Coordination of tetradentate X_2N_2 (X = P, S, O) ligands to iron(II) metal center and catalytic application in the transfer hydrogenation of ketones†

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A series of mixed tetradentate ligands associating two iminophosphorane moieties with two phosphino, thiophosphino, or phosphine oxide groups (labelled **2**, **3**, and **4** respectively) have been prepared from the corresponding aminophosphonium derivatives. Their coordination to the iron dichloride metal fragment was achieved using the $[FeCl_2(THF)_{1.5}]$ precursor leading to $[(P_2N_2)FeCl_2]$ (**5**), $[(S_2N_2)FeCl_2]$ (**6**), and $[(O_2N_2)FeCl_2]$ (**7**). These complexes were shown to be paramagnetic. Moreover, those ligands can act as bi, tri or tetradentate, as evidenced by X-ray structure analysis of the complexes, depending on the nature of the pendant PY coordinating ligand (Y = lone pair, S, O). Indeed, while only one phosphorus atom is coordinated to iron in **5** (PNN coordination), no thiophosphine moiety is connected to Fe in **6** (NN coordination), whereas both phosphine oxide arms are linked to the metal in **7** (ONNO) coordination. For ligand **2**, coordination reactions were also performed with a non-chlorinated iron precursor (either $[Fe(CH_3CN)_6](BF_4)_2$ or $[Fe(H_2O)_6](BF_4)_2$) leading to complexes **8** and **9** depending on the reaction conditions. The different iron(II) complexes **5–9** were tested in catalytic transfer hydrogenation of acetophenone, and were found to be efficient for reactions carried out at 82 °C.

Introduction

Development of efficient homogeneous catalysts able to achieve transformations at low economical and environmental cost is fundamental from an industrial point of view. In this context, the use of iron-based complexes is particularly attractive due to the availability and the cost of this metal. Thus in the last decade, a lot of effort was devoted to the development of easily available and cheap iron based catalysts featuring nitrogen based ligands. In particular, bis(iminopyridine) iron(II) complexes were shown to be excellent ethylene oligomerisation[1,2] or polymerisation catalysts.[3,4] More recently, Chirik and coworkers successfully reduced such (N,N,N) iron(II) precursors under nitrogen atmosphere to obtain efficient iron(0) precatalysts for the hydrogenation and hydrosilylation of olefins and alkynes.[5] The same group also reported the reduction of α-diimine iron(II) complexes in presence of alkynes or alkenes to prepare (N,N)Fe(0) complexes that are able to perform the catalytic hydrogenation of 1-hexene.[6]

However, while tetradentate mixed (P_2N_2) ligands (**1**, Chart 1) combining two "soft" phosphines and two "hard" nitrogen atoms, either imine or amide groups, were used with great success in palladium or ruthenium chemistry,[7] their coordination to iron was much less investigated. Whereas Gao and coworkers described the synthesis and structure of (P_2N_2)Fe(II) complexes in 1996,[8] the involvement of such complexes in catalytic processes was only reported this year by Morris's group,[9] who performed the first asymmetric hydrogenation of polar bonds using iron complexes. In this context, we recently developed the synthesis of the phosphorus analog of such tetradentate ligand bearing two phosphine and two iminophosphorane (P=N) moieties (**2**, Chart 1), having in mind that iminophosphoranes exhibit different electronic and steric properties than classical imines. Indeed, iminophosphoranes have no π-accepting ability because of the absence of a real π-system, and behave as strong π-donor ligands due to the presence of two lone pairs on the nitrogen atom. We studied the coordination of tetradentate ligand **2** to palladium and nickel centres, and demonstrated the potential of the corresponding complexes for Suzuki–Miyaura reactions in a biphasic medium.[10] Pursuing our investigations on this ligand, we report here our study concerning the coordination of ligands **2**, **3**, and **4**, which are the corresponding sulfated and oxygenated derivatives respectively (Chart 1), to iron(II) metal centres. Catalytic activity of these complexes in the transfer hydrogenation of ketones is also presented and discussed.

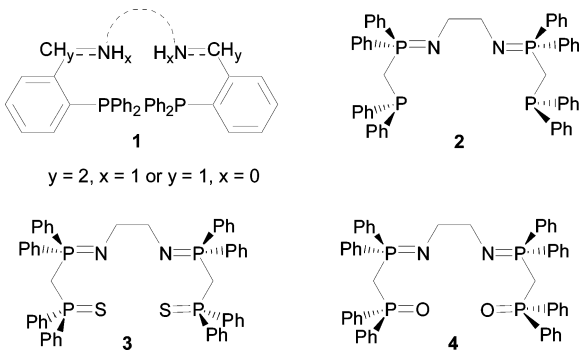

Chart 1 Tetradentate ligands.

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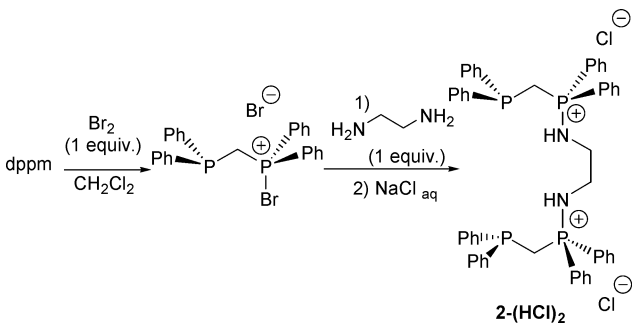
Results and discussion

