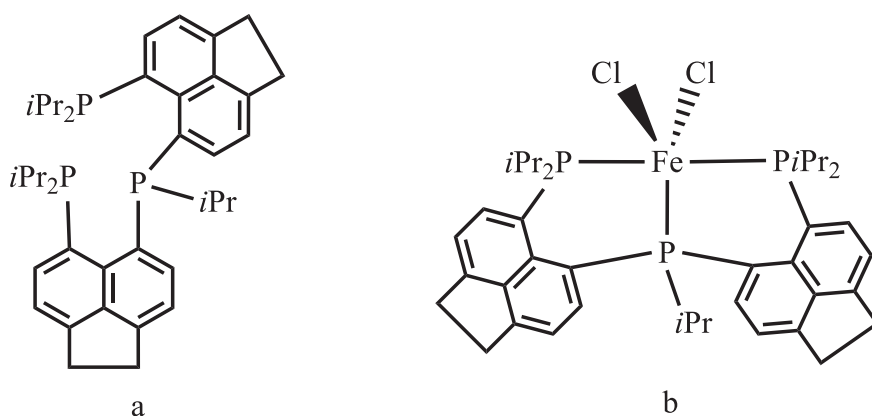


Fig. 54. Schematic representation of the structure of (a) dppadp and (b) $[\text{FeCl}_2(\text{dppadp})]$.

bridge between the two central P atoms, and we find similar possibilities for complex formation. For example, the *rac*-tetraphosm reacted with FeX_2 ($\text{X} = \text{Cl}, \text{Br}$) to give $[\text{Fe}(\text{rac-tetraphosm})\text{X}_2]$ with *cis- α* configurations, with both enantiomers present in each crystal structure. This phosphane in the *meso* form can act as tridentate, leaving an uncoordinated P with *mer* configuration and the other three positions occupied by monodentate ligands, to give non-chiral complexes based on NMR interpretation.[221] Furthermore, the low denticity of the phosphane provided the octahedral and chiral-at-metal $[\text{FeBr}(\text{meso-tetraphosm-}\kappa^2)]$ (*meso-tetraphosm-FeBr κ -3*) complex (Fig. 58), with two and one

terminal P atoms for the respective bidentate and tridentate ligands, unlinked to the Fe(II).[222] This compound crystallized as a racemic mixture within a centrosymmetric space group. When the bridge between the two central P atoms of the tetraphosmane is a propyl group, *trans* and *cis- α* iron derivatives were obtained for the *rac* and only the *trans* isomer for the *meso* form.[223] The compound with *cis- α* configuration is chiral, but the two enantiomers are found in the crystal.

The linear tetraphosphane tppropyl (Fig. 59a) has propyl groups between P atoms and all P atoms are stereogenic. It was prepared as a mixture of diastereoisomers (2 *meso* forms and 4 enantiomeric pairs) and

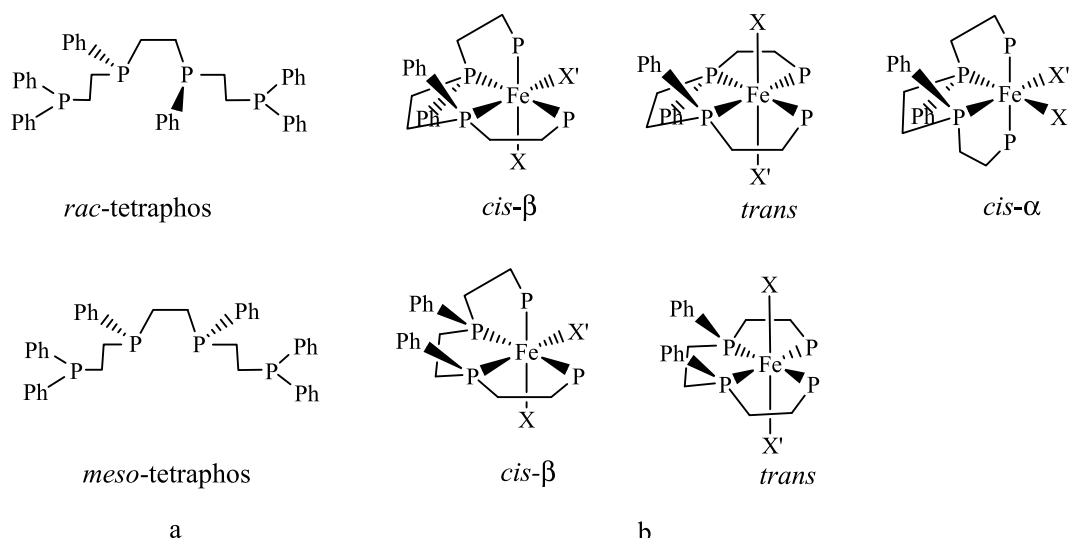


Fig. 55. Schematic representations of (a) tetraphos ligands and (b) derived octahedral iron complexes.

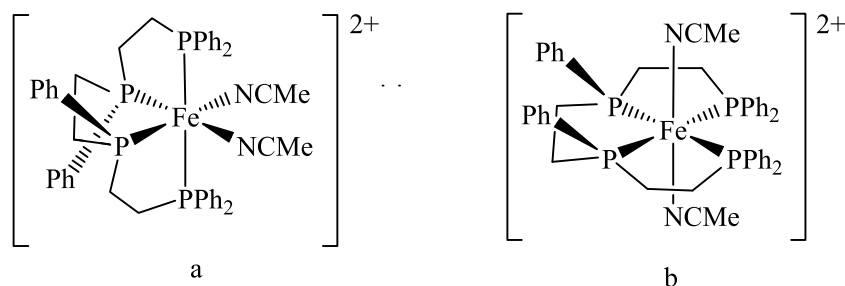


Fig. 56. Schematic representation of the hexacoordinated iron tetraphos complexes: (a) Λ -*cis*- α -[Fe(NCMe)₂(S,S-tetraphos)]²⁺ and (b) *trans*-[Fe(NCMe)₂(*meso*-tetraphos)]²⁺.

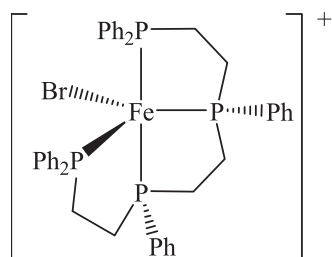


Fig. 57. Schematic representation of the pentacoordinate *cis*- β -[FeBr(*meso*-tetraphos)]⁺ complex.

reacted with FeCl₂ in THF to give *cis*- α -[FeCl₂(tppropyl)] (Fig. 59b). [153] This configuration was assigned by NMR and at least two diastereoisomers were identified in solution.

Another example of chiral iron polyphosphane structures bearing 4- and 5-membered rings is the Fe(II) *cis*- α -[Fe(CO)Cl(mhtp- κ^4)]Cl octahedral compound, in which the mhtp hexaphosphane is tetracoordinated leaving two terminal P atoms uncoordinated (Fig. 60). [224] This compound is chiral at the metal and central P atoms because of the formation of the complex. It means that the two central P atoms, which that were previously associated with the achiral polyphosphane, are now stereogenic. The *cis*- α configuration forces the P atoms to have different conformations. Considering exclusively the central P atoms, one is *R* and the other must be *S*, leading to a *meso* form comprised into the *cis*- α configuration of the iron complex. This behavior contrasts with that previously described for *meso*-tetraphos, which after coordination with Fe(II) gives the *cis*- β instead *cis*- α configurations. Concerning metal, the two Δ - and Λ -*cis*- α -[Fe(CO)Cl(mhtp- κ^4)]⁺ enantiomers are present in the crystal structure. The authors proposed the separation of the enantiomers by crystallization with a chiral anion, but we have not found any published work on the matter.

A different hexaphosphane is ehtp, which contains an ethyl group bridging the two central P atoms. The position of P atoms resembles the positions of the donor atoms in EDTA, which would allow ehtp to be a hexadentate ligand. Surprisingly, the reaction of ehtp with FeCl₂·6H₂O

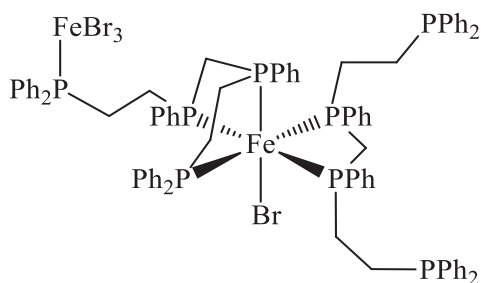


Fig. 58. Schematic representation of [FeBr(*meso*-tetraphosm- κ^2)(*meso*-tetraphosm-FeBr₃- κ^3)].

in the presence of ammonium hexafluorophosphate afforded [FeCl(ehtp)]PF₆. [225] The presence of the tetradentate phosphane in the pentacoordinated [FeCl(ehtp)]⁺ complex was proposed in the basis of its magnetic moment (2.3 BM), but no information about its structure and chirality was provided.

4.1.3. Tridentate ligands with different donor atoms

Polydentate ligands (with denticity equal to or greater than 3) containing different donor atoms represent an interesting area in the field of iron stereochemistry, due to the possibilities of formation of isomers with different coordination modes.

The modes of coordination of tridentate ligands around the iron metal determine the number of expected isomers due to geometrical conditions provided by the rigidity and the asymmetry of the ligand on one hand, and the number of coordination and the possibilities of ligand coordination to the metal, on the other hand. These factors are crucial in the selective preparation of chiral at iron complexes. Accordingly, in octahedral iron complexes, tridentate ligands can give a *fac* or *mer* coordination depending on their flexibility, thus providing more possibilities of isomerism centred at metal. This flexibility is also extended to pentacoordinated complexes.

Most of these ligands contain at least one P and one N atom, and the rest of the donor atoms are highly variable, encompassing O, C, and S atoms. In most of these ligands, their asymmetry is responsible for chirality upon iron coordination. We will describe the derived iron compounds according to the donor atoms.

Without a doubt, the most numerous and most studied ligands are those that contain 2P and one N as donor atoms. The complexes formed by Fe and PNP ligands have been used as effective catalysts in organic transformations and this interest has increased in the last years. [226–231] However, among the stereoisomers identified, there are only a few examples of chiral-at-iron compounds with this kind of ligands.

