Configurational landscapes of chiral iron (II) bis(phosphane) complexes†

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The reaction of the chiral $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]^+$ ($(\text{R},\text{R})\text{-Me-DuPhos}$ = (-)-1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene) complex with ethers and halides is investigated by NMR techniques. From this study, it is apparent that the dihydrogen ligand exchange by poorly-donor molecules, such as THF or Et_2O , is feasible in mild conditions. The *cis*- $[\text{FeH}(\text{THF-d}_8)\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]^+$ complex is identified as product in THF- d_8 solution. A mixture of the *cis*- and *trans*- $[\text{FeH}(\text{ether})\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]^+$ isomers are obtained after the addition of small quantities of THF or Et_2O to a CD_2Cl_2 solution of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]^+$. The reaction between $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]^+$ with an excess of iodide or chloride salts in THF- d_8 or CD_2Cl_2 affords initially the *cis*- and *trans*- $[\text{FeHX}\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]$ (X = Cl or I) isomers. The *trans* complex is the thermodynamic product when X = Cl, whereas the *cis* isomer is obtained when X = I. These complexes evolve, and the pentacoordinated $[\text{FeX}\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2](\text{A})$ (X = Cl, A = BF_4 ; X = A = I) and hexacoordinated *trans*- $[\text{FeCl}_2\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]$ compounds are obtained as air-stable crystals, and identified by X-ray diffraction and NMR techniques. Experiments done with (*S,S*)-Me-DuPhos ((+)-1,2-bis[(2*S*,5*S*)-2,5-dimethylphospholano]benzene) give similar results, and the $[\text{Fe}\{(\text{S,S})\text{-Me-DuPhos}\}_2](\text{ClO}_4)$ compound has been crystallographically characterized.

Introduction

Several hydrido and dihydrogen transition metal catalysts play a crucial role in many catalytic hydrogen transfer, hydrogenation and hydrosilylation reactions.^{1–4} Dihydrogen metal compounds can evolve to dihydrido complexes by oxidative addition of H_2 , or to hydrido complexes by heterolytic deprotonation of H_2 . The substitution reaction of dihydrogen by other ligands also participates in some catalytic cycles. In recent years, many efforts have been devoted to the development of hydrido and dihydrogen catalysts using inexpensive, abundant and environmentally benign metals, such as iron, nickel and cobalt.^{5–10} In the field of asymmetric catalysis, only few optically pure hydrido and/or dihydrogen derived metal compounds are involved in efficient enantioselective reduction reactions.^{11–13} Among them, the design and preparation of well-defined chiral hydrido or dihydrogen iron complexes directed to catalytic asymmetric hydrogenation of ketones have attracted much attention.^{13–25} Alternatively, the active species can be *in situ* generated in the catalytic process by combining a chiral ligand with cheap, stable and readily available iron compounds.⁹ As a paradigmatic example, Beller and coworkers reported one of the firsts examples of iron (II)-catalyzed asymmetric hydrosilylation of ketones, with excellent enantioselectivities obtained from highly hindered aromatic ketones by using a combination of $\text{Fe}(\text{OAc})_2$, two equivalents of (*S,S*)-Me-DuPhos, and a reducing agent ($(\text{EtO})_2\text{MeSiH}$ or PMHS (PMHS = polymethylhydrosiloxane)) in THF.²⁶ Often, the

concentration, composition and structure of the metallic active species involved in the reaction mechanism is not identified, and it makes difficult the control of the appropriate catalytic reaction conditions. The characterization of the complexes formed along the reaction is crucial to know the properties of the species active in catalysis, and this will allow the development of new catalysts directed to specific transformations.

R-DuPhos (R = Me, Et, ⁱPr) are chiral phosphanes ligands commonly used for asymmetric transformations of prochiral substrates, and consist of two dialkyl-substituted phospholane rings connected by an *ortho*-phenyl bridge, with two stereocenters in each phospholane ring (Fig. 1).^{27–33} The C_2 -symmetry of these phosphanes allows high levels of enantiocontrol in many metal-catalyzed reactions. Three distinctive features embody these ligands compared to other chiral bis(phosphane) compounds: their donor-acceptor properties, the pseudo-chirality on the phosphorous atoms, and the rigidity of the P-C-C-P skeleton. These properties limit the number of possible active metal stereoisomers involved in the catalytic cycle,^{29, 34} and are responsible of the development of similar DuPhos reagents with success in enantioselective transformations.^{32, 35} In this context, in the case of the reported ketone hydrosilylation catalytic reaction, it is expected that two (*S,S*)-Me-DuPhos, one hydrido and one monodentate ligand will fulfill the 18-electron iron(II) intermediate, and one of the three possible optically active stereoisomers, namely *trans*-isomer and the *cis*- Δ and *cis*- Λ -diastereomers, represented in Fig. 1, would be the active species in the asymmetric catalytic reaction.

The design and preparation of efficient asymmetric hydrido iron(II) bis(R-DuPhos) catalysts must be directed by the selective synthesis of one of the three above mentioned isomers. Whereas the chemistry of hydrido iron(II) complexes with *o*-phenylene bis(phosphane) ligands has been poorly investigated, the iron compounds with bis(phosphane) ligands bearing a 1,2-ethylene

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† Electronic supplementary information (ESI) available: Experimental details, NMR tables and figures, and detailed X-ray structural descriptions. Computed (DFT) bond lengths and angles of Λ and Δ isomers for the $[\text{Fe}\{(\text{R},\text{R})\text{-Me-DuPhos}\}_2]^+$ complex, Cartesian coordinates and Gibbs free energies reported in this paper are included. This material is available free of charge. CCDC 1952454–1952457. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

Fig. 1. Representation of (S,S)-Me-DuPhos and the three possible iron active species involved in the most efficient enantioselective hydrosilylation of ketones catalyzed reactions reported by Beller *et al.*²⁶ L represents a neutral monodentate ligand.