A Ligand syntheses and coordination studies

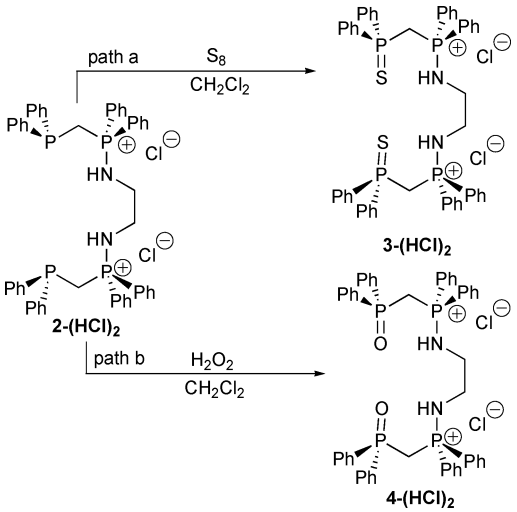
Iminophosphorane-based ligands are, in most cases, straightforwardly prepared by the Staudinger reaction involving the thermal reaction of azides and phosphines.[11] However, with this methodology, the substitution pattern at the nitrogen atom is generally restricted to trimethylsilyl, bulky aryl, sulfonate or phosphonate groups due to the poor availability of functional azides. Thus, we employed a different strategy based on the Kirsanov reaction.[12] This approach consists in the bromination of the phosphine followed by reaction of the formed bromophosphonium with a primary amine in the presence of a base to yield finally the corresponding aminophosphonium, which is perfectly air and moisture stable. Moreover, the use of diamines opens the way to iminophosphorane ligands which would be very difficult to access using azides.

As already described,[10] compound **2-(HCl)$_2$** (Scheme 1) was readily obtained by reaction of bromine with dppm (bis-(diphenylphosphino)methane), followed by the addition of one equivalent of ethylenediamine (half the equivalent behaving as a nucleophile, the second as a base). In order to avoid any scrambling of the bromide counteranions with the chlorides of iron precursors, the dication was isolated as the chloride derivative in 72% yield after washing with saturated brine solution. The tetradentate phosphine-iminophosphorane ligand (**2**) will then be generated *in situ* before coordination experiments by addition of two equivalents of base.



Scheme 1 Synthesis of **2-(HCl)$_2$**.

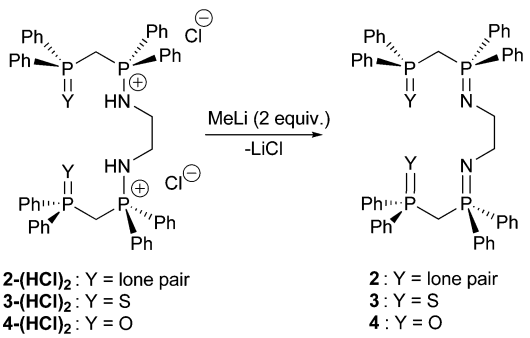
The thio and oxo derivatives have been prepared by a similar strategy involving the corresponding cations **3-(HCl)$_2$** and **4-(HCl)$_2$** respectively. Reaction of the dicationic **2-(HCl)$_2$** with a stoichiometric amount of S_8 in dichloromethane at 40 °C induced within 30 min the precipitation of the sulfide derivative **3-(HCl)$_2$** as a white powder (Scheme 2, path a). **3-(HCl)$_2$** was obtained in excellent yield (92%) and was characterized by multinuclear NMR techniques and elemental analysis. $^{31}P\{H\}$ NMR spectrum show two singlets at 37.0 and 44.7 ppm corresponding respectively to the thiophosphinoyl and aminophosphonium groups. Interestingly, no coupling between the two non-equivalent phosphorus could be measured. The phosphine oxide derivative **4-(HCl)$_2$** was prepared by oxidation of the phosphino groups of the dicationic **2-(HCl)$_2$** by hydrogen peroxide (1.5 equiv.) in dichloromethane at room temperature (Scheme 2, path b). After washing with water then drying, **4-(HCl)$_2$** was isolated as a white powder in 85% yield. It was characterized by multinuclear NMR techniques and elemental



Scheme 2 Synthesis of **3-(HCl)$_2$** and **4-(HCl)$_2$**.

analysis. Contrary to what is observed in the case of the sulfide derivative **3-(HCl)$_2$**, the $^{31}P\{H\}$ NMR spectrum of **4-(HCl)$_2$** exhibits a characteristic AB spin system pattern centered at δ($CDCl_3$) 44.6 ppm ($^2J_{PP}$ = 8 Hz) for the phosphonium group and at 28.6 ppm ($^2J_{PP}$ = 8 Hz) for the phosphine oxide moiety.

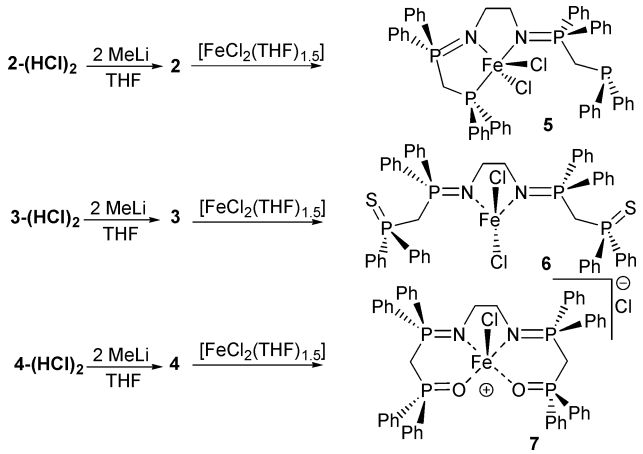
As described for the synthesis of **2** from **2-(HCl)$_2$**,[10] the iminophosphorane based ligands **3** and **4** were prepared by deprotonation of the corresponding dications using 2 equivalents of MeLi in toluene at low temperature (Scheme 3). The $^{31}P\{H\}$ NMR data of **3** and **4** were found to be very similar, both exhibiting a characteristic AB spin system pattern centered at δ(d_8-toluene) = 38.0 ($^2J_{PP}$ = 26.0 Hz) and 38.7 ($^2J_{PP}$ = 12 Hz), for the thio- or oxo-phosphino group respectively and at 27.9 ppm in **3** and at 33.2 ppm in **4** for the iminophosphorane moiety.



Scheme 3 Preparation of iminophosphorane-based ligands.

These ligands could be isolated as air and moisture sensitive white powders after removal of precipitated LiCl salts and evaporation of solvents. Because of their sensitivity **3** and **4** were only characterized by multinuclear NMR techniques.