The most common PNP ligands are the pyridine derivatives with substituents at positions 2 and 6. Given their rigid structure, the complexes formed have the *mer* configuration and generally the chirality is absent in penta- and hexacoordinated complexes. These PNP pincer ligands generally react with FeX₂ (X = Cl, Br) to form pentacoordinate [Fe(PNP)X₂] complexes, with a more or less distorted SP geometry and one halide in apical position (Fig. 61a). [232–236] In the presence of L, octahedral *cis*- and *trans*-[FeL(PNP)X₂] (L = CO, N₂) (Fig. 61b and c) were obtained. [237,238] In the strict sense, the two 5-membered rings present in each compound are not coplanar and the molecule is not symmetrical, the deviation from regularity is small and in solution, the configurations of the rings would exchange easily. Thus, chirality is absent in common PNP iron complexes, however, the substituents on P atoms influence the structure of the iron complex. It is evidenced if we consider two similar phosphanes dpmpy and dbmpy, the latter has *tert*-butyl while the former has *iso*-propyl as substituents on the P atoms. Both reacted with FeCl₂ to form [FeCl₂(PNP)] and after reduction in the presence of CO, provided the [Fe(CO)₂(PNP)] derivatives. In the case of the *iso*-propyl derivative, the geometry is TB [238] as would be expected for a compound of Fe(0), but in the case of the *tert*-butyl derivative, its

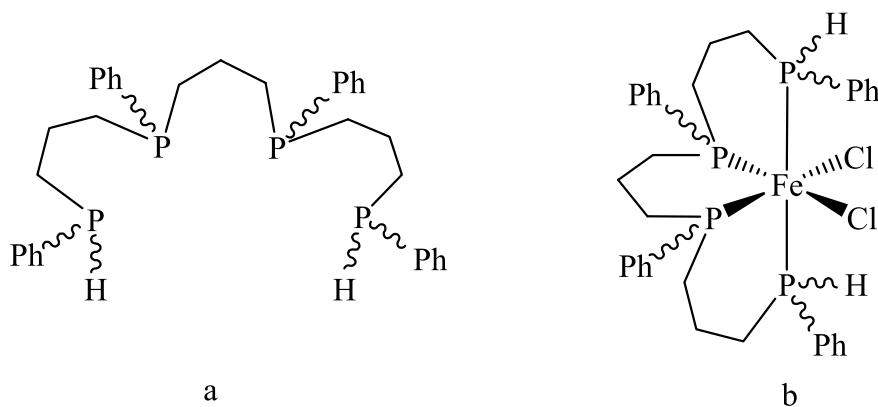


Fig. 59. Schematic representation of (a) tppropyl and (b) *cis-α*-[FeCl₂(tppropyl)].

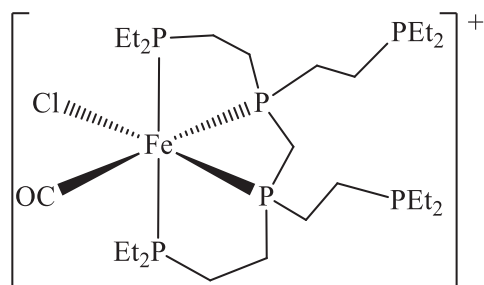


Fig. 60. Schematic representation of Δ-*cis-α*-[Fe(CO)Cl(mhtp-κ⁴)]⁺.

geometry is SP. [233] In whatever case, both compounds are achiral.

The change of the CH₂ bridge by NH leads to a similar reactivity of the derived PNP ligands, however, the rigidity imposed by the pyridino group again prevented the formation of iron chiral derivatives in most of the cases, although, in these compounds, the deviation from planarity is more pronounced when the substituents of the P atoms are smaller (Me or Et versus Ph). [239–242] For this kind of PNP ligand, only the presence of stereogenic P atoms allowed the synthesis of chiral complexes. [241,243].

Other PNP iron compounds with κN,κ²P and κN,κP coordination forms were reported. [244–246] They are not chiral, (the deviation from planarity is small) and even if various isomers are possible, only one of them was detected.

Ligands that contain different substituents on the terminal P atoms, that is, PNP' ligands, could form chiral-at-iron compounds more easily. Whereas they involve a less simple preparation than symmetric PNP analogues, have similar behaviour and complexes formed have less symmetry. Kirchner studied iron complexes with PNP' ligands, in which the bridge was derived from 2,6 di-amino-pyridine. [247].

Hexacoordinated complexes of the form *mer*-[FeBr₂(CO)(PNP')] (Fig. 62) can be identified as *cis* (Fig. 62) or *trans*. [248] The *trans* isomer

is not chiral, but the *cis* is chiral. The crystal structure of *cis* isomer contains both enantiomers.

In the case that the 3 additional ligands to PNP' ligand are different (Fig. 63), several isomers can be formed, and the diastereoisomers obtained are inseparable. [229,249].

In the case of PONOP ligands, in which the two terminal groups of the PNP ligand are phosphites or phosphinites, their tridentate coordination and rigidity prevent the isolation of chiral iron complexes. [250–252].

The use of more flexible ligands can lead to different modes of coordination that may involve the formation of chiral-at-iron compounds. However, the reaction of FeCl₂ with NH(CH₂CH₂PR₂)₂ (R = *i*Pr, Cy, *t*Bu) (PNP^R) led to the formation of the non-chiral pentacoordinate [FeCl₂(PNP^R)] compounds, that crystallize in SP and TB distorted structures. In the former, the apical position is occupied by a Cl, while in the latter, the axial positions are occupied by an N and a Cl. [253] Whereas this distortion provides some kind of asymmetry for each compound, it is expected to disappear in solution. The expected non-chiral hexacoordinated *trans,mer*-[Fe(CO)(PNP^{iPr})X₂] (X = Cl, Br) compounds were reported, with CO *trans* to the N atom. [254–256].

The reaction of dmea with FeCl₂ in methanol allowed the synthesis of *fac*-[Fe(dmea)₂]²⁺ with two tridentate ligands. [257] Although three isomers with meridional, symmetric facial, and asymmetric facial

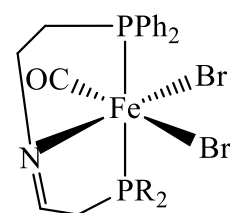


Fig. 62. Schematic representation of one enantiomer of *cis*-[FeBr₂(CO)(PNP')] (R = Cy, *i*Pr).

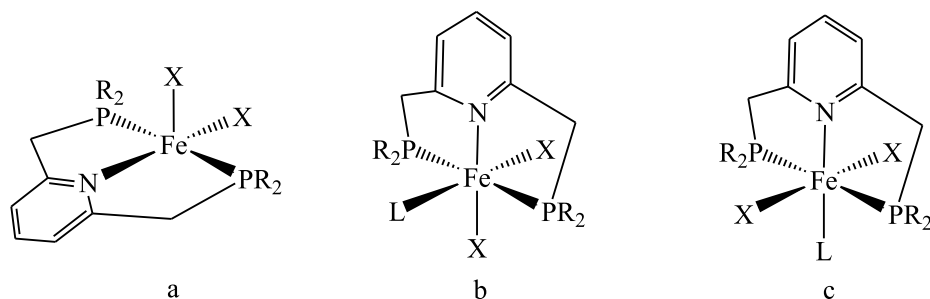


Fig. 61. Schematic representation of PNP complexes (X = Cl, Br, L = CO, N₂).

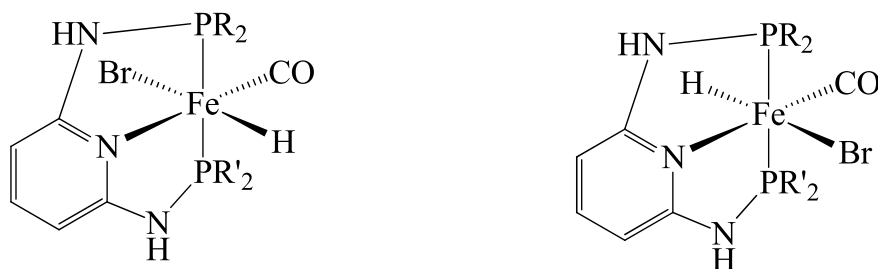


Fig. 63. Schematic representation of two hexacoordinated iron isomers with PNP'.

structures are possible for the former complex, only one isomer with *fac* structure and N *trans* to P atom was isolated (Fig. 64). This structure is chiral, although both enantiomers are found in the crystal structure. Probably, the strong *trans* influence of the P prevents the formation of the more symmetric isomers (*mer* and *fac*) with two P-Fe-P groups in *trans* positions.

Other tridentate linear ligands containing the sequence NPN, such as bppp, reacted with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to form the $[\text{Fe}(\text{bppp})_2]^{2+}$ octahedral complex, with the ligands disposed in *fac* and with the P atoms in *cis* (Fig. 65). [258] Various structures can be formulated with this stoichiometry, but given the strong *trans* effect of P atoms, the isomer with P in *trans* is expected to be less stable, and only the isomer with *cis* P atoms was obtained. The compound is chiral and crystallized as a racemic mixture.

A different ligand distribution around the Fe atom is observed with PNN-type ligands derived from 2,6-disubstituted pyridines. When the terminal N donor group is a pyridine, as dipp, its reaction with FeX_2 ($X = \text{Cl}, \text{Br}$) provided $[\text{Fe}(\text{dipp})\text{X}_2]$ or the bis-chelate $\text{mer}-[\text{Fe}(\text{dipp})_2]^{2+}$ (Fig. 66) complexes, with distorted TB and octahedral structures, respectively. [259] Because of the rigidity imposed by the bipyridyl group, the ligand adopts a *mer* configuration. These compounds are chiral and appear as both enantiomers in their crystalline state.

Similar mono- and bis-tridentate iron (II) compounds were obtained containing another kind of PNN ligands, in which the pivotal N atom does not belong to the pyridine ring but an imino group, with preservation of the phosphane and pyridine terminal groups. These compounds crystallized as racemic mixtures. [260] Bis-tridentate *mer*- $[\text{Fe}\{\text{R}_2\text{PCH}_2\text{CH}=\text{NCH}_2(\text{C}_5\text{H}_4\text{N})\}_2]^{2+}$ ($\text{R} = \text{Ph}, \text{Cy}$) octahedral complexes have been prepared by Morris *et al.* [261] Whereas this ligand is more flexible than the 2,6-disubstituted pyridine analogues, the *mer* configuration was obtained for these complexes being the origin of its chirality and C_2 symmetry. The low quality of the diffraction data only confirmed the *mer*-octahedral arrangement.

The reaction of different types of PNN ligands (in which the terminal N group is a dialkyl amine, as dbap, or quinoline, as aqpn) with FeCl_2 provided pentacoordinate $[\text{FeCl}_2(\text{dbap})]$ (Fig. 67) or $[\text{Fe}(\text{aqpn})\text{Cl}_2]$ compounds, both with SP structure and a Cl atom in the apical position. The reported compounds are chiral, and the crystal structure contains both enantiomers. [232,262].