Fig. 2. Stereoselective formation of *trans*-[FeHL(PP)₂]⁺ complexes.

bridge, such as [FeHX(PP)₂],^{36–39} and [FeHL(PP)₂]⁺ (PP = chelating 1,2-ethylene-bis(phosphane), X = Cl, Br and L = neutral ligand) complexes, has been deeply developed. These complexes are generally obtained as *trans* isomers, while *cis* isomers, such as *cis*-[FeH(N₂H₄)(dmpe)₂]⁺, can be prepared.⁴⁰ The formation of *trans*-[FeHL(PP)₂]⁺ compounds takes place in a two-step reaction process. In a first reaction step, the protonation of the *trans*-[Fe(H)₂(PP)₂] precursors, the heterolytic cleavage of molecular dihydrogen by *trans*-[FeCl₂(PP)₂] complexes (Fig. 2) or the sodium assisted exchange (Cl by H₂) in *trans*-[FeHCl(PP)₂] leads an (dihydrogen)(hydrido) iron(II) intermediates, [FeH(η²-H₂)(PP)₂]⁺, which show fluxional behaviour at room temperature.^{41–50} These complexes react in a second reaction step with other neutral ligands (L = N₂, D₂, CO, C₂H₄, DMSO, RCN (R = Me, Ph), MeNC) to lead to *trans*-[FeHL(PP)₂]⁺ complexes as unique stereoisomers (Fig. 2).^{41–44, 48, 50–54} Alternatively, the substitution of dihydrogen can be extended to anionic ligands, for instance, the [FeH(η²-H₂)(dmpe)₂]⁺ complex reacts with halides to afford the neutral *trans*-[FeHX(dmpe)₂] (X = Cl, Br) compounds.^{46, 47}

The high selectivity of the dihydrogen ligand exchange from the fluxional [FeH(η²-H₂)(PP)₂]⁺ precursor towards the formation of the *trans* isomer is not evident, and this stereospecificity is presumably due to the less steric hindrance of the *trans* disposition of the two bis(phosphane) ligands. Kinetic experiments reported on dihydrogen substitution reactions by other nucleophiles on [FeH(η²-H₂)(PP)₂]⁺ (PP = dppe,^{53, 54} depe⁵⁵) support different mechanisms for the formation of the *trans*-[FeH(nucleophile)(PP)₂]⁺ compound, and the isomerization towards the *cis* isomer is not observed.

Recently, we have synthesized the first chiral [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂]⁺ and [FeH(η²-H₂){(*S,S*)-Me-DuPhos}₂]⁺ complexes by

heterolytic cleavage of H₂ promoted by the iron(II)-hexaquo tetrafluoroborate and the corresponding optically pure bis(phosphane).⁵⁶ This complex is fluxional in deuterated dichloromethane at room temperature, analogously to other [FeH(η²-H₂)(PP)₂]⁺ complexes. The dihydrogen by CO and CH₃CN substitution at room temperature gives a mixture of *cis*- and *trans*-[FeHL(Me-DuPhos)₂]⁺ (L = CO, CH₃CN) complexes quantitatively. NMR experiments confirmed the formation of the *cis*-[FeHL(Me-DuPhos)₂]⁺ isomers in greater proportion, and the configurational rigidity of *cis* and *trans* isomers at room temperature. In this study we conclude that the presence of sterically hindered phosphanes does not prevent the formation of *cis* conformers. Among the iron hydrido complexes bearing two bis(phosphane) ligands with a 5-membered chelate ring, to the best of our knowledge, these and the *trans*-[FeHCl{o-C₆H₄(PEt₂)₂]₂ and *trans*-Fe(H,D)₂{o-C₆H₄(PEt₂)₂]₂ complexes are the only examples of hydrido complexes bearing functionalized 1,2-phenylene bis(phosphane) ligands reported in the literature.^{56, 57}

The latest experiments done in our laboratory showed that the [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂]⁺ complex and the (S,S)-Me-DuPhos analogue react in THF-d₈ under inert atmosphere to give unexpected products. In this work, we describe the NMR identification of a new stereochemically-rigid molecule, namely the *cis*-[FeH(THF-d₈){(*R,R*)-Me-DuPhos}₂]⁺ complex, and its evolution to new species in solution. Both *cis*- and *trans*-[FeHL{(*R,R*)-Me-DuPhos}₂]⁺ isomers (L = THF, Et₂O) appeared when a small quantity of ether is added to a solution of [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂]⁺ in CD₂Cl₂. The reaction of [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂]⁺ with halide salts are explored, and a mixture of the *cis*- and *trans*-[FeHX{(*R,R*)-Me-DuPhos}₂] (X = Cl, I)

isomers are identified by NMR. The pentacoordinated $[\text{FeX}\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ ($\text{X} = \text{Cl}, \text{I}$) and $[\text{Fe}\{(\text{S,S})\text{-Me-DuPhos}\}_2]^+$ complexes, and the hexacoordinated $[\text{FeCl}_2\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ compounds were isolated from complicated mixtures as final air-stable products, and identified by NMR and X-ray techniques.