As previously explained, coordination experiments were directly conducted from the dications, without isolating the free ligands **2–4**. Thus, their deprotonation was achieved in THF at low temperature, followed by the addition of [$FeCl_2(THF)_{1.5}$] (Scheme 4). The coordination reaction could be monitored by $^{31}P\{H\}$ NMR showing the total disappearance of the AB spin system pattern corresponding to the free ligands **2–4**. In each case the coordination was accompanied by a marked colour change of



Scheme 4 Coordination with $[FeCl_2(THF)_{1.5}]$.

the reaction mixture which became yellow upon forming **5**, brown upon forming **6** and **7**.

After completion of the reaction, THF was evaporated *in vacuo*, dichloromethane was introduced, inducing the precipitation of the LiCl salts which were eliminated by filtration. After removal of CH_2Cl_2, and washing with hexanes, complexes **5** and **6** were isolated as air and moisture sensitive yellow and brown powders respectively, whereas **7**, which appeared a lot more air and moisture sensitive was isolated as a yellow brown powder. The latter indeed decomposes when handled in air even for a few seconds as evidenced by an instant colour change to red.

The $^{31}P\{H\}$ NMR spectra of complexes **5–7** solutions are poorly definite, because of their paramagnetism. Nevertheless, significant differences can be observed depending on the ligand used. Indeed, while for **5** and **6**, after long acquisition time, a broad singlet can be observed at $\delta(THF) = -27$ ppm and 57 ppm respectively, which may correspond to uncoordinated phosphine and thiophosphine arms respectively, no signal could be seen for solutions of complex **7**, which might indicate the coordination of both iminophosphorane and phosphine oxide moieties.

To confirm the paramagnetic nature of complexes **5–7**, the magnetic moments of these complexes were determined using the method of Evans in $CDCl_3$ at 20 °C employing tetramethylsilane as reference. These measurements gave values of 4.36 μ_B for **5**, 3.87 μ_B for **6**, and 4.03 μ_B for **7**, which are in the range of those determined for other iron(II) complexes.[1,3,14]

However, definitive evidences concerning the structures of complexes **5–7** were furnished by X-ray crystal structure analysis of these complexes. Suitable crystals were grown by slow diffusion of hexanes into concentrated dichloromethane solution of complexes. An ORTEP plot of one molecule of **5** is presented in Fig. 1. Complex **5** adopts a bipyramid trigonal geometry with both iminophosphoranes and only one phosphine arm being coordinated to the metal centre, the other one being remote from iron (5.729 Å for the Fe–P4 distance). The Fe, N1, N2, and P2 atoms are almost coplanar with a small deviation of 4.52° from the planarity (N1–N2–Fe–P2 dihedral angle). The coordination sphere is completed by two chloride atoms, the Fe–Cl bonds measuring 2.406(7) and 2.350(7) Å. As expected for this d^6 metal centre in a trigonal bipyramidal complex, a triplet spin configuration is preferred for the d-block and justified the

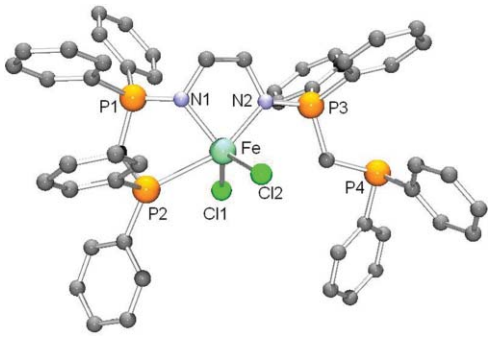


Fig. 1 Molecular structure of complex **5**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (°): P4–Fe = 5.296; N1–Fe = 2.074(2); N2–Fe = 2.116(2); P2–Fe = 2.676(8); Fe–Cl2 = 2.406(7); Fe–Cl1 = 2.350(7); P1–N1 = 1.593(2); P3–N2 = 1.581(3); Cl1–Fe–Cl2 = 123.84(3); Cl1–Fe–N2 = 96.26(8); Cl2–Fe–N2 = 100.98(8); Cl1–Fe–N1 = 116.28(7); Cl2–Fe–N1 = 119.06(7); Cl1–Fe–P2 = 98.27(3); Cl2–Fe–P2 = 85.13(2); P2–Fe–P4 = 145.64; N1–Fe–P2 = 77.30(7); N1–Fe–N2 = 80.8(1); N2–Fe–P2 = 157.38(7); Fe–P2–N1–N2 = 4.52; P2–N1–N2–P4 = 6.34; P2–P1–P3–P4 = 24.70; Fe–N1–Cl2–Cl1 = 6.04.

observed paramagnetism. The broad signal observed in ^{31}P NMR for the free phosphine moiety also suggests that, in solution, the phosphine groups are in permanent exchange.

A view of complex **6** is shown in Fig. 2. In this case, the geometry around the iron(II) centre is tetrahedral since only the two iminophosphorane arms and two chloride atoms are coordinated, all the angles around iron being relatively close (angles : Cl1–Fe–Cl2 = 118.42(3)°; Cl1–Fe–N2 = 113.88(6)°; Cl2–Fe–N2 = 110.46(6)°; Cl1–Fe–N1 = 111.26(6)°). On the other hand, the Cl–Fe bond distances were measured at 2.301(7) and 2.312(7) Å.