The reaction of FeCl_2 with a more flexible ligand, such as dppba, provided a chiral $[\text{FeCl}_2(\text{dppba})]$ (Fig. 68a) species, with TB geometry and halides in the equatorial position. [263] The asymmetric disposition of the two 6-membered metallacycles is the origin of the asymmetry to

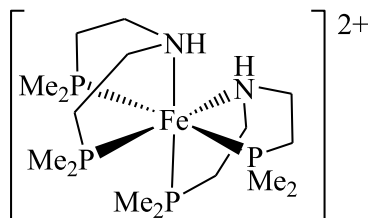


Fig. 64. Schematic representation of *fac*- $[\text{Fe}(\text{dmea})_2]^{2+}$.

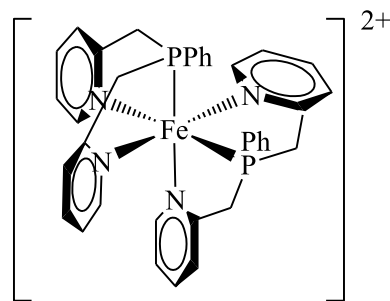


Fig. 65. Schematic representation of *fac*- $[\text{Fe}(\text{bppp})_2]^{2+}$.

the iron complex (Fig. 68b).

Chiral bis-tridentate complexes with *mer* configuration were prepared from a PNN ligand, with a terminal amino group in place of pyridine. These can be classified according to the aliphatic skeleton between the two N atoms: in the case of being achiral ($-\text{CH}_2-\text{CH}_2-$), the compound obtained shows C_2 symmetry and the crystal structure contains the two enantiomers; in the case of a chiral bridge ($-\text{CH}(\text{Ph})-\text{CH}(\text{Ph})-$), only one isomer was formed with complete diastereoselectivity at iron (Fig. 69). [261,264].

Flexible PNN ligands are also present in chiral tetracoordinate compounds, such as that represented in Fig. 70, which crystal structure contains both enantiomers. [265].

Ligands with more than 3 donor atoms, such as the PN_3 ligands, could behave as a tridentate NPN ligand. This is the case of the *tpmp*

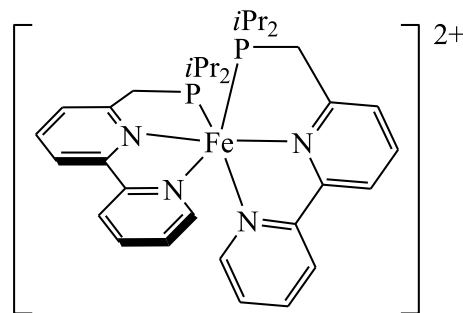


Fig. 66. Schematic representation of *mer*- $[\text{Fe}(\text{dipp})_2]^{2+}$.

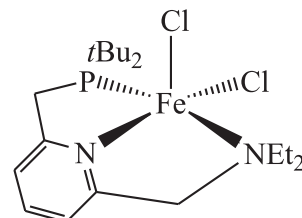


Fig. 67. Schematic representation of $[\text{FeCl}_2(\text{dbap})]$.

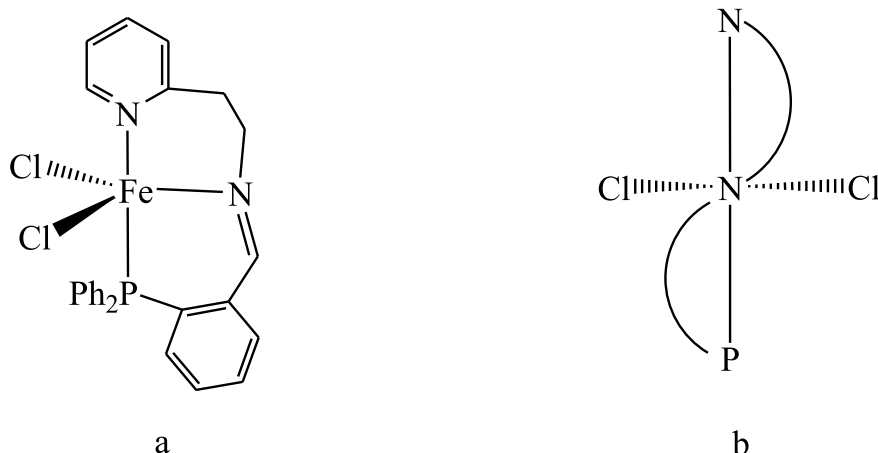


Fig. 68. (a) Schematic representation of $[\text{FeCl}_2(\text{dppba})]$ and (b) simplified vision of one enantiomer through N(imino)-Fe axis.

which reacts with FeBr_2 to form $\text{fac}-[\text{Fe}(\text{tpmp}-\kappa^3\text{N},\text{N}',\text{P})_2]^{2+}$ (Fig. 71). [266] Various structures can be formulated with this stoichiometry, but since the $^{31}\text{P}\{^1\text{H}\}$ NMR signal is unique and the strong *trans* effect of P, the two isomers with *trans* P atoms (*fac* and *mer*) are expected to be less stable and only the isomer with *cis* P atoms was obtained. This structure only has a C_2 axis and the two enantiomers are present in the solid.

The substitution of a terminal N donor group by other O-, S- or C-donors leads to an increase of possible iron isomers. This is illustrated by the case of the PNO ligands, such as pnoH (Fig. 72a), which after reaction with FeCl_2 led the *mer*- $[\text{Fe}(\text{pnoH})_2]^{2+}$ (Fig. 72b) octahedral complexes. [263] Given the asymmetry of the ligand, the Fe complex is chiral, and the crystal structure shows the presence of both enantiomers. The *mer*- $[\text{Fe}(\text{pno})_2]$ compound, which was prepared by deprotonation of the ligand and subsequent addition of FeCl_2 , shows in the ^1H and ^{31}P NMR spectra broad signals at room temperature that sharpen when the temperature decreases. This fluxionality was interpreted based on the decoordination of one end of the ligand to form a pentacoordinated species with the isomerization between the two configurations. More interesting is the reaction of this same ligand with FeCl_3 . This reaction produces the dinuclear $[\text{Fe}_2\text{Cl}_6(\text{pnoH})_2]$ compound, which contains the *mer*- $[\text{Fe}(\text{pnoH})_2]^{3+}$ cation, and a mixture of Cl^- , $[\text{FeCl}_4]^{2-}$ and $[\text{FeCl}_5]^{2-}$ as anion. The cation is chiral and isostructural to the above-mentioned Fe(II) complexes, and its structure shows a homochiral chain of complexes.

The reaction between the iron atom and a tridentate ligand with P, N and S as donor atoms afforded the bimetallic and chiral *mer*- $[\text{Fe}(\mu\text{-S}\{\text{R}_2\text{PCH}_2\text{CH}=\text{N}(\text{C}_6\text{H}_4)\text{S}\})_2\text{FeBr}_2]$ (R = Ph, Cy) species. [261] The compound with R = Ph (Fig. 73) crystallized in a centrosymmetric group with both stereoisomers in the structure. This compound shows a C_2 symmetry and a pseudo-octahedral and a pseudo-tetrahedral

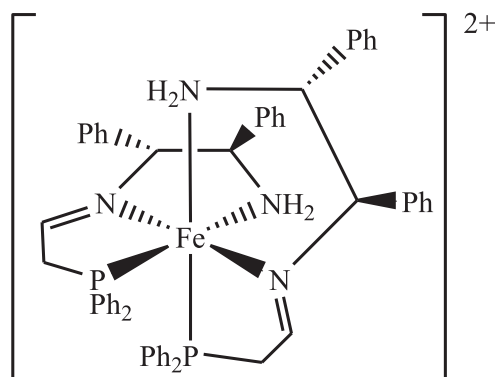


Fig. 69. Schematic representation of $\text{mer}-[\text{Fe}(\text{NNP})_2]^{2+}$.

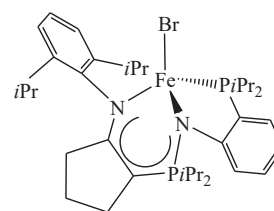


Fig. 70. Schematic representation of a tetrahedral $[\text{FeBr}(\text{NNP})]$ compound.

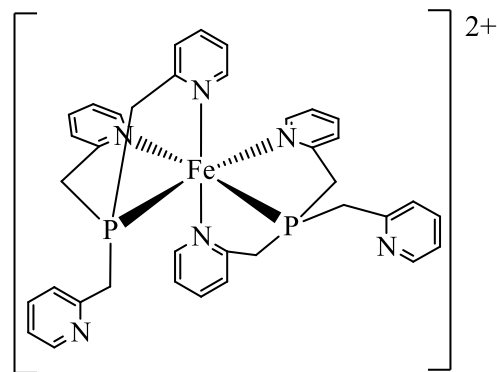


Fig. 71. Schematic representation of $\text{fac}-[\text{Fe}(\text{tpmp}-\kappa^3\text{N},\text{N}',\text{P})_2]^{2+}$.

environments for the respective Fe atoms.

Another type of asymmetric tridentate ligands is those containing PNC as donor atoms. Complexes with ligands of this type were obtained by the insertion of CO in the reaction of $[\text{Fe}(\text{CO})_4\text{I}_2]$ with 2,6-diaminopyridine derivatives (pnc), forming chiral *cis*- $[\text{Fe}(\text{CO})_2(\text{pnc})(\text{X})]^{n+}$ (X = I, OTf, n = 0; X = H_2O , n = 1; Fig. 74) complexes. [267] In all cases, the solids are present as racemic mixtures. The reaction of *cis*- $[\text{Fe}(\text{CO})_2\text{I}(\text{pnc})]$ with AgBF_4 in NCMe provided $[\text{Fe}(\text{CO})(\text{NCMe})_2(\text{pnc})](\text{BF}_4)$, and both the *cis* and *trans* isomers co-crystallized in the crystal.

4.1.4. Tetradentate ligands with different donor atoms

Ligands with a denticity greater than 3 and with different donor atoms represent an area that has experienced great growth in recent years due to their application as catalysts. [268–273] Within these ligands, those with a P_2N_2 group as donor atoms were widely studied. These ligands contain the sequence PNNP as donor atoms with different bridges between donor atoms (2 or 3C atoms) and different substituents in the P atoms (Fig. 75). The N atoms belong to the imino or amino groups.

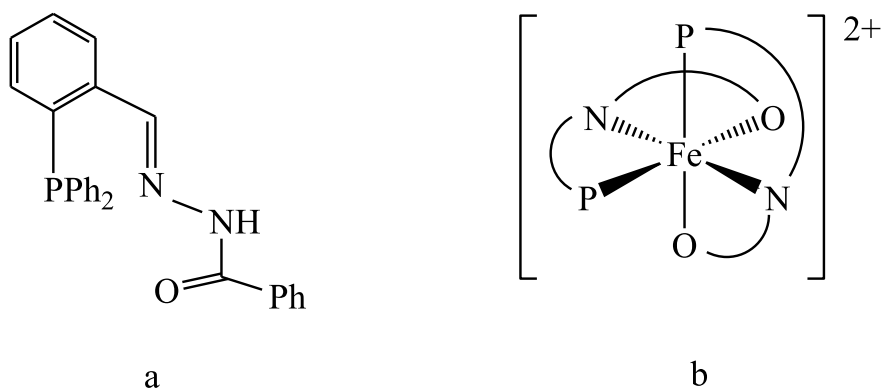


Fig. 72. Schematic representation of: (a) pnoH and (b) *mer*-[Fe(pnoH)₂]²⁺.