Results and discussion

In a previous work, the *cis*- and *trans*- $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ stereoisomers have been characterized in CD_2Cl_2 by NMR techniques at low temperature.⁵⁶ In order to describe them in a larger temperature range, we found that the $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex is not soluble in toluene, but slightly soluble in THF-d_8 . Typically, this compound is dissolved in THF-d_8 in a sealed NMR tube at room temperature under inert atmosphere (see Table S1 in ESI[†]), and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the solution were acquired just after dissolution. The characteristic signals of the fluxional dihydrogen-hydrido iron(II) precursor, at room temperature, appeared at 108 ppm and -10.1 ppm in the $^{31}\text{P}\{^1\text{H}\}$ and ^1H spectra, respectively. After four hours, at room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was registered, the signal of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ disappeared, and a new pattern of three complex multiplets appeared as different signals at 94, 111, and 116 ppm, that integrate 1:1:2 respectively (Fig. 3). This new pattern of multiplets is associated to the formation of a new stereochemically-rigid molecule with four different P atoms. Similar systems with four

non-equivalent phosphorous in *cis* disposition have been reported by Field *et al.*⁵⁸ Other minor signals appeared as singlets at higher fields, which are attributed to decomposition products (*vide infra*). The hydride region of the proton spectrum shows a new resolved multiplet signal at -10.3 ppm (Fig. 4), due to coupling of proton with 4 different P. The experimental and gNMR simulated ^1H (hydride region) and $^{31}\text{P}\{^1\text{H}\}$ chemical shifts and coupling constants of the new product obtained after solution of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2](\text{BF}_4)$ in THF-d_8 are listed in Table S2[†], and the corresponding ^1H NMR spectra are illustrated in Fig. S1[†].

Several ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired at different temperatures. After cooling from room temperature to -50 °C or heating to 40 °C the spectra did not change, which implies the absence of fluxional behavior and the stereochemical rigidity of the *in situ* generated product. Since no dihydrogen signal was detected in the ^1H NMR spectra, we hypothesized that the H_2 ligand is lost in the course of the reaction through a dihydrogen by dinitrogen exchange. The experiments done under argon gave identical results and, in consequence, none of the *cis* or *trans*- $[\text{FeH}(\text{N}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complexes were formed. Moreover, the $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ does not react in dichloromethane.⁵⁶ This behaviour is unexpected, given that dihydrogen ligand is commonly replaced by dinitrogen in the $[\text{FeH}(\eta^2\text{-H}_2)(\text{PP})_2]^+$ complexes.^{48, 50-52} In addition, we discard the presence of the pentacoordinated $[\text{FeH}\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex in solution because we assume that this species would be fluxional at room temperature.

Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after 4 hours at room temperature of a solution of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2](\text{BF}_4)$ in THF-d_8 .

Fig. 4. ^1H NMR spectrum after 4 hours at room temperature of a solution of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2](\text{BF}_4)$ in THF-d_8 .

Fig. 5. Dihydrogen substitution by THF- d_8 in $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ to lead $[\text{FeH}(\text{THF-}d_8)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ stereoisomers.

Fig. 6. Schematic representation of the reactions of iron complexes with halides (I^- and Cl^-). Only one *cis* diastereoisomer is represented for clarity.

The NMR results suggest that the chiral iron precursor reacts with the poor-coordinating THF- d_8 by losing dihydrogen to give one of three possible hexacoordinated stereoisomers, one *trans* and two *cis*- $[\text{FeH}(\text{THF-}d_8)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ (Fig. 5). The formation of the *trans* isomer is discarded considering the NMR results. An AA'BB' spin system would be expected for the phosphorous nuclei in this *trans* configuration. The spectrum of $^{31}\text{P}\{^1\text{H}\}$ NMR indicates the presence of an ABCD system with 4 different P, which allows us to point out that the complex has a *cis* arrangement. Since narrow and well defined signals are observed in the ^1H (hydride region) and ^{31}P NMR spectra (Figs. 3-4), we deduce that only one diastereoisomer is formed.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired after addition of small amounts Et_2O or THF in a CD_2Cl_2 solution of the iron precursor under inert atmosphere. Four multiplets, and two additional minor multiplets were detected and assigned to the formation of the *cis*- and *trans*- $[\text{FeHL}\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ (L = Et_2O or THF) stereoisomers, respectively (Fig. S2†), being the *trans* the minor isomer. Both compounds decompose slowly, the *trans* isomer first and the characteristic signals of *cis* isomers are visible in the NMR spectra after one month under inert atmosphere. Additional experiments with poorly-coordinating O-donors, such as acetone- d_6 , did not give new species and not new signals were observed in the NMR spectra.

There are only few reports about the direct substitution of dihydrogen by poorly-coordinating ligands, such as ethers, in $[\text{FeH}(\eta^2\text{-H}_2)(\text{PP})_2]^+$ complexes. The bright red *trans*- $[\text{FeH}(\text{THF})(\text{dppe})_2]^+$ complex is the only reported analogue, and it is obtained by direct reaction of THF with the blue-green $[\text{FeH}(\text{dppe})_2]^+$.⁵⁹ The *trans*- $[\text{FeH}(\text{THF})(\text{dppe})_2]^+$ complex loses THF by heating from temperatures below 0 °C to above 40 °C in a reversible equilibrium.⁶⁰ The pentacoordinated compound also reacts with N_2 to give *trans*- $[\text{FeH}(\text{N}_2)(\text{dppe})_2]^+$.^{60,61} It is worth noting that the $[\text{FeH}(\text{dppe})_2]^+$ precursor is paramagnetic, and the complexes with N_2 or THF- d_8 are diamagnetic at room temperature.⁶¹