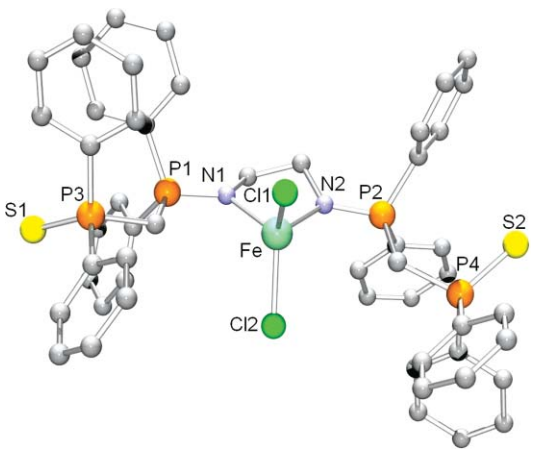


Fig. 2 Molecular structure of complex **6**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (°): P4–Fe = 5.046; N1–Fe = 2.018(2); N2–Fe = 2.019(2); P3–Fe = 5.045; Fe–Cl2 = 2.301(7); Fe–Cl1 = 2.312(7); P1–N1 = 1.599(2); P2–N2 = 1.592(2); P3–S1 = 1.948(1); P4–S2 = 1.949(8); Cl1–Fe–Cl2 = 118.42(3); Cl1–Fe–N2 = 113.88(6); Cl2–Fe–N2 = 110.46(6); P3–Fe–P4 = 156.88; Cl1–Fe–N1 = 111.26(6); N1–Fe–N2 = 82.74(8); N1–Fe–Cl2 = 114.79(6); N2–Fe–Cl2 = 110.46(6); N1–N2–P4–P3 = 12.98; P1–P2–P4–P3 = 8.46.

As can be seen the thiophosphine groups are rejected away from the metal centre, Fe–S distances being greater than 6.32 Å. The tetrahedral geometry around the d^6 metal centre explains the observed paramagnetism of complex **6**. It is noteworthy that the uncoordinated thiophosphine arms appeared deeply deshielded compared to the free ligand ($\Delta\delta \sim 19$ ppm).

A view of complex **7** is presented in Fig. 3. As can be seen, complex **7** adopts a square pyramidal geometry. The five coordination sites being occupied by both iminophosphorane and phosphine oxide arms, together with one chloride atom. Contrary to complex **6**, complex **7** is monocationic, pentacoordinated and extremely electron rich because of the coordination of the phosphine oxide side arms. This might explain the greater sensitivity towards air of **7** in comparison to **5** and **6**. Indeed, in presence of oxygen, **7** instantly changes from yellow to red, being oxidized into iron(III), whereas **5** and **6** could be isolated easily and handled for a few minutes without any apparent oxidation.

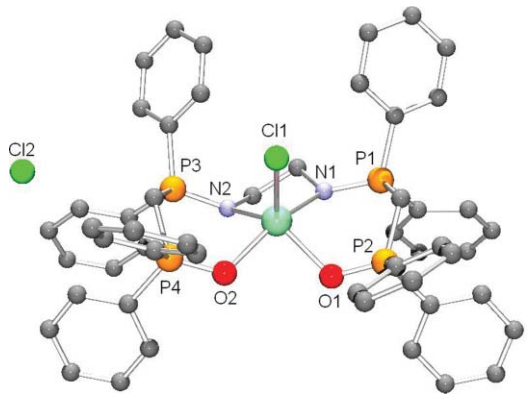
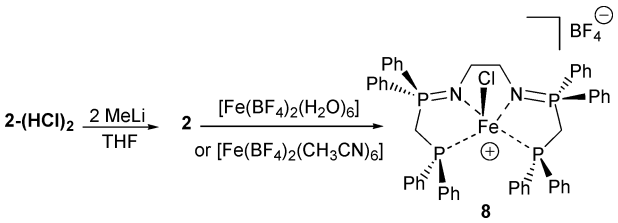


Fig. 3 Molecular structure of complex **7**. Hydrogen atoms solvent molecules have been omitted for clarity. Selected distances (Å) and angles (°): O1–Fe1 = 2.132(2); N1–Fe1 = 2.097(2); N2–Fe1 = 2.100(2); O2–Fe1 = 1.127(2); Fe1–Cl1 = 2.332(8); Fe1–Cl3 = 6.861; P1–N1 = 1.585(2); P3–N2 = 1.596(2); P4–O2 = 1.507(2), P2–O1 = 1.504(2), O2–Fe1–O1 = 83.69(7); N1–Fe–N2 = 80.0(1); O2–Fe–N2 = 89.80(8); O1–Fe–N1 = 90.78(1); O1–Fe–Cl1 = 107.89(6), O2–Fe–Cl1 = 99.23(6), N1–Fe–Cl1 = 102.54(7), N2–Fe–Cl1 = 114.85(6), N1–O1–O2–N2 = 13.84; P1–P2–P4–P3 = 9.02.

In order to evaluate the potential of dicationic iron(II) complexes in transfer hydrogenation reactions, we then logically attempted the removal of chloride ligands from complex **5** using two equivalents of $AgBF_4$, but despite many efforts, whatever the experimental conditions employed, this reaction failed. To obtain the desired dicationic complex of general formula $[Fe(P_2N_2)]^{2+}$, coordination of ligand **2** was achieved using either the available dicationic $[Fe(H_2O)_6](BF_4)_2$ or $[Fe(CH_3CN)_6](BF_4)_2$ precursors. Two different procedures were tested. In a first approach, both iron precursors were added to a THF solution of free ligand **2** still containing LiCl salts resulting from the reaction with methyl lithium (Scheme 5). However, no reaction yielded the expected tetracoordinated dicationic species but the pentacoordinated complex **8** (see Scheme 5). The structure of **8** could not be established from NMR data (**8** is ^{31}P NMR silent) and definitive evidence on its formulation was given by a X-ray crystal structure analysis. Note that it was checked that both reactions yielded the



Scheme 5 Synthesis of complex **8**.

same complex, single crystals being grown in separate experiments. A view of one molecule of complex **8** is presented in Fig. 4.