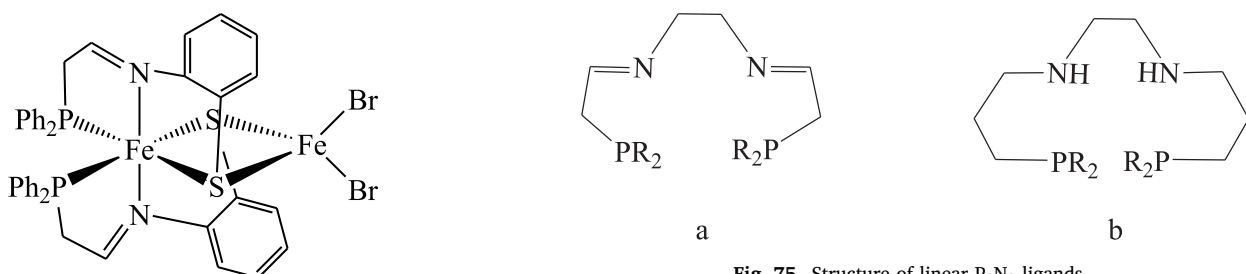


Fig. 73. Schematic representation of *mer*-[Fe(μ-S{Ph₂PCH₂CH=N(C₆H₄)S}₂)FeBr₂].

The first iron PNNP complexes studied contain imino groups and skeletons of 2 and/or 3C atoms as linkers and octahedral complexes are obtained with two additional ligands occupying *trans* positions (Fig. 76). [264,274–278] Pentacoordinate complexes have also been described in the form of SP, with the fifth ligand occupying the axial position. [272] If the ligand is symmetric, the complexes formed are achiral.

Similar PNNP iron compounds were prepared, in which the N atoms belong to amino groups and the N become stereogenic centres in the formation of complexes, and in this case, the *trans* compounds formed are mixtures of two isomers. In one of them, the crystal structure shows that the two NH groups point in opposite directions concerning with the plane defined by the P atoms and the Fe atom, while in the other, the two NH groups probably have the same orientation. [275] Together with these compounds with configuration *trans*, in the case of the analogous iron compound bearing imino PNNP ligand, the reduction of imino to amino supposes the formation, with a lower yield, of hydrido complexes [Fe(CO)(H)(PNNP)]⁺ with *cis-β* configuration. Their structure shows that the metal is Δ -*cis-β*, while the conformation of both N is *S* (Fig. 77). [279].

Linear PNNP phosphanes that contain 2 chiral carbons in the bridge between N atoms appear in iron complexes with a similar *trans* configuration depicted in Fig. 76. [270] The reduction of only one imino group to amino supposed the appearance of a new stereogenic centre and the

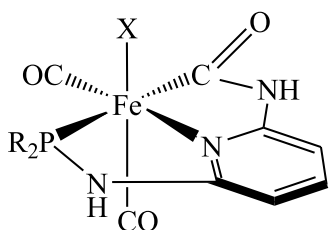


Fig. 74. Schematic representation of *cis*-[Fe(CO)₂(pnc)(X)] (X = I, OTf; R = Ph, *i*Pr).

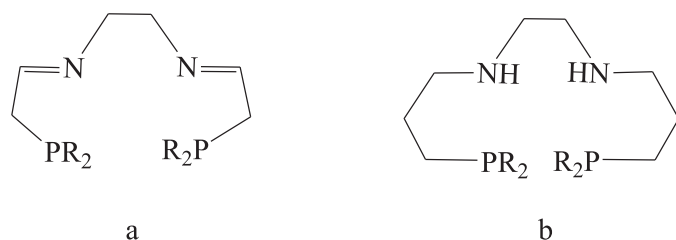


Fig. 75. Structure of linear P₂N₂ ligands.

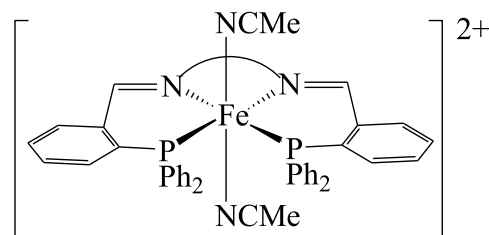


Fig. 76. Schematic representation of *trans*-[Fe(NCMe)₂(PNNP)]²⁺.

iron compounds were obtained in the form of two diastereoisomers, which were initially formulated as *trans*, [269] although a more detailed study showed that the configuration was *cis-β*. In this case, we have two chiral centres, the metal and N, but only two diastereoisomers are observed, one that is Δ -*cis-β* for the metal and *R* for N and the other that is Λ -*cis-β* for the metal and *S* for N. [41,280,281] The two diastereoisomers co-crystallized in the asymmetric unit (Fig. 78).

A different behavior is observed when the sequence of donor atoms in the P₂N₂ ligand is NPPN instead of PNNP, with bridges containing 2 or 3C atoms between donors. In this case, the P atoms are chiral and three diastereoisomers are possible. An octahedral iron complex involving the

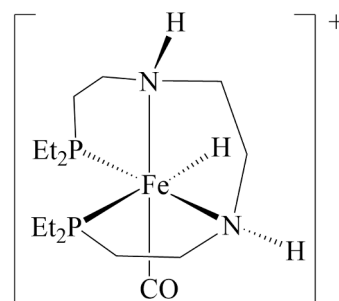


Fig. 77. Schematic representation of Δ -*cis-β*-[Fe(CO)(H)(*S,S*)-(PNNP)]⁺.

S,S isomer of NPPN (Fig. 79a) was described with *cis-α* configuration (Fig. 79b). The compound is chiral at iron, and only the Λ isomer can be obtained with the *S,S* isomer of phosphane. [282].

Ligands with other sets of donor atoms, such as P_2S_2 or PNSP, are analogous to those already described for P_2N_2 , and form octahedral complexes with Fe, mostly with a *cis-α* configuration, leaving two vacant *cis* positions. Thus, the pssp ligand (Fig. 80a) reacted with $[Fe(NCMe)_6]$ (CF_3SO_3)₂ forming $[Fe(NCMe)_2(pssp)]^{2+}$, as a *cis-α* chiral octahedral complex (Fig. 80b). [283] The crystal structure contains both enantiomers. Substitution of an NCMe for a hydride or a carbonyl gave rise to the $[Fe(NCMe)H(pssp)]^+$ complex, which can exist in the form of 4 diastereoisomers.

The reaction of $[Fe(H_2O)_6](BF_4)_2$ with pnsP ligand (Fig. 81a) gave $[Fe(NCMe)_2(pnsP)]^{2+}$ complex (Fig. 81b) with *cis-α* configuration. [284] The two NCMe ligands that complete the coordination sphere are not stereochemically equivalents, and the substitution of one of them by a hydride led to the selective formation of the complex with the hydride *trans* to the amine group.

Iron compounds with ligands of the P_2O_2 form have been prepared by different routes from that described for compounds with P_2N_2 or P_2S_2 ligands, and show similar structures to those described in section 2.3.

4.2. Cyclic polyphosphanes

Macrocyclic polyphosphanes with 3 or 4P atoms in 9–14 membered rings present diverse diastereoisomers (due to stereocenters of P atoms) and only some of them can form chelate iron complexes. After coordination, those polyphosphanes with 3P atoms exhibit *fac* isomerism, while those with 4P atoms and rigid rings present SP geometries. [285] Iron complexes with this type of phosphanes are scarce, probably due to the difficulty in their synthesis, their air instability, and the formation of stereoisomeric mixtures. [286–288] In addition, iron polyphosphane complexes were used as a scaffold for the preparation of polyphosphanes. [286,289–291] Although the isolation of the resulting free phosphane has hardly been reported, [292] in other cases it is not simple and an oxidized phosphane was obtained. [293].

Other iron complexes with cyclic polyphosphanes and with additional donor atoms, like O, S or N, were reported but did not always correspond to chiral-at-metal complexes. We have classified these polyphosphanes into two groups, depending on the interaction with iron: (i) those in which the coordinating atoms are exclusively P, and (ii) those in which the coordinating atoms are P and other donors.

The polyphosphane represented in Fig. 82 belongs to the group (i). [294,295] This complex contains a macrocycle P_2N_2 , with two P atoms, bonded terminally to each N. Whereas P_2N_2 show different potential anchoring points for iron, the N atoms are not coordinated to iron and the phosphane binds exclusively through four P atoms, with two additional ligands in the *cis* position to complete the coordination. Given the ligand symmetry, this complex lacks chirality.

Similar behavior is observed with another P_2N_2 cycle, which contains two additional phosphane groups bonded to each P atom of the

cycle. In this case, an octahedral Fe(II) complex is formed (Fig. 83a) in which the N atoms are not bonded to the metal, the 4P atoms occupy equatorial positions, and the two additional ligands are placed in *trans* positions. This compound can be reduced to a paramagnetic Fe(I) pentacoordinate complex, with the fifth ligand in the apical position (Fig. 83b). [296,297] None of these compounds are chiral.

Within the second group (ii) of cyclic polyphosphanes, those with a P_2N_2 group as donor atoms have been widely studied. In these cases, the P atoms are stereogenic and if amino groups are present, the N atoms are also stereogenic. Therefore, phosphanes present various diastereoisomers and only specific isomers, in which the free electronic pairs of the donor atoms have the appropriate orientation, can form chelates. [298] Macrocyclic P_2N_2 ligands with 14- or 16-member rings (Fig. 84) and with the NPPN sequence of donor atoms can be prepared and isolated in the form of various optical isomers. Only when the orientation of the free electronic pairs of the donor atoms is appropriate can form chelates. [298] Octahedral complexes with this kind of macrocyclic ligands can be *trans* or *cis*.

The *trans* complexes with macrocyclic P_2N_2 ligands do not provide more chirality than that provided by the cyclic P_2N_2 ligand. As in the case of linear P_2N_2 ligands with amino groups, the formation of the complex involves the appearance of two new chiral centres in the N atoms, and in this case, given the symmetry of the ligand, there are two *trans* diastereoisomers. In contrast, the *cis* compounds with macrocyclic P_2N_2 have metal-centered chirality with a *cis-β* coordination (Fig. 85). As in the case of polyphosphanes, the configuration of the P atoms determines which of the two *cis-β* isomers (Δ or Λ) is formed. With the *S,S* isomer of phosphane, only the Λ isomer is possible. Reducing the imino to amino groups increases the number of chiral centres in the molecule, but given the configuration of the complex, only a few configurations are possible at the new chiral centres. Thus, in this Λ -*cis-β* case, the N atoms must be *R*. The substitution of NCMe ligands by other monodentate ligands (Br, CO) allowed the synthesis of new complexes, in which the configuration Λ around the metal is maintained. [299].