By prolonged heating at 40 °C in THF- d_8 , we observed that the *cis*- $[\text{FeH}(\text{THF-}d_8)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex evolved with the formation of the free bis(phosphane) and other unidentified reaction intermediates with signals between 65 and 1 ppm in the $^{31}\text{P}\{^1\text{H}\}$ spectra. After a few days, high-quality red crystals appeared in the NMR tube. These crystals were identified by single-crystal X-ray diffraction as the pentacoordinate $[\text{Fe}\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex (*vide infra*). The presence of iodine in these crystals is surprising, which led us to look for the origin of it. The analysis by inductively coupled plasma mass spectrometry (ICP-MS) of the starting compound $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ showed that it contained iodine as an impurity, but in quantity enough to explain the origin of iodine in the crystal. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of the isolated crystals, once dissolved in CD_2Cl_2 , showed only one signal as singlet at 65.8 ppm. To confirm the isolation of the $[\text{Fe}\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex, we followed two synthetic routes: i) the addition of an excess of iodide (KI or TBAI (TBA = tetrabutylammonium)) to a solution of the $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex, and ii) the self-assembly reaction between $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$, an excess of TBAI and two equivalents of (R,R)-Me-DuPhos (**Fig. 6**). Along the reaction i) we detected the formation of dark-orange crystals after 2-3 days in THF- d_8 , which were identified by NMR. A singlet was obtained as a unique signal at 64.8 ppm in THF- d_8 . This result implies that a new diamagnetic compound was obtained. In the second reaction (ii), also done in THF- d_8 , the initial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum registered at room temperature showed the free phosphane at 3.4 ppm, and after prolonged heating to 50 °C, the expected singlet became the main signal. The presence of a single signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature could be due to fluxional character of the compound formed, so an additional NMR study was carried out at different temperatures. In the temperature range from -93 to 25 °C, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra only shows a signal without multiplicity (**Fig. S3**[†]), and the ^1H NMR spectra does not show any signal in the hydride region within the same temperature range. No variation of the multiplet of the aromatic protons was detected, and we assign this result to the presence of only one fluxional compound in the temperature range studied.

The reports about the synthesis of pentacoordinate $[\text{Fe}(\text{PP})_2]^+$ compounds bearing a similar P-C-C-P skeleton are scarce. Leigh *et al.* described the synthesis of the $[\text{Fe}(\text{opdp})_2]\text{I}\cdot 2\text{CH}_2\text{Cl}_2$ (opdp = o-phenylenebis(diphenylphosphane)) analogue by direct reaction of the FeI_2 precursor with two equivalents of opdp, and this compound results diamagnetic from Mössbauer analyses.⁶² The $[\text{Fe}\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex is diamagnetic from the NMR studies. However, the ethylene-bridge bis(phosphane) iron(II) complex, $[\text{Fe}(\text{dppen})_2]\text{BPh}_4$ (dppen = *cis*-1,2-

bis(diphenylphosphano)ethylene), which is isolated following the same reaction procedure, gives a magnetic moment value (3.30 μ_B) associated to a triplet ground state.⁶³ Thus, the spin-iron configuration of the iodide iron(II) bis(phosphane) complexes seems to be influenced by the structural and electronic characteristics of the P-C-C-P skeleton.

Reaction of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ with halide salts was monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR. The reaction with a stoichiometric quantity of KI in THF- d_8 favored the slow formation of iodide substituted species in *cis* and *trans* configurations, with formula $[\text{FeHI}\{(\text{R,R})\text{-Me-DuPhos}\}_2]$, which were identified by $^{31}\text{P}\{^1\text{H}\}$ NMR (**Fig. S4**[†]), in addition to the *cis*- $[\text{FeH}(\text{THF-}d_8)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex, and other products. Finally, the *cis*- $[\text{FeHI}\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ stereoisomers were formed as the main product after 1 week in solution. Since these species were detected together with the *cis*- $[\text{FeH}(\text{THF-}d_8)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ complex, we chose CD_2Cl_2 as a non-coordinating solvent to follow the same reaction with halides. The use of KI in CD_2Cl_2 did not provide the substituted compounds because of the low solubility of the salt. The addition of a small quantity of THF gave a signal at 66.8 ppm as unique signal after 1 week. Since TBA salts are soluble in dichloromethane, the reaction of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ with TBAI (5 eq) in CH_2Cl_2 during 4 h at room temperature provided an orange solution. Once the reaction mixture was evaporated and dissolved in CD_2Cl_2 , the *cis*- $[\text{FeHI}\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ was identified by NMR and it decomposed slowly in solution.

We studied the reaction between $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$ and TBACl (5 eq) in CD_2Cl_2 (**Fig. 6**). The initial spectrum only showed the starting complex, but after 2 h the *cis* and *trans*- $[\text{FeHCl}\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ complexes together with the starting compound and other unidentified products were identified in ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ spectra (**Fig. 7**). In the ^1H spectrum, the signal at -15 ppm does not have the appearance of a proton coupling to 4 P of a system $\text{AA}'\text{BB}'$, however, the $^1\text{H}\{^{31}\text{P}\}$ spectrum shows that it is a singlet, which confirms the ^1H - ^{31}P coupling (**Fig. S5**[†]). Both species evolved with time, as observed for the iodide analogue, and after 24 h at room temperature only the *trans* isomer was observed in the spectrum.

This *trans* isomer is not stable and goes forward slowly to other products. After 7 days in solution, no hydride and phosphorous signals associated to the $[\text{FeHCl}\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ complexes were detected in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, respectively (**Fig. S6**[†]). The remaining signals on the phosphorous spectra, which appear between 66 and 3 ppm, agree with the formation of other symmetric Me-DuPhos species and free Me-DuPhos. Among them, the singlet at 64.6 ppm is assigned to the formation of the *trans*- $[\text{FeCl}_2\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ compound. This compound was identified crystallographically after isolating a single crystal from a dichloromethane solution of $[\text{FeH}(\eta^2\text{-H}_2)\{(\text{R,R})\text{-Me-DuPhos}\}_2]^+$. The complex *trans*- $[\text{FeCl}_2\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ crystallizes as an enantiomerically pure compound. This compound lies in a C_2 symmetry axis on the plane defined by the iron and the phosphorous atoms, and which bisects the P-Fe-P angle of the two chelating phosphanes. The iron atom in the *trans*- $[\text{FeCl}_2\{(\text{R,R})\text{-Me-DuPhos}\}_2]$ molecule is coordinated by two chlorine atoms and by the four phosphorous atoms of the two bis(phosphane) ligands within a distorted *trans*-octahedral geometry (**Fig. S7**[†]). Selected bond