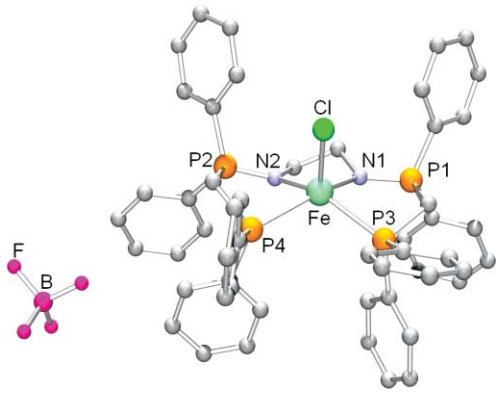
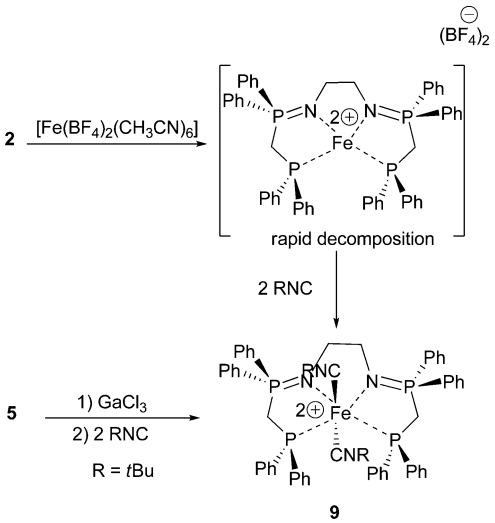


Fig. 4 Molecular structure of complex **8**. Hydrogen atoms solvent molecules have been omitted for clarity. Selected distances (Å) and angles (°): P4–Fe = 2.528(5); N1–Fe = 2.088(1); N2–Fe = 2.080(1); P3–Fe= 2.483(5); Fe–Cl = 2.316(5); P1–N1 = 1.598(1); P2–N2 = 1.597(1); P4–Fe–Cl = 95.20(2), P3–Fe–Cl = 100.82(2), N1–Fe–Cl = 109.42(4), N2–Fe–Cl = 111.40(4), P3–Fe–P4 = 106.55(2); N1–Fe–N2 = 79.38(5); P3–Fe–N1 = 82.21(4), P4–Fe–N2 = 79.42(4), N1–P3–P4–N2 = −4.59; P1–P3–P4–P2 = 1.21.

As can be seen, **8** is a monocationic iron(II) complex, which adopts a square pyramidal geometry. The five coordination sites are occupied by both iminophosphorane and phosphine arms, together with one chloride ligand. In comparison with complex **5**, all phosphines are strongly coordinated to the metal center (P4–Fe = 2.528(5) and P3–Fe = 2.483(5) Å in **8** *versus* P2–Fe = 2.674 Å in **5**). The Fe–Cl distance was measured at 2.316(5) Å. Though the two phosphorus and the nitrogen atoms are almost coplanar (dihedral angle N1–P3–P4–N2 = 4.59°), the iron metal centre is located above the square base of the pyramid (dihedral angles P3–N1–N2–Fe = 22.81° and P4–N2–N1–Fe = 15.88°). In this strongly distorted square base pyramidal d^6 complex of a first period element, a triplet or a higher spin configuration of the d block can be expected. Indeed, here the complex is paramagnetic with a measured magnetic moment of 4.17 μ_B. No additional experiments were undertaken to rationalize the mechanism accounting for the formation of complex **8** but one may propose that it results from a ligand exchange between co-ligands (H_2O and CH_3CN) and chloride anions which are present in solution.

In order to circumvent this limitation further experiments were carried out using LiCl-free solutions of ligand **2**. Moreover, an ionizing solvent such as acetonitrile was used. Under these conditions (Scheme 6), addition of a stoichiometric amount of $[Fe(CH_3CN)_6](BF_4)_2$ to an acetonitrile solution **2** induced an



Scheme 6 Synthesis of complex **8** from **2** and from complex **5** by chloride abstraction with $GaCl_3$.

instant colour change from colourless to purple. Unfortunately, monitoring the reaction by $^{31}P\{H\}$ NMR did not bring significant information on the nature of the compound formed since no signal could be detected. However, a rapid decomposition was observed as evidenced by the fading of the purple colour and the appearance of many unidentified peaks in the $^{31}P\{H\}$ NMR spectrum.

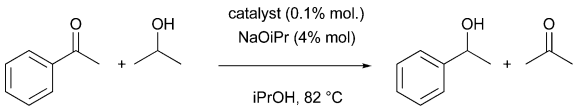
Anticipating that this decomposition may result from the high reactivity of the putative transient $[Fe(P_2N_2)(CH_3CN)_2](BF_4)_2$ complex, two equivalents of *tert*-butylisocyanide (*t*BuNC) were added to the purple solution as soon as it formed resulting in the immediate appearance of an orange colour. The $^{31}P\{H\}$ NMR spectrum of the crude mixture also revealed the presence of an A_2B_2 spin system pattern consisting of two virtual triplets centered at ($^3J_{PP}$ = 14.5 Hz) at δ(CH_3CN) = 43.2 and 65.2 ppm.‡ This complex proved to be diamagnetic and was fully characterized by multinuclear NMR spectroscopies and elemental analyses. It is noteworthy that the same complex, labelled **9**, was obtained by chloride abstraction of complex **5** using $GaCl_3$ followed by addition of two equivalents of *tert*-butylisocyanide ligand. Conventional work-up yielded a pale orange solid, which unfortunately could not be further characterized by X-ray diffraction since no suitable crystal could be obtained despite numerous crystallization attempts. However, considering the coupling figures obtained in the NMR spectrum, we propose that **9** adopts a pseudo-octahedral geometry as depicted in Scheme 6.

B Catalytic transfer hydrogenation of acetophenone

Complexes **5–9** were evaluated in the catalytic transfer hydrogenation of acetophenone in isopropanol using 4% of base and a low catalyst loading of 0.1%. Different bases were tested (KOH, *t*-BuOK, and *i*-PrONa); no significant difference being observed. Reactions were conducted with sodium isopropanolate. The results are gathered in Table 1. No reaction took place at room temperature, and the evolution was only very sluggish at 50 °C (48% conversion after 18 h with complex **8**, entry 1). However

‡ When only one equivalent of isocyanide was added, a mixture of complex **9** and the transient $[(P_2N_2)Fe^+]$ complex was observed.