The bridge between the P atoms in macrocyclic P_2N_2 ligands can be a group propane-1,3-diyl or a group ethane-1,2-diyl and, whereas in both cases different iron isomers are initially formed, only the *cis-β* isomer is obtained as thermodynamic product, and with an Λ environment around the metal. [300].

Macrocycles of 14, 16, 18, 20 and 22 atoms with a P_4N_2 combination and NPPNPP sequence were prepared. Given the high inversion barrier of the phosphanes, these cycles can be presented in two *rac* forms and three *meso* forms. [301–304] For the phosphane nppnpp, the 5 diastereoisomers have been characterized. [305,306] Only the 4*R*,7*R*,13*S*,16*S* (or the equivalent 4*S*,7*S*,13*R*,16*R*) diastereoisomer (Fig. 86a) reacted with Fe(II), giving an octahedral complex (Fig. 86b) with 4P atoms in the equatorial plane and the axial positions are occupied by N atoms. [307] This complex shows no chirality in iron

These macrocycles were obtained by reaction of a diastereoisomeric mixture (*rac* and *meso* isomers) of diphosphanes $Ph(H)P(CH_2)_n P(H)Ph$ ($n = 2-5$) with paraformaldehyde and the corresponding primary amine.

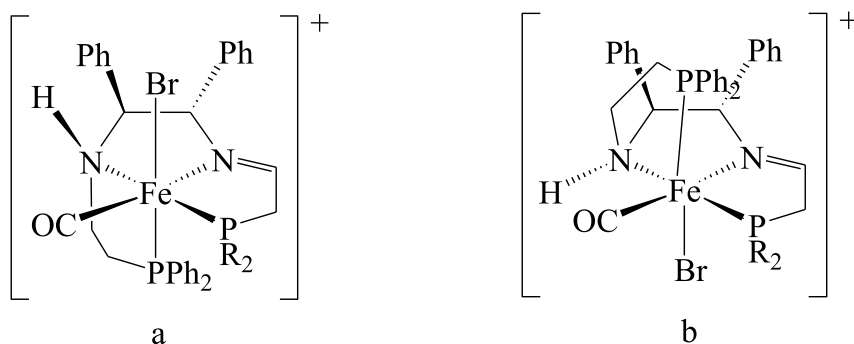


Fig. 78. Iron PNNP isomers with *cis-β* configurations (a) Δ and (b) Λ ($R = Et, iPr, Cy, Ph$).

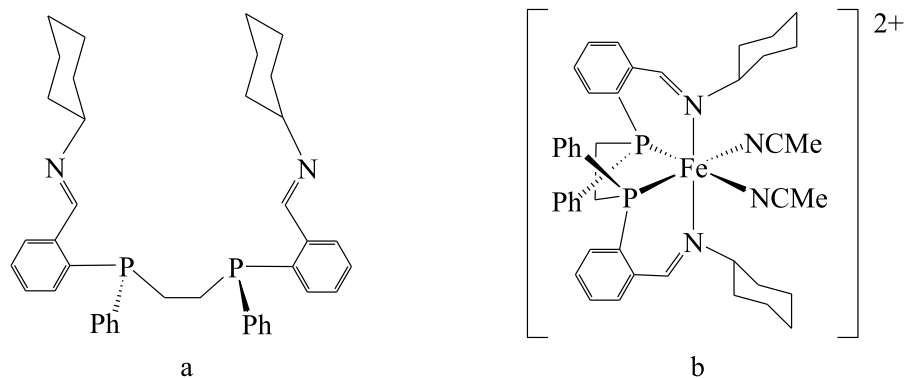


Fig. 79. Schematic representation of (a) linear (S,S)-NPPN ligand and (b) the iron Λ -cis- α enantiomer involving (S,S)-NPPN ligand.

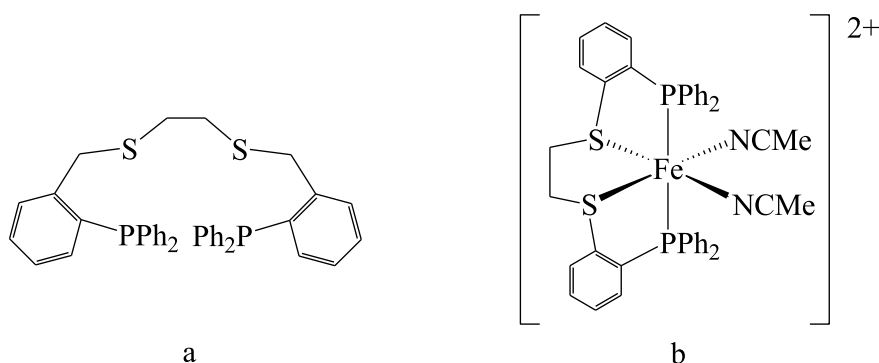


Fig. 80. Schematic representation of (a) pssp ligand and (b) one enantiomer of the complex with Fe.

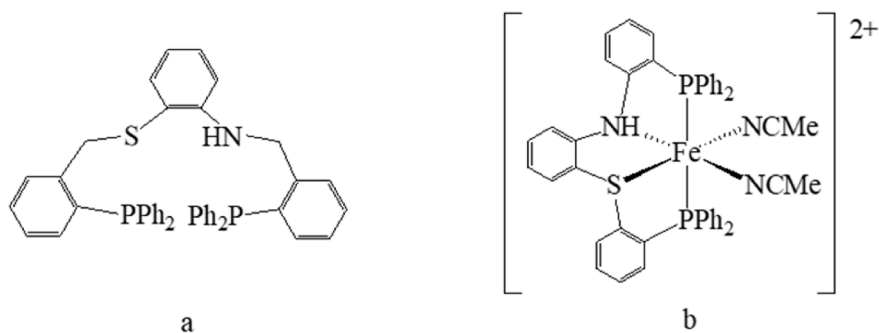


Fig. 81. Schematic representation of (a) pnp ligand and (b) its complex with iron.

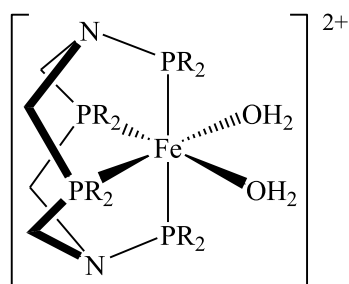


Fig. 82. Schematic representation of an iron (II) complex containing a macrocycle P₂N₂ ligand (R = CH₂OH).

[301] The number of diastereoisomers of these cyclic tetraphosphanes is 5, but the above reaction produces only one stereoisomer in moderate to good yields.[303] Complex formation is only possible in the case of the enantiomer having the appropriate configuration of the P atoms. In

some cases, in the formation of a complex, the corresponding interconversion to an enantiomer with the appropriate configuration was observed. The complexes with Fe have been little studied, and for the 16-membered cycle, octahedral complexes are formed with tetraphosphane and two NCMe ligands in *trans* positions.[308,309].

22-membered macrocycles with two P atoms in the ring are known, but the different isomers of these cycles, as well as the complexes they form with iron, are not well characterised.[310,311].

4.3. Non-linear ligands

4.3.1. Tripodal ligands

The tripodal phosphanes have the general formula E{(CH₂)_nPR₂}₃ or E{(o-Ph)PR₂}₃, with E = CR', SiR', N, BR'; n = 0–2; R = alkyl or aryl groups and R' usually H, Me or Ph. In the case of E = P, the resulting tetraphosphane will be treated in the next section. In general, the geometry of the tripodal phosphanes could infer a behavior as tridentate ligands, or as tetradentate when the apical atom interacts with the metal

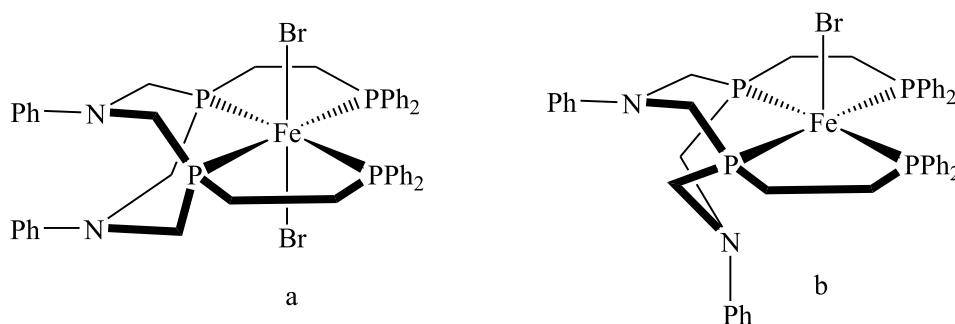


Fig. 83. Schematic representation of (a) and (b) complexes with P_2N_2 ligand.

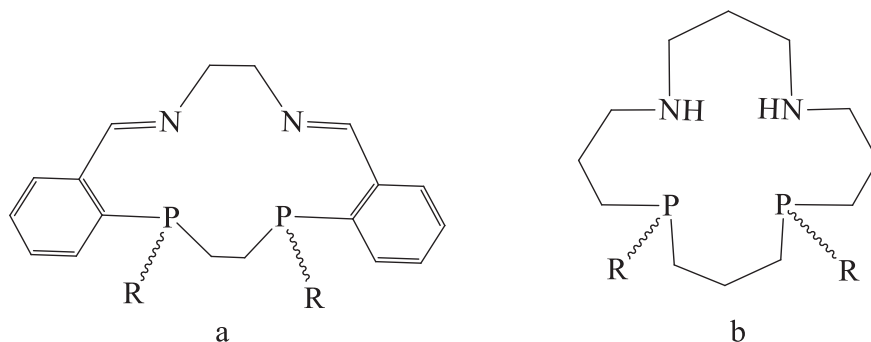


Fig. 84. Structure of macrocyclic P_2N_2 ligands.