distances and angles of this structure and of similar *trans*-[FeCl₂(PP)₂] compounds bearing two bis(phosphane) ligands with o-phenylene or ethylene bridges are listed in **Table S3**[†]. The symmetry independent Fe-Cl and Fe-P distances for the *trans*-[FeCl₂{(*R,R*)-Me-DuPhos}₂] compound differs in only 0.01-0.05 Å than those corresponding in *trans*-[FeCl₂(opdp)₂]⁶⁴ and *trans*-[FeCl₂(dppen)₂].⁶³ It suggests that the differences between the bis(phosphane) skeletons, and the differences of the donor abilities and the steric hindrance between the phospholane and the PPh₂ groups do not affect in the interatomic Fe-P and Fe-Cl distances. This is not obvious, since the structure of the *trans*-[FeCl₂{(o-C₆H₄)(PHⁱPr)₂}]₂ compound shows the shortest Fe-P distances.⁶⁵ The steric hindrance of the phospholane groups in *trans*-[FeCl₂{(*R,R*)-Me-DuPhos}₂] increases the P-Fe-P bite angle in 4° with respect to that observed for *trans*-[FeCl₂(opdp)₂]. The *trans* structure of [FeCl₂{(*R,R*)-Me-DuPhos}₂] contrasts with the *cis* structure reported for the [FeCl₂(BPE5)₂] (BPE5 = 1,2-diphospholanoethane) compound.⁶⁶ A comparison between both structures suggests that the presence of the o-phenylene bridge and the methyl substituents in the phospholane ring favor the *trans* configuration around the iron atom in [FeCl₂{(*R,R*)-Me-DuPhos}₂].

Red crystals were obtained from a solution of [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂]⁺ in the NMR tube in the presence of halides, and they were isolated and characterized by using ³¹P{¹H} NMR, and single-crystal X-ray crystallographic methods. Three enantiomerically pure pentacoordinate iron (II) complexes were identified, two with (*R,R*)-Me-DuPhos ([Fe{(*R,R*)-Me-DuPhos}₂]⁺·H₂O and [FeCl{(*R,R*)-Me-DuPhos}₂](BF₄)) and one with (*S,S*)-Me-DuPhos ([Fe{(*S,S*)-Me-DuPhos}₂](ClO₄)), which have been obtained from the [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂](BF₄) and KClO₄ salts in THF-d₈. The simplified representations of the corresponding cations (see **Figs. S8-S10**[†]) are illustrated in **Figs. 8 and 9**.

The structure of each iodide compound shows two independent cations in the crystal. The iron atom is five coordinated with an approximately trigonal-bipyramidal coordination (the geometry for pentacoordinated compounds is described on the basis of the structural parameter τ, known as the Addison parameter,⁶⁷ and mean τ values is calculated for both independent molecules in the unit cell to give τ = 0.97 for [Fe{(*R,R*)-Me-DuPhos}₂]⁺ and 0.96 for [Fe{(*S,S*)-Me-DuPhos}₂]⁺), with one iodine and two phosphorous atoms which form the equatorial triangle of the trigonal bipyramid. This geometry contrasts to that reported for the [Fe(opdp)₂]⁺·2CH₂Cl₂ structure, which shows a slightly distorted square-pyramidal structure (τ(mean) = 0.13).⁶⁴ The o-phenylene groups in [Fe{(*R,R*)-Me-DuPhos}₂]⁺ and [Fe{(*S,S*)-Me-DuPhos}₂]⁺ compounds are tilted in the opposite direction of the Fe-I bond, blocking the access to the sixth coordination site, and the methyl groups and the phospholane rings surround the iodide so that its large size can be accommodated. The trigonal-bipyramidal geometry of these cations seems to be caused by the steric characteristics of the iodine atom and the phospholane rings. The averaged Fe-I distance is 2.587 Å, and the Fe-P distances span 2.265-2.299 Å with a mean value of 2.278 Å (**Tables 1 and S4**[†]). These mean bond distances are shorter than those obtained for [Fe(opdp)₂]⁺ (Fe-I = 2.640 Å and Fe-P = 2.344 Å) due to the stabilizing interactions of the Me-DuPhos ligand.⁶⁴ The P-Fe-I angles agree with slightly distorted trigonal-bipyramidal geometries. The averaged P-Fe-P bite angles about 81° is typical for o-phenylene bis(phosphane) iron (II) compounds.

Fig. 7. ¹H and ³¹P{¹H} NMR spectra after 2 h of reaction of TBACl and [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂](BF₄) at room temperature in CD₂Cl₂. The *, +, and # notations correspond to the characteristic signals of [FeH(η²-H₂){(*R,R*)-Me-DuPhos}₂]⁺, *trans*-[FeHCl{(*R,R*)-Me-DuPhos}₂] and *cis*-[FeHCl{(*R,R*)-Me-DuPhos}₂] compounds, respectively.