Table 1 Catalytic transfer hydrogenation of acetophenone



Entry	Complex	Reaction time/h	NMR conversion (%)
1[a]	**8**	18	48
2	**5**	8	80
3	**6**	8	91
4	**7**	6	89
5	**8**	8	75
6	**9**	8	78

[a] Reaction performed at 50 °C.

at 82 °C (propanol reflux), a minimal conversion of 75% was observed in ^1H NMR after 8 h, all reactions being completed after 24 h.

Comparing the different results, complex **7** appeared slightly more efficient but, taken as a whole, the performances of the complexes **5–9** were found to be comparable. Moreover, having in mind that a cationic iron(II) hydride complex may be the active catalytic species, the reaction was monitored by $^1H\{P\}$ NMR, but no putative iron hydride complex could be detected. The synthesis of this iron hydride complex by reduction of **5** with sodium tetraborohydrate or lithium triethylborohydride in THF was also attempted but did not yield convincing results, each experiment resulting in the formation of many unidentified species. Nevertheless iron hydride complexes are not always powerful catalysts, since Bianchini's group synthesised such a complex, which only exhibited a low catalytic activity in transfer hydrogenation of acetophenone.[15] On the other hand, Casey developed an elegant use of Knölker's iron hydride complex as a racemic hydrogenation catalyst under mild conditions (room temperature, low pressure of dihydrogen).

To complete this study, complexes **5**, **8** and **9** were also tested as catalytic precursors for the hydrogenation of acetophenone to 1-phenylethanol under H_2 atmosphere. The results were found to be disappointing since no reaction was observed for **5** and **9** after 20 h at 60 °C. With **8** the conversion only reached 10%.

While ruthenium-based systems for the transfer hydrogenation of ketones are well known in the literature,[16] examples of active iron-based systems are still very rare. Aside from the system reported by Morris's group at the beginning of 2008, which turns out to be the most efficient reported so far (room temperature activity, good enantioselective excess),[9] complexes **5–9** can be considered as quite competitive, though racemic and requiring higher temperature. At 0.1% molar catalyst loading, these complexes compete favorably with the racemic system developed by Beller in 2006 based on iron sources and porphyrins (1% molar of iron, 50% base, 100 °C, 90% conversion of acetophenone in 7 h).[17] Even Casey's catalyst required higher catalyst loading (1% molar) for the racemic transfer hydrogenation reaction, 87% of acetophenone being converted in 1-phenylethanol within 16 h at 75 °C.

Conclusions

In summary, we have developed a series of well-defined iron catalyst based on a family of readily accessible mixed tetradentate

ligands bearing two iminophosphorane moieties and either two phosphine, thiophosphine or phosphine oxide groups. All those ligands are easily synthesised from the same bis(phosphine-aminophosphonium) salt, prepared from commercial reagents. The variety of the coordination sites in this family of ligands accounts for the structural diversity of the prepared iron(II) complexes **5–9**. All present different geometries: trigonal bipyramidal, pseudo-octahedral, square based pyramidal, or tetrahedral. Moreover, neutral, monocationic, and dicationic iron species were prepared using the same tetradentate phosphine-iminophosphorane ligand **2** by simply modifying the nature of the iron(II) precursor. Most of these complexes were paramagnetic and were characterized by X-ray diffraction analysis. All these complexes constitute well-defined iron catalysts for the transfer hydrogenation of acetophenone. Active at 0.1% mol, those precatalysts give satisfactory TON (1000) and TOF (150 h^{-1} for complex **7**) and are among the best iron catalysts reported so far for the transfer hydrogenation of ketones. Mechanistic studies and the development of pure enantiomeric derivatives of these new systems are currently underway in our laboratories.

Experimental section

General considerations

All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glove box techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, diethylether, petroleum ether), from P_2O_5 (dichloromethane). Aminophosphonium salt 2-$(HCl)_2$,[10] sodium isopropanolate, $[Fe(MeCN)_6](BF_4)_2$[18] and $[FeCl_2THF_{1.5}]$[19] were prepared according to literature procedures. All other reagents and chemicals were obtained commercially and used without further purification, except for isopropanol which was distilled under dry nitrogen from calcium hydride. Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Magnetic moments were determined by the Evans method[13] in $CDCl_3$ using a solution of Me_4Si in $CDCl_3$ (1 : 100, V/V) as reference. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France.

Syntheses

Synthesis of thiophosphine/aminophosphonium salt 3-$(HCl)_2$. S_8 (36 mg, 0.140 mmol) was added to a solution of **2-$(HCl)_2$** (500 mg, 0.557 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 30 min at 40 °C and a white precipitate was rapidly formed. The solvents were removed under vacuum to yield a white solid, which was washed with diethylether.