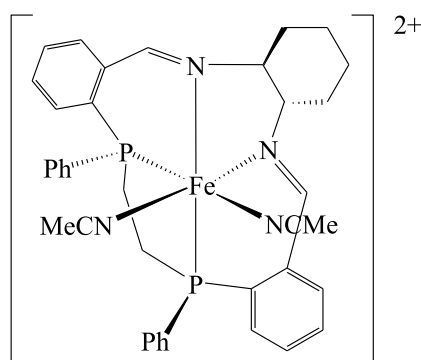


Fig. 85. Schematic representation of a *cis-β* complex with a macrocyclic (S_P, S_P)- P_2N_2 ligand.

atom. Their facial disposition in SP , TB or octahedral configurations leaves *cis* positions vacant for other ligands, a situation that is useful in many catalytic processes.[202] Moreover, in many cases the tripodal

phosphanes shows great flexibility in their modes of coordination, in fact, they could act as bidentate ligand with a free phosphane,[312] and show a reversible κ^3/κ^2 interconversion, which is highly relevant in catalytic processes.[313].

The reactivity of tripodal phosphanes $CH_3C((CH_2)PR_2)_3$ ($R = Et, Ph$) and iron began to be investigated more than 40 years ago. From *tdpme* and FeX_2 ($X = Cl, Br$) precursors, various complexes with general formula $[Fe(tdpm)_2(\mu-X_3)]^+$ were prepared, with a structure formed by two octahedra sharing a face and *tdpme* adopting a facial disposition (Fig. 87).[200,314] In this facial arrangement of the ligand, the carbon skeleton of the phosphane arms adopts a helix-like configuration that confers chirality to the compound.[315] This phenomenon occurs not only in dinuclear but also in mononuclear complexes and it is a consequence of the coordination to the metal since the tripodal ligand is not chiral. The description of this kind of chirality at metal was reported only on a few occasions and it is revisited in this section. In the cases in which the structure was determined, it is verified that the two enantiomers are present. In the case of the dinuclear compounds described, the configuration of the two phosphanes arms is the same, which means that the plane containing the three X atoms is a plane of symmetry and

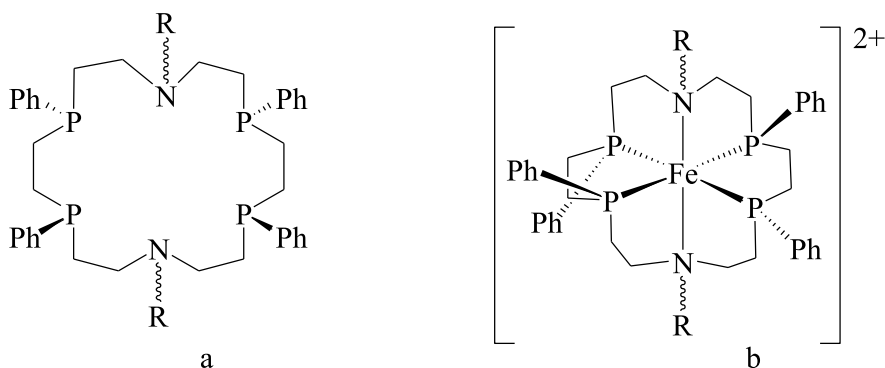


Fig. 86. Schematic representation of *nppnpp* (4*R*,7*R*,13*S*,16*R* diastereoisomer; $R = Propyl$) and the derived $[Fe(nppnpp)]^{2+}$ compound.

the molecule is not chiral.

The reaction of Fe(II) halides and the tdpme in THF gave the tetra-coordinate $[\text{Fe}(\text{tdpme-}\kappa^2)\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes, with the phosphane as bidentate. After dissolution of $[\text{Fe}(\text{tdpme-}\kappa^2)\text{X}_2]$ in NCMe, an octahedral $[\text{Fe}(\text{NCMe})_3(\text{tdpme-}\kappa^3)]^{2+}$ complex is obtained, with the phosphane in *fac* position (Fig. 88).[312] The helix-like configuration of the carbon skeleton of the phosphane arms prevents the existence of a plane of symmetry, and this molecule is chiral because of the helix-like ligand disposition, with both enantiomers present in the crystal, although the interconversion of the enantiomers is likely to have low activation energy and easy racemization in solution.[316].

The reaction of $[\text{Fe}(\text{NCMe})_3(\text{tdpme-}\kappa^3)]^{2+}$ complex with bdt gives rise to the formation of the 16 electrons $[\text{Fe}(\text{bdt})(\text{tdpme})]$ compound (Fig. 89), with a distorted SP environment and with a phosphorous atom in the apical position. The oxidation with $[\text{Fe}(\text{Cp})_2]\text{PF}_6$ gave $[\text{Fe}(\text{bdt})(\text{tdpme})]^+$ with the same distorted SP structure.[317,318] Both compounds are chiral due to the helix-like configuration of tripodal ligand and appear as racemic mixtures in the solid state.

The chirality of the $[\text{FeL}_3(\text{tdpme-}\kappa^3)]^{2+}$ octahedral complex depends, not only on the helix-like configuration of the carbon skeleton but also on the nature of the three ligands L. If the ligands L are different, we obtain chiral compounds with the iron atom as a stereocenter. This is the case of the $[\text{Fe}(\text{CO})\text{H}(\eta^2\text{-H}_2)(\text{tdpme-}\kappa^3)]^+$ complex (Fig. 90), which was obtained in a single step by mixing tdpme, Fe(II) halides and BH_4 . The fluxionality of this compound, even at very low temperatures, prevented the isolation of possible stereoisomers.[319–321].

The homoleptic $[\text{Fe}(\text{tdmme})_2]^{2+}$ compound was prepared from tdmme and FeCl_2 . [315] The Fe atom is surrounded by six phosphorus atoms of two facially coordinated tdmme ligands to form a slightly distorted octahedron (Fig. 91). Also in this compound, the tdmme ligands are twisted to the same hand around the C_3 axis, affording chirality to the cationic complex due to the skeleton dispositions of the two ligands. A racemic mixture of isomers is present in the crystallographic unit cell.

The $\text{HC}(\text{PPh}_3)_3$ (tdppm) can act as monodentate, bidentate, tridentate or bridging ligand. The reaction of $[\text{Fe}(\text{Cp})(p\text{-xylene})]\text{PF}_6$ with tdppm gave $[\text{Fe}(\text{Cp})(\text{tdppm-}\kappa^3)]\text{PF}_6$. [322] This compound is strongly stressed, due to the 4-membered rings it contains and reacts rapidly in NCMe displacing one arm of the tdppm ligand by an NCMe and afforded $[\text{Fe}(\text{Cp})(\text{NCMe})(\text{tdppm-}\kappa^2)]^+$. Based on NMR data, only one of the two possible isomers (*exo* or *endo* at C central) is formed.

Tripodal phosphanes, in which the P atoms are different because they are not bonded to the same terminal groups, have the form $\text{RC}(\text{P}(\text{P}'))(\text{P}'')$ and are chiral due to C. These ligands form octahedral complexes whose chirality lies in the ligand. Complexes with this type of ligands containing three NCMe as additional ligands have been described, so the chirality at iron has not been studied until present. [323].

A range of tripodal ligands containing B, Si, N or other elements as apical atoms and with varied functionality is known. [324] Dinuclear compounds were obtained with the phosphane as tridentate, in a facial disposition and Si as central atom, similarly to those obtained with C. The same lack of symmetry appears in the crystal structure due to the twist of the skeleton around the C_3 axis as in bridge carbon derivatives. A notable difference between the phosphanes with Si concerning those

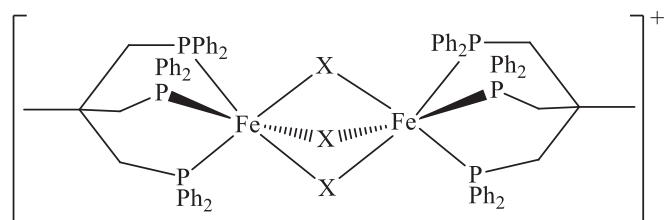


Fig. 87. Schematic representation of $[\{\text{Fe}(\text{tdpme})\}_2(\mu\text{-X}_3)]^+$.

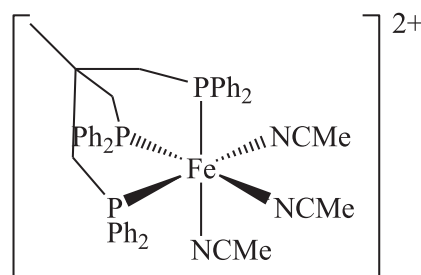


Fig. 88. Schematic representation of $[\text{Fe}(\text{NCMe})_3(\text{tdpme-}\kappa^3)]^{2+}$.

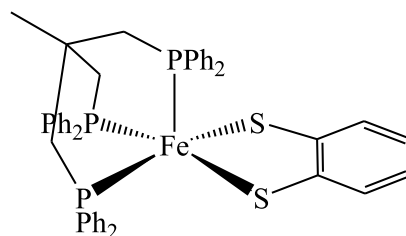


Fig. 89. Schematic representation of $[\text{Fe}(\text{bdt})(\text{tdpme})]$.

with C as central atoms is the greater facility of the former to act as a bidentate, leaving an uncoordinated arm in the formation of tetra-coordinate iron species. [312,325] For example, $\text{PhSi}(\text{CH}_2\text{PPh}_2)_3$ (tpps) reacted with FeCl_2 to give the tetrahedral and paramagnetic $[\text{FeCl}_2(\text{tpps-}\kappa^2)]$ product. When this complex is dissolved in coordinating solvents, such as NCMe, the $[\text{Fe}(\text{NCMe})_3(\text{tpps-}\kappa^3)]^{2+}$ complex is formed, which results to be diamagnetic and wherein the phosphane is tridentate occupying *fac* positions. The equilibrium between octahedral and tetrahedral species depends on the solvent used and the temperature. [325].

The reaction of $[\text{Fe}(\eta^6\text{-C}_6\text{H}_6)(\text{PMe}_3)_2]$ with $\text{MeSi}(\text{CH}_2\text{PMe}_2)_3$ (tmps) afforded the dinuclear chiral compound $[\{\text{Fe}(\text{tmps})\}_2(\mu\text{-C} = \text{CH}_2)(\mu\text{-H})_2]$ (Fig. 92). [326,327] It crystallized in the P212121 non-centrosymmetric space group.

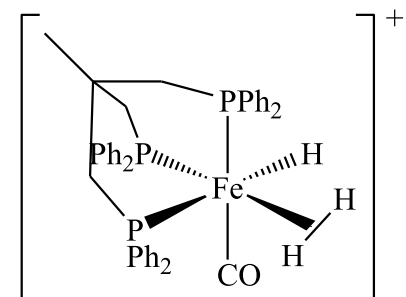


Fig. 90. Schematic representation of one of the isomers of $[\text{Fe}(\text{CO})\text{H}(\eta^2\text{-H}_2)(\text{tdpme-}\kappa^3)]^+$.