The structure of each iodide compound shows two independent cations in the crystal. The iron atom is five coordinated with an approximately trigonal-bipyramidal coordination (the geometry for pentacoordinated compounds is described on the basis of the structural parameter τ , known as the Addison parameter,⁶⁷ and mean τ values is calculated for both independent molecules in the unit cell to give $\tau = 0.97$ for **[Fe{(R,R)-Me-DuPhos}₂]⁺** and 0.96 for **[Fe{(S,S)-Me-DuPhos}₂]⁺**, with one iodine and two phosphorous atoms which form the equatorial triangle of the trigonal bipyramid. This geometry contrasts to that reported for the **[Fe(opdp)₂]⁺**·2CH₂Cl₂ structure, which shows a slightly distorted square-pyramidal structure ($\tau(\text{mean}) = 0.13$).⁶⁴ The o-phenylene groups in **[Fe{(R,R)-Me-DuPhos}₂]⁺** and **[Fe{(S,S)-Me-DuPhos}₂]⁺** compounds are tilted in the opposite direction of the Fe-I bond, blocking the access to the sixth coordination site, and the methyl groups and the phospholane rings surround the iodide so that its large size can be accommodated. The trigonal-bipyramidal geometry of these cations seems to be caused by the steric characteristics of the iodine atom and the phospholane rings. The averaged Fe-I distance is 2.587 Å, and the Fe-P distances span 2.265–2.299 Å with a mean value of 2.278 Å (Tables 1 and S4[†]). These mean bond distances are shorter than those obtained for **[Fe(opdp)₂]⁺** (Fe-I = 2.640 Å and Fe-P = 2.344 Å) due to the stabilizing interactions of the Me-DuPhos ligand.⁶⁴ The P-Fe-I angles agree with slightly distorted trigonal-bipyramidal geometries. The averaged P-Fe-P bite angles about 81° is typical for o-phenylene bis(phosphane) iron (II) compounds.

Both **[Fe{(R,R)-Me-DuPhos}₂]⁺** and **[Fe{(S,S)-Me-DuPhos}₂]⁺** complexes have a C₂ axis passing through the Fe-I bond (Fig. 8). They are chiral-at-metal complexes with four additional stereocenters of each bis(phosphane). They show an helical arrangement of the bis(phosphane) ligands with an opposite configuration at the metal center, namely Δ for **[Fe{(S,S)-Me-DuPhos}₂]⁺** and Λ for **[Fe{(R,R)-Me-DuPhos}₂]⁺**. These descriptors are used to define the absolute configuration of dissymmetric pentacoordinated complexes: Δ is used when the rings describe the right-handed helix as the complex is viewed along the C₂ axis, and Λ is used when they describe a left-handed helix.^{68, 69} Since the (R,R)- and (S,S)-Me-DuPhos ligands are chiral, in principle, both Δ and Λ diastereomers of each iron-bis(phosphane) complex could be formed. The structure of each bis(phosphane) could facilitate the preferential formation of one diastereomer, and even though the stereocenters of the phosphane lie far from the iron atom, the formation of only one diastereomer seems to be favoured. We have chosen the iron-(R,R)-Me-DuPhos system for the study of the structural and energetic differences between Δ and Λ configurations for **[Fe{(R,R)-Me-DuPhos}₂]⁺** by using a DFT methodology. The optimized Gibbs free energies confirms that the Λ configuration is the most stable, with an energetic stabilization of 14.5 kcal·mol⁻¹. In addition, the Δ structure of the complex is the most distorted (see Fig. S11 and Table S5[†]). The structure of the **[FeCl{(R,R)-Me-DuPhos}₂]⁺** cation depicts the iron center is surrounded by two Me-DuPhos and one chloride distributed in an intermediate square-pyramidal and trigonal-bipyramidal geometry ($\tau = 0.49$, Fig. 9).⁶⁷ This distortion is similar to those reported for the crystal structures of the iron (II) **[FeX(dppe)₂]** (X = Cl, $\tau = 0.43$; X = Br, $\tau = 0.41$) complexes, which have a triplet ground state with large zero-field splitting.⁷⁰ However,

the iron (I) **[FeX(dppe)₂]** (X = Cl, $\tau = 0.83$; Br, $\tau = 0.82$),⁷¹ and **[FeX(opdp)₂]** (X = Cl, $\tau = 0.79$; Br, $\tau = 0.81$) complexes show distorted trigonal-bipyramidal structures.⁷² These geometries contrast with the square-pyramidal geometries reported for the **[FeCl(DMeOPrPE)₂](BPh₄)** ($\tau = 0.13$) and **[Fe(opdp)₂]** compounds.^{50, 64} The geometries of the **[FeX(PP)₂]** and **[FeX(PP)₂]⁺** (X = halogen) complexes seem to be closely related to the type of the bis(phosphane) and the charge of the iron. Because the geometry of the **[FeCl{(R,R)-Me-DuPhos}₂]⁺** cation, additional stereoisomers are not possible, and the chirality of the complex is only provided by the DuPhos. The chlorine atom occupies the apical position, approximately perpendicular to two of the four phosphorous atoms. The Fe-Cl bond length (2.267 Å) is quite short in comparison to similar iron (II) pentacoordinated compounds (Table 2), and is close to the pseudo-octahedral **[FeCl₂{o-C₆F₄(PMe₂)₂}(BF₄)** compound (2.234 Å).⁷³ The Fe-P distances span 2.279–2.302 Å, and the mean Fe-P distance (2.292 Å) and the bite P-Fe-P angles are similar to analogous Fe(II) compounds (Tables 2 and S6, ESI[†]).

These crystals are air stable and their identification by NMR at room temperature confirmed that **[FeX{(R,R)-Me-DuPhos}₂]⁺** (X = Cl, I) and **[Fe{(S,S)-Me-DuPhos}₂]⁺** complexes are diamagnetic, as reported for the iron (II) **[Fe(opdp)₂]** complex.⁶⁴ A singlet appeared at around 66 ppm in the ³¹P{¹H} NMR spectra at room temperature (Figs. S12 and S13[†]). This chemical shift is analogous to the main signal observed in the ³¹P{¹H} NMR spectra acquired after long periods of time reaction between **[FeH(η²-H₂){(R,R)-Me-DuPhos}₂]⁺** and halide salts. The presence of a narrow signal without couplings in the ³¹P{¹H} spectrum in the range -70 to 25 °C of the temperatures studied is indicative of a fluxional behavior. The absence of hydride resonances in the ¹H NMR spectrum confirmed the X-ray determined composition of the crystals.