3-$(HCl)_2$ (457 mg, 92%). ^{31}P $\{^1H\}$ (121.5 MHz, $CDCl_3$) δ 37.0 (s, $P^{(V)}$(S), 44.8 (s, $P^{(V)}$(N). ^1H (300 MHz, $CDCl_3$) δ 2.79 (4H, bs, N-CH_2), 5.03 (4H, dd, $^2J_{HP}$ = 13.2 Hz, $^2J_{HP}$ = 3.4 Hz, PCH_2P), 7.27 (20H, m, p-H ($Ph_2P^{(V)}$(S) and m-H ($Ph_2P^{(V)}$(N)), 7.46 (4H, m, p-H ($Ph_2P^{(V)}$(N)), 7.77 (8H, dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 13.4 Hz, o-H ($Ph_2P^{(V)}$(N)), 7.87 (8H, dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 14 Hz, o-H $Ph_2P^{(V)}$(S), NH not seen. ^{13}C $\{^1H\}$ (75.5 MHz, $CDCl_3$) δ_C 27.3 (dd, $^1J_{CP}$ = 49.0 Hz, $^1J_{CP}$ = 66.5 Hz, PCH_2P), 40.5 (d, $^2J_{CP}$ = 8.5 Hz, NCH_2), 118.3 (d, $^2J_{CP}$ = 100.0 Hz C_{ipso}-(Ph_2 $P^{(V)}$)), 127.7 (d, $^3J_{CP}$ = 13.1 Hz, m-CH-($Ph_2P^{(V)}$(S)), 128.1 (d, $^3J_{CP}$ = 13.6 Hz, m-CH-($Ph_2P^{(V)}$(N)), 130.1 (d, $^2J_{CP}$ = 11.4 Hz, o-CH-($Ph_2P^{(V)}$(S)), 130.4 (dd, $^1J_{CP}$ = 81.8 Hz, $^3J_{CP}$ = 3.5 Hz, C_{ipso}-(Ph_2 $P^{(V)}$)), 130.6 (d, $^4J_{CP}$ = 2.7 Hz, p-CH-($Ph_2P^{(V)}$(S)), 133.3 (d, $^2J_{CP}$ = 11.5 Hz, o-CH-($Ph_2P^{(V)}$(N)), 133.7 (d, $^4J_{CP}$ = 2.7 Hz, p-CH-($Ph_2P^{(V)}$(N)). Anal. Calcd. for $C_{52}H_{50}Cl_2N_2P_4S_2$: C, 64.93; H, 5.24; N, 2.91%. Found: C, 64.87; H, 5.21; N, 2.94%.

Synthesis of phosphine oxide/aminophosphonium salt 4-$(HCl)_2$. A solution of H_2O_2 in water (35% wt) (74 µL, 0.84 mmol) was slowly (the reaction is exothermic) added to a suspension of **2-$(HCl)_2$** (500 mg, 0.557 mmol) in dichloromethane (5 mL). The suspension was stirred for 5 min at room temperature. The solution was washed twice with water (5 mL), the organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum to deliver a white solid, which was washed with diethyl ether.

4-$(HCl)_2$ (440 mg, 85%).^{31}P $\{^1H\}$ (121.5 MHz, $CDCl_3$) δ 28.7 (d, $^2J_{PP}$ = 7.6 Hz, $P^{(V)}$(O), 44.6 (d, $^2J_{PP}$ = 7.6 Hz, $P^{(V)}$(N). ^1H (300 MHz, $CDCl_3$) δ 3.20 (4H, bs, N-CH_2), 4.88 (4H, dd, $^2J_{HP}$ = 12.7 Hz, $^2J_{HP}$ = 17.0 Hz, PCH_2P), 7.28 (8H, m, p,m-H (Ph_2 $P^{(V)}$(O)), 7.33 (8H, m, m-H ($Ph_2P^{(V)}$(N)), 7.49 (8H, t, $^3J_{HH}$ = 7.5 Hz, p-H ($Ph_2P^{(V)}$(N)), 7.82 (8H, dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 12.6 Hz, o-H ($Ph_2P^{(V)}$(O)), 7.90 (8H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HP}$ = 13.7 Hz, o-H ($Ph_2P^{(V)}$(N)), NH not seen. ^{13}C $\{^1H\}$ (75.5 MHz, $CDCl_3$) δ_C 28.0 (dd, $^1J_{CP}$ = 56.6 Hz, $^1J_{CP}$ = 60.0 Hz, PCH_2P), 42.2 (d, $^2J_{CP}$ = 9.0 Hz, NCH_2), 120.7 (d, $^1J_{CP}$ = 100.6 Hz, C_{ipso}-(Ph_2 $P^{(V)}$(O)), 129.0 (d, $^3J_{CP}$ = 12.8 Hz, m-CH-(Ph_2 $P^{(V)}$(O)), 129.6 (d, $^3J_{CP}$ = 13.7 Hz, m-CH-(Ph_2 $P^{(V)}$(N)), 131.0 (d, $^3J_{CP}$ = 10.5 Hz, o-CH-($Ph_2P^{(V)}$(N)), 132.2 (dd, $^1J_{CP}$ = 100.6 Hz, $^3J_{CP}$ = 3.2 Hz, C_{ipso}-($Ph_2P^{(V)}$(N)), 132.4 (d, $^2J_{CP}$ = 2.7 Hz, p-CH-($Ph_2P^{(V)}$(O)), 134.0 (d, $^2J_{CP}$ = 12.0 Hz, o-CH-($Ph_2P^{(V)}$(N)), 134.8 (d, $^2J_{CP}$ = 2.8 Hz, p-CH-($Ph_2P^{(V)}$(N)). Anal. Calcd. for $C_{52}H_{50}Cl_2N_2P_4O_2$: C, 67.17; H, 5.42; N, 3.01%. Found: C, 67.13; H, 5.39; N, 3.06%.

Synthesis of thiophosphine/iminophosphorane 3. MeLi (130 µL, 0.208 mmol) was added to a suspension of ligand **3-$(HCl)_2$** (100 mg, 0.104 mmol) in toluene (5 mL) cooled at-78 °C. The cold bath was removed and the solution allowed to warm to room temperature. The insoluble lithium salts were centrifuged from the yellow solution and after removal of solvent under vacuum, the obtained white solid was washed with hexanes (10 mL).