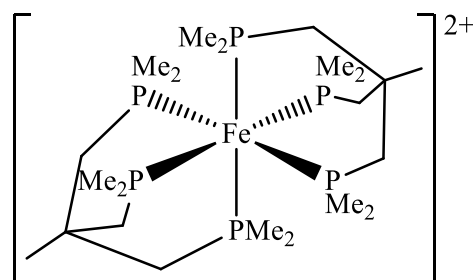


Fig. 91. Schematic representation of $[\text{Fe}(\text{tdmme})_2]^{2+}$.

If the silane has a *t*Bu group instead of the Me, the dinuclear $\{[\text{Fe}(\text{tmpstBu})_2(\mu\text{-Cl}_3)]\text{Cl}$ compound is obtained, which by reaction with diphosphane ligands (PP) led to $[\text{FeCl}(\text{PP})(\text{tmpstBu})]^+$ (Fig. 93a), which is a hexacoordinated Fe(II) compound with tmpstBu in facial arrangement.[328,329] The twist of the phosphane arms is the only property that makes the iron complex asymmetric. Interestingly, the $[\text{FeCl}(\text{PP})(\text{tmpstBu})]\text{A}$ compound crystallized as a racemic mixture when $\text{A} = \text{Cl}^-$, whereas it resolved spontaneously into a unique enantiomer when $\text{A} = \text{BPh}_4^-$. [328] The reduction of this mononuclear compound with Na gave the pentacoordinated asymmetric Fe(0) species, $[\text{Fe}(\text{PP})(\text{tmpstBu})]$, with a distorted SP structure (Fig. 93b).

Studies of reactivity between iron and tripodal phosphinites, with general formula $\text{R}^i\text{Si}(\text{OPR}_2)_3$, are scarce, and no chiral-at-iron derivative was reported. The *tppos* phosphinite, as well the analogue *tpps* phosphane, reacted with $\text{Fe}(\text{O}_3\text{SCF}_3)_2$ in NCMe giving the respective octahedral $[\text{Fe}(\text{NCMe})_3(\text{tppos})]^{2+}$ and $[\text{Fe}(\text{NCMe})_3(\text{tpps})]^{2+}$ complexes. [330] The chirality at the iron of these complexes is due to the helix-like configuration of the phosphinite.

In the most common tripodal phosphanes, both in the case of being C and Si the apical atoms, its metalation can be produced to form both Fe (II) and Fe (I) $[\text{FeL}(\text{phosphane-}\kappa^1\text{E},\kappa^3\text{P})]$ species, being $\text{E} = \text{C}$ or Si and L diverse ligands, such as H, Cl, Br, N_2 , CO, H_2 , which structures show little deformed TB geometries.[331–334] The coordination of the central atom (E) to iron provided three helix-like 5-membered metallacycles, in contrast to the tripodal complexes described above, which are 6-membered. Tripodal phosphanes with *ortho*-phenylene bridges, such as $\text{HC}\{(o\text{-C}_6\text{H}_4)\text{PiPr}_2\}_3$ (*tippm*), reacted with FeX_2 ($\text{X} = \text{Br}, \text{I}$) to give the tetracoordinate $[\text{Fe}(\text{tippm-}\kappa^2)\text{X}_2]$ complexes. The reduction of these compounds with Na afforded also tetracoordinate complexes but with a tridentate phosphane, $[\text{Fe}(\text{tippm-}\kappa^3)\text{X}]$. In this complex, the methine proton is located within the ligand cage pointed linearly to the iron atom. This molecule is chiral, and the crystal structure shows both enantiomers. Further reduction gives the octahedral $[\text{FeH}(\text{N}_2)(\text{tippm-}\kappa^1\text{C},\kappa^3\text{P})]$ and N_2 placed *trans* to metallated carbon (Fig. 94).[331] Similar metalation reactions occur when the apical atom is Si with the formation of pentacoordinated chiral compounds of Fe(I) or Fe(II) $[\text{Fe}(\text{phosphane-}\kappa^3\text{P},\kappa^1\text{Si})\text{X}]$ ($\text{X} = \text{Cl}, \text{CO}, \text{N}_2$), in the form of distorted TB.

When the apical atom is N and the arm is ethyl, the phosphane generally acts as a tetradentate ligand. Octahedral complexes with two auxiliary ligands (usually a hydride and a neutral ligand, as N_2 or CO, in *cis* position (Fig. 95a)), [335,336] or pentacoordinate compounds (containing a halogen or a nitrosyl ligand) with a distorted TB structure (Fig. 95b) were formed.[337,338] These complexes are chiral due to helix-like chiral octahedral or BP structure, and both enantiomers are present in the crystal.

The asymmetric ligands of the $\text{NP}_2\text{N}'$ form derived from NP_3 , in which a P donor is replaced by an N, led hexacoordinated iron compounds with two auxiliary ligands in which the P atoms occupy *trans* positions, and with a symmetric disposition of the carbon skeletons, and the plane containing the N and Fe atoms is a symmetry plane. In consequence, these compounds do not present chirality (Fig. 96). [262,339] The analogous pentacoordinate complex $[\text{FeCl}(\text{NP}_2\text{N}')^+]$ has a TB structure with Cl and amine N in axial positions, similar to the compound depicted in Fig. 95b. This structure is chiral because of the

helix disposition of the aliphatic chains, with both enantiomers in the crystal structure.

Tripodal phosphanes with B as an apical atom compound afforded pseudo-tetrahedral compounds, with a halide or N_2 as the fourth ligand. This last compound resulted successfully in the catalytic conversion of N_2 to ammonia.[340,341] These compounds are chiral due to the helix-like configuration of the phosphane ligand, and the complex $[\text{FeCl}\{\text{PhB}(\text{CH}_2\text{PiPr}_2)_3\text{-}\kappa^3\text{P}\}]$ crystallized as only one stereoisomer in the P212121 group.[340].

The apical atom can also be Al or Ga, and in these cases, the ligand corresponds to the EP_3 anion, which formed pseudo-tetrahedral $[\text{Fe}(\text{EP}_3\text{-}\kappa^3\text{P})\text{X}]$, ($\text{X} = \text{Cl}, \text{Br}$) or pentacoordinated $[\text{Fe}(\text{EP}_3\text{-}\kappa^1\text{E},\kappa^3\text{P})\text{X}]$ species with TB structure and with X and E in axial positions. Reduction of these species with Na and under a nitrogen atmosphere provided $[\text{Fe}(\text{EP}_3\text{-}\kappa^1\text{E},\kappa^3\text{P})(\text{N}_2)]$ with the same TB structure.[340,341] As in the previous case, the compounds are chiral due to the helix-like configuration of the phosphane.

The presence of different substituents on the P atoms in tripodal ligands allowed the formation of iron complexes with less symmetry. [339] For example, the synthesis of $\text{EP}_2\text{P}'$ ligands is not simple and limits their use as ligands in complex formation. Penta- and hexa-coordinated iron complexes were prepared with $\text{NP}_2\text{P}'$ ligands, but the two P atoms with the same substituents occupy *trans* positions and, in consequence, the compounds do not exhibit chirality. As far as we know, there is no report about iron complexes bearing $\text{EPP}'\text{P}'$ ligands.

An NP_4 ligand (Fig. 97a) reacts with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol at 50°C giving the complex depicted in Fig. 97b. This reaction involved the C-P bond cleavage in NP_4 to provide the hexacoordinated iron complex with a phosphinite and a tripodal pentadentate ligand, the last involving an agostic interaction between the Fe atom and a methyl group. At room temperature, the reaction leads to the metalation of a methyl group provided by the compound shown in Fig. 97c. Both compounds are chiral-at-iron and crystallized as racemic mixtures.[342,343].

4.3.2. Tripodal tetraphosphanes

Tetraphosphanes, PP'_3 , with general formula $\text{P}\{(\text{CH}_2)_n\text{PR}_2\}_3$ or $\text{P}\{(o\text{-Ph})\text{PR}_2\}_3$ ($n = 2, 3$; $\text{R} = \text{alkyl}$ or aryl), are tripodal tetradentate ligands upon iron coordination, and form penta- or hexacoordinate complexes. Hexacoordinate $[\text{Fe}(\text{PP}'_3)\text{X}_2]$ and $[\text{FeH}(\text{PP}'_3)\text{X}]$ ($\text{X} = \text{halogen}$) complexes are chiral-at-iron complexes known for a long time, in which the halido is located *trans* to the central P atom.[344–348] The substitution of a chlorido in $[\text{FeCl}_2(\text{tdmep})_3]$ ($\text{tdmep} = \text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$) by H or Me originates only one isomer with the new ligand occupying a *cis* position concerning the central P atom, whereas the substitution with PPh_3 originates the isomer with the new ligand in *trans* position to the central P atom. The reaction with CO gives rise to the two isomers, with the CO in *cis* and *trans* positions concerning the central P atom.[349] Alternatively, the same iron precursor reacted with acetaldehyde to form the $[\text{Fe}(\text{CH}_3)(\text{CO})\{\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3\}]^+$ chiral-at-iron complex, with CO *trans* to the central P atom.[350].

The hydride $[\text{FeH}(\text{tdmep})\text{X}]$ complexes readily reacted with dinitrogen or dihydrogen to form $[\text{FeH}(\text{tdmep})(\text{Y}_2)]^+$ ($\text{Y} = \text{N}, \text{H}$) or the $[\{\text{FeH}(\text{tdmep})\}_2(\mu\text{-N}_2)]^{2+}$ dimer.[349,351,352] These species are chiral-at-metal because of the helix-like disposition of the carbon skeletons and, when reacted with a base, were reduced to the Fe(II)-Fe(0) $[\{\text{FeH}(\text{tdmep})\}_2(\mu\text{-N}_2)]^+$ and the Fe(0)-Fe(0) $[\{\text{Fe}(\text{tdmep})\}_2(\mu\text{-N}_2)]$ dimers,[353] or to Fe(0) $[\text{Fe}(\text{N}_2)(\text{tdmep})]$ species.[354].

The presence of asymmetry in the tripodal tetraphosphanes ($\text{PP}_2\text{P}'$) through the incorporation of different alkyl chains between the P atoms would increase the number of iron isomers. This occurs with the phosphanes *dmdep* (Fig. 98a), and *dmdpe* (Fig. 98b). The two phosphanes form diamagnetic octahedral complexes with Fe(II). With *dmdpe*, two isomers exist in the solution and for *dmdep* only one unsymmetric iron isomer was obtained (Fig. 98c).[355] These complexes have not yet been fully characterized.

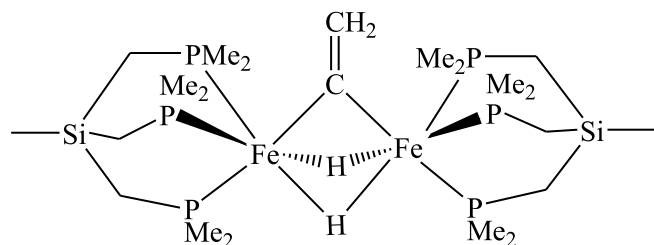


Fig. 92. Schematic representation of $\{[\text{Fe}(\text{tmps})_2]_2(\mu\text{-C}=\text{CH}_2)(\mu\text{-H})_2\}$.