Conclusions

NMR experiments show that the dihydrogen ligand in **[FeH(η²-H₂){(R,R)-Me-DuPhos}₂]⁺** is easily substituted by ethers and halides. The **[FeH(η²-H₂){(R,R)-Me-DuPhos}₂]⁺** complex reacts in CD₂Cl₂ at 40 °C with small quantities of ether (THF or Et₂O) to give the *cis*- and *trans*-**[FeHL{(R,R)-Me-DuPhos}₂]⁺** (L = Et₂O or THF) isomers. In THF-d₈ as solvent only the *cis* isomer is obtained. Reaction between **[FeH(η²-H₂){(R,R)-Me-DuPhos}₂]⁺** and ethers evolves with time to free phosphane and other bis(phosphane)-symmetric species. The reaction of **[FeH(η²-H₂){(R,R)-Me-DuPhos}₂]⁺** with iodide or chloride affords *cis* and *trans* mixtures of **[FeHX{(R,R)-Me-DuPhos}₂]** (X = Cl or I). At the end of the reaction, air-stable crystals are obtained and identified by single-crystal X-ray diffraction, and NMR techniques as pentacoordinated **[FeX{(R,R)-Me-DuPhos}₂]⁺** (X = Cl or I) and **[Fe{(S,S)-Me-DuPhos}₂]⁺** complexes. The **[Fe{(R,R)-Me-DuPhos}₂]⁺** and **[Fe{(S,S)-Me-DuPhos}₂]⁺** structures shows that both are chiral-at-metal complexes with trigonal-bipyramidal geometries, which adopt Δ and Λ configurations, respectively. DFT calculations confirms that the helical distribution of the (R,R)-Me-DuPhos around the iron center is favoured to the Λ configuration. In contrast, the chlorine **[FeCl{(R,R)-Me-DuPhos}₂]⁺** complex adopts a near square-pyramidal geometry. The formation of the **[FeCl₂{(R,R)-Me-DuPhos}₂]** complex is also obtained as final product and identified by

Table 1. Selected averaged bond distances and angles for compounds Δ -[Fe{(S,S)-Me-DuPhos}₂](ClO₄) and Λ -[Fe{(R,R)-Me-DuPhos}₂](H₂O) and comparison with the structurally similar [Fe(opdp)₂](I·2CH₂Cl₂) compound.

Distances (Å) ^[a]	Δ -[Fe{(S,S)-Me-DuPhos} ₂] ⁺	Λ -[Fe{(R,R)-Me-DuPhos} ₂] ⁺	[Fe(opdp) ₂] ⁺ ⁶⁴
Fe-P(1)	2.2989[24]	2.2896[13]	2.368[11]
Fe-P(2) ^[b]	2.2857[36]	2.2835[24]	2.368[12] ^[c]
Fe-P(3)	2.2693[1]	2.2646[27]	2.320[4]
Fe-P(4)	2.2678[36]	2.2668[20]	2.320[4] ^[c]
Fe-I	2.5920[5]	2.5816[56]	2.639[7]
Angles (°) ^[a]			
P(1)-Fe-P(2)	121.89[18]	120.73[4]	166.1[16]
P(3)-Fe-P(4)	178.98[13]	178.63[21]	174.1[4]
P(1)-Fe-P(3)	81.24[22]	81.25[14]	80.4[2]
P(2)-Fe-P(4)	81.30[9]	81.57[4]	80.4[2] ^[c]
P(1)-Fe-P(4)	97.92[2]	98.62[43]	98.9[1]
P(3)-Fe-P(2)	99.61[13]	99.66[3]	98.9[1] ^[c]
P(1)-Fe-I	121.76[14]	121.34[1]	95.5[23]
P(2)-Fe-I	116.36[21]	117.94[3]	95.5[23] ^[c]
P(3)-Fe-I	89.77[12]	89.01[18]	94.5[17]
P(4)-Fe-I	89.22[30]	89.93[18]	94.5[17] ^[c]

[a] Standard deviations for averaged values are given in brackets. [b] For all the compounds, P(2) lies in the plane defined by P(1)-Fe-I. [c] Distances and angles generated by symmetry operations of the space group.

Table 2. Selected bond distances and angles for compound [FeCl{(R,R)-Me-DuPhos}₂](BF₄) and comparison with other structurally similar compounds.

Distances (Å) ^[a]	[FeCl{(R,R)-Me-DuPhos} ₂] ⁺	[FeCl(depe) ₂] ⁺ ⁷⁰	[FeCl(DMEOPrPE) ₂] ⁺ ⁵⁰
Fe-P(1)	2.2793(16)	2.3198(9)	2.3130(8)
Fe-P(2) ^[b]	2.2893(16)	2.3340(9)	2.3175(11)
Fe-P(3)	2.2971(16)	2.2740(9)	2.2803(8)
Fe-P(4)	2.3021(16)	2.2792(9)	2.2792(8)
Fe-Cl	2.2666(18)	2.3634(9)	2.35004(10)
Angles (°) ^[a]			
P(1)-Fe-P(2)	146.15(6)	152.52(3)	163.47(4)
P(3)-Fe-P(4)	175.68(6)	178.51(4)	171.25(4)
P(1)-Fe-P(3)	84.39(6)	84.46(3)	82.64(4)
P(2)-Fe-P(4)	85.15(6)	84.36(3)	82.86(4)
P(1)-Fe-P(4)	96.85(6)	96.45(3)	95.81(4)
P(3)-Fe-P(2)	96.14(6)	95.40(3)	96.17(4)
P(1)-Fe-Cl	108.51(8)	101.11(3)	98.94(4)
P(2)-Fe-Cl	105.34(8)	106.37(3)	97.59(4)
P(3)-Fe-Cl	88.46(7)	90.20(3)	96.06(3)
P(4)-Fe-Cl	87.22(7)	88.45(3)	92.70(4)

[a] Standard deviations of the measurement are given in parenthesis. [b] For all the compounds, P(2) lies in the plane defined by P(1)-Fe-Cl.