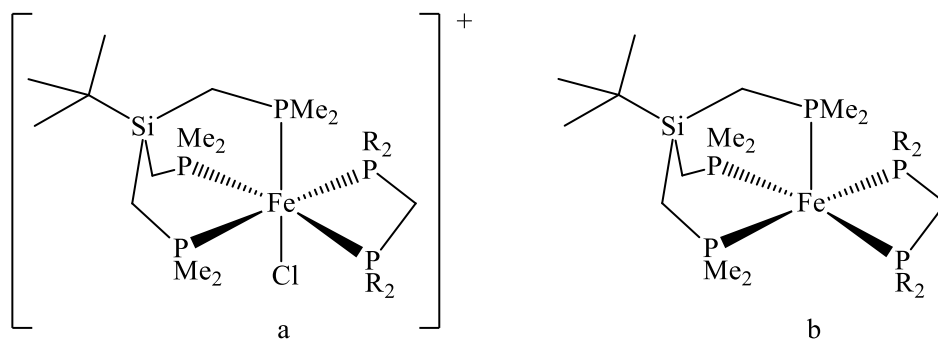


Fig. 93. Schematic representation of (a) $[\text{FeCl}(\text{PP})(\text{tmpstBu})]^+$ and (b) $[\text{Fe}(\text{PP})(\text{tmpstBu})]$.

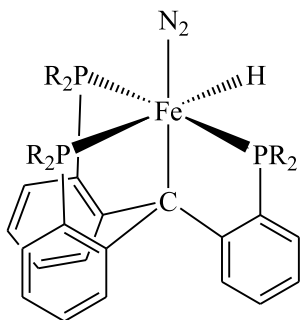


Fig. 94. Schematic representation of $[\text{FeH}(\text{N}_2)(\text{tippm-}\kappa^1\text{C},\kappa^3\text{P})]$ ($\text{R} = i\text{Pr}_2$).

Pentacoordinate $[\text{Fe}(\text{PP}'_3)\text{L}]^+$ ($\text{L} = \text{halogen}$, [337,338,352,354,356] H , [357] N_2 , [358] NO , [359] HS , [197] alkyne, [360]) $[\text{Fe}(\text{PP}'_3)\text{L}]$ (N_2 , [348,354,358] alkyne [360]) and $[\text{Fe}(\text{PP}'_3)\text{H}(\eta^2\text{-H}_2)]^+$, [361] complexes are well-known and some of them were applied in the catalytic transformations. [348,356,357] These compounds are structurally similar to the NP_3 iron complex (Fig. 95b), show chirality because of the helicity of the metallacycles and were isolated as racemic mixtures.

5. Conclusion and perspectives

The use of iron compounds as catalysts, for covering a wide range of reactions, has increased significantly in recent years. Enantioselective syntheses require the presence of chiral catalysts and this review focuses on the preparation and characterization of chiral-at-iron complexes with phosphanes. These materials constitute potential catalysts for the preparation of optically active compounds in fine chemistry and as building blocks for the synthesis of optically active materials. The great advantage of the use of chiral-at-iron compounds with phosphanes is not only the low toxicity, high abundance and low price of iron versus other noble metals but also the presence of P ligands that contribute to stabilising the iron complexes. However, little is known about the technological applications of these compounds, and the reports are limited to

the synthesis and characterization of complexes. In the catalytic field, only a few studies have been reported and in some cases, there is no characterization of the possible/transient catalytic species.

The strategies for the synthesis of chiral-at-iron complexes with donor P ligands are diverse and generally not straightforward, and the composition of the resulting compounds is highly dependent on the reaction conditions, such as solvent and temperature used. Frequently, the possible formation of different isomers is not considered, limiting itself to the characterization of the compounds that are easiest to isolate and purify.

Numerous iron phosphane complexes that are chiral-at-iron have been synthesized, while, in general, authors do not explicitly indicate the metal-centered chirality of the compounds obtained, with no consideration of the possible separation of the enantiomers. Hence, many chiral compounds are found for which the possible separation of the isomers has not been taken into account, and only in a few cases the separation of the isomers has been attempted.

In other cases, given the geometry of the ligand and/or the coordination sphere of the iron atom, the synthesis has enabled the preparation of only one of the possible stereoisomers, although the reasons that lead to this stereoselective preparation are not clear. Often, the chiral-at-iron compounds crystallize in centrosymmetric groups with the presence of both enantiomers in the crystal. In other cases, a pure enantiomer crystallizes as a non-centrosymmetric crystal, but it is not clear whether a single enantiomer has formed, or if in the case of a racemic mixture

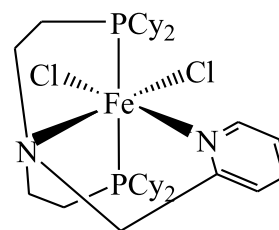


Fig. 96. Schematic representation of a hexacoordinated complex with an $\text{NP}_2\text{N}'$ ligand.

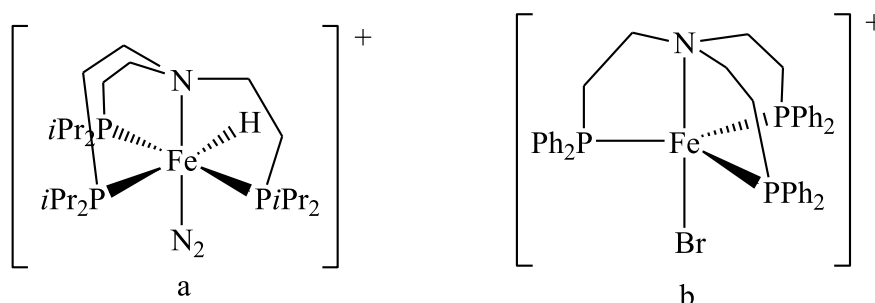


Fig. 95. Schematic representation of complexes with tripodal ligands with an apical N atom.

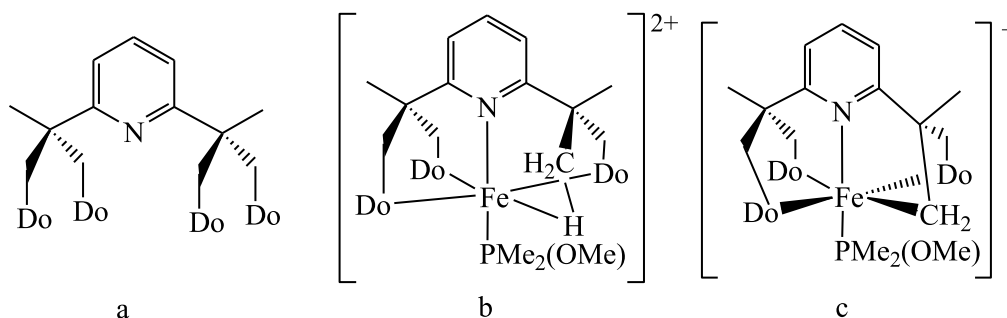


Fig. 97. Schematic representation of: (a) NP_4 and (b) iron (II) complex with NP_4 , being $\text{Do} = \text{PMe}_2$.

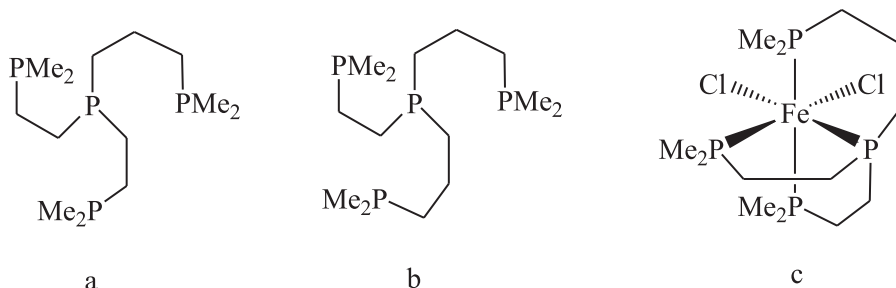


Fig. 98. Schematic representation of (a) dmdep , (b) dmdpe and (c) $[\text{FeCl}_2(\text{dmdep})]$.

formed, there is a spontaneous resolution of the enantiomers. The enantiomeric excess of the crystals and the possible reasons that lead to spontaneous separation are not discussed by the authors. Likewise, among other crystals formed, the possible presence of other isomers obtained in the reaction mixture is not considered.

We remark that the structure of the reported iron compounds is often assumed the same in solution and the solid state. Although, often the structure in solution deduced from the NMR data coincides with the crystalline structure obtained by X-ray diffraction. Considering that the structural stability in solution is crucial for reactivity purposes, fluxionality is a phenomenon to take into account when formulating an iron complex with phosphanes. In general, this phenomenon is more frequent in pentacoordinated compounds and the increase in the denticity/hapticity of the ligand decreases the possibility that the compounds formed are fluxional.

The structural analyses of the compounds described in this review support the identification of the iron atom as the unique stereocenter in most cases. The discovery of stereogenicity at the metal of the already synthesized iron compounds paves the path for the application of chiral-at-iron compounds in asymmetric catalysis and in the molecular design of iron stereoisomers using available non-chiral phosphanes. The factors that determine the stereochemistry of the compounds formed are not always obvious. While the hapticity/denticity and the electronic/steric characteristics of the phosphane ligands contribute to the structural rigidity, other variables such as the geometry of the compounds, the (hemi)lability of the phosphanes, and the nature of the remaining ligands, should also be taken into account.

To our knowledge, the isolation of enantiomerically pure chiral-at-iron complexes is scarce and is derived from the use of optically pure phosphanes. Some authors have considered the separation of enantiomers with non-chiral phosphanes, but they have not described their results.

Although great advances have been made in recent years in the use of chiral iron compounds as catalysts, they have been much less developed in comparison to the noble metal analogues. Until to our knowledge, the application of chiral-at-iron compounds with phosphanes in asymmetric catalysis is limited to the use of chiral phosphanes. Whereas the metal stereocenter would be relevant in the determining step of the

stereochemical transformation, the stereoselectivity of iron catalysts is commonly associated with the chirality of the ligand and the structure of the iron intermediates and transition states involved in the asymmetric transformation remains unknown.

We expect that this review will open new pathways for the design of chiral-at-iron catalysts and the development of further synthesis procedures, using readily accessible and cheap ligands, mostly non-chiral ligands as alternatives to the expensive chiral ligands, and considering the coordination modes of already known ligands and the scope of the coordination environments depicted in this review.

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.

Data availability

Data will be made available on request.

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