Fig. 8. Simplified X-ray structures of the cation in the Δ -[Fe{(S,S)-Me-Duphos}₂](ClO₄) (left) and Λ -[Fe{(R,R)-Me-Duphos}₂](H₂O) (right) salts, and their representations along the C₂ axis: a) front view, b) lateral view. The phospholane rings and the hydrogen atoms are omitted for clarity.

Fig. 9. Simplified X-ray structure of the cation in the [FeCl{(R,R)-Me-Duphos}₂](BF₄) salt. The phospholane rings and the hydrogen atoms are omitted for clarity.

using the same techniques. The pentacoordinated and [FeCl₂[(R,R)-Me-Duphos]₂] complexes are air-stable, and are proposed as catalysts for enantioselective transformations for the preparation of high value functionalized molecules. Experiments in this area are underway in our laboratory.

Experimental

Material and methods

All manipulations were carried out in a N₂-filled MBraun glove box and on a Schlenk line using nitrogen or argon. The reactions were carried out in NMR tubes (5 mm) sealed with assembled screw caps, Fisher-Porter tubes (5 mL) or Schlenk flasks (10 mL). The specific reaction conditions (reactants and solvents, type of reactor,

atmosphere used, and temperature and reaction time) are detailed in **Table S1**[†]. The reaction with KClO₄ has been done uniquely to confirm the identification of the counterion in the structure refinement. **Caution!** Perchlorate salts as potentially explosive and should be handled in small amounts and with necessary precautions. Yields are not reported because the syntheses are done at low scale, several unidentified compounds are formed in solution and only a small quantity of crystals are isolated. HPLC grade THF and CH₂Cl₂ (Sigma-Aldrich) was dried and deoxygenated by passing it through commercial columns of CuO followed by alumina under nitrogen atmosphere. Deuterated solvents (Eurosotop) were used as received and were kept in the drybox. Compounds [FeH(η²-H₂){[(R,R)-Me-Duphos]₂}⁺ and [FeH(η²-H₂){[(S,S)-Me-Duphos]₂}⁺ were prepared by following literature procedures.⁵⁶ ¹H and ³¹P{¹H} NMR experiments were recorded on a Bruker AVANCE 300 or 400 MHz spectrometer, in CD₂Cl₂, THF-d₈, or acetone-d₆ solutions. ³⁵Cl NMR experiments were acquired on a Bruker AVANCE 500 MHz spectrometer in CD₃CN. Chemical shifts (δ) are given in ppm relative to TMS (¹H), 85% H₃PO₄ in aqueous solution (³¹P) or NaCl 0.1 M in D₂O (³⁵Cl). Coupling constants (*J*) are in Hertz. Iodine content was determined using an ICP-MS Agilent 7900.

Crystallography

Suitable crystals of Δ -[Fe{(S,S)-Me-Duphos}₂](ClO₄), Λ -[Fe{(R,R)-Me-Duphos}₂](H₂O), [FeCl{(R,R)-Me-Duphos}₂](BF₄), and *trans*-[FeCl₂[(R,R)-Me-Duphos]₂] were grown by slow crystallization in the liquid-gas interphase of the reaction mixture in contact to the walls of the reactor vessel (see the reaction conditions in **Table S1**[†]). Diffraction data were collected on a Agilent Supernova diffractometer equipped with an Atlas CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Data collections, data reductions and absorption corrections were performed with the program CrysAlisPro.⁷⁴ The structures were solved using direct methods in SHELXS⁷⁵ and refined by the full-matrix least squares method based on F² with SHELXL⁷⁶ program with the aid of the OLEX2 (vs 1.2)⁷⁷

software package. The X-ray structure determination and a summary of the crystal data (Tables S6 and S7) are given in the ESI† file.

Computational studies

The calculations were conducted with the Gaussian 09 program suite.⁷⁸ Density functional theory was applied with the Becke hybrid B3P86 functional.^{79–80} Relativistic electron core potentials (RECP) from the Stuttgart group (also known Stoll-Preuss pseudopotentials) and its associated basis set was used to represent the iron,⁸¹ the phosphorus atoms, and the iodide atoms,⁸² and augmented in the case of Fe by an f polarization function (Fe: $\alpha = 2.462$),⁸³ in the case of the P and I with a d polarization function (P: $\alpha = 0.387$; I: $\alpha = 0.289$).⁸⁴ The 6-31G basis set was used to represent the remaining atoms (C and H) of the system. The geometry optimizations were performed in gas phase without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum has been reached. The identity of the minima was confirmed as no imaginary frequencies were obtained. gNMR 4.1 spectral simulation program was used to interpret the ¹H and ³¹P{¹H} data by providing calculated chemical shifts and coupling constants.⁸⁵

Conflicts of interest

There are no conflicts to declare.

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The $[\text{FeH}(\eta^2\text{-H}_2)\{\text{Me-DuPhos}\}_2]^+$ complex reacts with ethers and halides to give *cis*- and *trans*-dihydrogen substituted isomers, and $[\text{FeX}\{\text{Me-DuPhos}\}_2]^+$ (X = Cl, I) complexes.