3 (76 mg, 76%).^{31}P $\{^1H\}$ (121.5 MHz, C_7D_8) δ 33.2 (d, $^2J_{PP}$ = 26.2 Hz, $P^{(V)}$(N)), 34.8 (d, $^2J_{PP}$ = 26.2 Hz, $P^{(V)}$(S)). ^1H (300 MHz, C_7D_8), 3.12 (4H, bs, N-CH_2), 4.59 (4H, d, $^2J_{HP}$ = 6.5 Hz, PCH_2P), 7.19–7.35 (24H, m, p,m-H (Ph_2 $P^{(V)}$)), 7.79 (8H, dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 12.0 Hz, o-H ($Ph_2P^{(V)}$(S)), 7.93 (8H, m, o-H ($Ph_2P^{(V)}$(N)). ^{13}C $\{^1H\}$ (75.5 MHz, C_7D_8) δ_C 12.0 (dd, $^1J_{CP}$ = 106.8 Hz, $^1J_{CP}$ = 135.5 Hz, PCH_2P), 41.2 (d, $^2J_{CP}$ = 8.1 Hz, NCH_2), 126.7 (d, $^3J_{CP}$ = 12.0 Hz, m-CH-($Ph_2P^{(V)}$),127.6 (d, $^3J_{CP}$ = 12.4 Hz, m-CH-($Ph_2P^{(V)}$), 128.5 (d, $^4J_{CP}$ = 2.3 Hz, p-CH-($Ph_2P^{(V)}$), 130.0 (d, $^2J_{CP}$ = 10.7 Hz, o-CH-($Ph_2P^{(V)}$(S)), 130.4 (d, $^4J_{CP}$ = 2.1 Hz, p-CH-($Ph_2P^{(V)}$(N)), 131.4 (d, $^2J_{CP}$ = 10.0 Hz, o-CH-($Ph_2P^{(V)}$(S)), 133.7 (d, $^4J_{CP}$ = 2.7 Hz, p-CH-($Ph_2P^{(V)}$(N)), 132.8 (dd, $^1J_{CP}$ = 109.2.0 Hz, $^4J_{CP}$ = 5.6.0 Hz,

C_{ipso}-($Ph_2P^{(V)}$)), 141.9 (dd, $^1J_{CP}$ = 84.4 Hz, $^4J_{CP}$ = 4.1 Hz, C_{ipso}-($Ph_2P^{(V)}$)).

Synthesis of phosphine oxide/iminophosphorane 4. MeLi (135 µL, 0.215 mmol) was added to a suspension of ligand **4-(HCl)$_2$** (100 mg, 0.107 mmol) in toluene (5 mL) cooled at −78 °C. The cold bath was removed and the solution allowed to warm to room temperature. The insoluble lithium salts were removed by centrifugation from the colourless solution. After removal of solvent under vacuum, the obtained white solid was washed with hexanes (10 mL).

4 (73 mg, 82%).^{31}P {^{1}H} (121.5 MHz, C_7D_8) δ 27.9 (d, $^2J_{PP}$ = 12.0 Hz, $P^{(V)}$(N)), 38.7 (d, $^2J_{PP}$ = 12.0 Hz, $P^{(V)}$(O)). ^{1}H (300 MHz, C_7D_8) δ 1.78 (4H, bs, PCH_2P), 2.64 (4H, bs, N-CH_2), 7.18 (4H, m, p-H (Ph_2 $P^{(V)}$O), 7.25 (16H, m, m, o-H ($Ph_2P^{(V)}$(N), 7.46 (4H, m, o-H ($Ph_2P^{(v)}$O). ^{13}C {^{1}H} (75.5 MHz, C_7D_8) δ_C 36.5 (t, $^1J_{CP}$ = 94.0 Hz, $^1J_{CP'}$ = 135.5 Hz, PCH_2P), 49.5 (d, $^2J_{CP}$ = 16.0 Hz, NCH_2), 126.7 (d, $^3J_{CP}$ = 6.0 Hz, p-CH-($Ph_2P^{(V)}$(O)), 127.7 (d, $^3J_{CP}$ = 10.0 Hz, o-CH-($Ph_2P^{(V)}$(O), 130.5 (d, $^2J_{CP}$ = 5.0 Hz, p-CH-($Ph_2P^{(V)}$(N)), 131.0 (d, $^4J_{CP}$ = 9.0 Hz, m-CH-($Ph_2P^{(V)}$(O)), 131.8 (d, $^2J_{CP}$ = 9.0 Hz, m-CH-($Ph_2P^{(V)}$(N)), 132.1 (d, $^4J_{CP}$ = 10.0 Hz, o-CH-($Ph_2P^{(V)}$(O)), 139.8 (d, $^1J_{CP}$ = 36.5 Hz, C_{ipso}-($Ph_2P^{(V)}$)), 141.7 (d, $^1J_{CP}$ = 30.5 Hz C_{ipso}-($Ph_2P^{(V)}$)).

Synthesis of complex [$P_2N_2FeCl_2$] 5. MeLi (140 µL, 0.222 mmol) was added to a suspension of ligand **4-(HCl)$_2$** (0.111mmol) in THF (5 mL) cooled at −78 °C. The cold bath was removed and the solution allowed to warm to room temperature. Then, [$FeCl_2THF_{1.5}$)] (26 mg, 0.111 mmol) was added and the solution turned immediately from colourless to yellow. After stirring 30 min at room temperature, THF was evaporated and the resulting solid was dissolved into CH_2Cl_2 (5 mL) to remove the insoluble lithium salts. After evaporation of solvents under vacuum, the obtained very air-sensitive yellow solid was washed with Et_2O (10 mL) then dried. Crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a solution of **5** in dichloromethane at room temperature. **5** (83 mg, 78%).^{31}P {^{1}H} (121.5 MHz, $CDCl_3$) δ −27.0 (bs, non coordinated $P^{(III)}$). ^{1}H (300 MHz, $CDCl_3$) δ 4.21 (4H, bs, N-CH_2), 4.99 (4H, bs, PCH_2P), 7.45 (16H, bs, H (Ph_2 P), 7.77 (8H, bs, H (Ph_2 P), 8.97 (6H, m, H (Ph_2P)). μeff (Evans balance): 4.36 μ_B. Anal. Calcd. for $C_{53}H_{50}Cl_2FeN_2P_4$: C, 65.92; H, 5.22; N, 2.90%. Found: C, 66.03; H, 5.29; N, 2.88%.

Synthesis of complex [$S_2N_2FeCl_2$] 6. The preparation of **6** (yielded as a very air-sensitive light brown solid) and the obtainment of crystals were carried out using the same methods already described for **5**. **6** (95 mg, 85%).^{31}P {^{1}H} (121.5 MHz, $CDCl_3$) δ 57 (bs, not coordinated $P^{(V)}$(S). ^{1}H (300 MHz, $CDCl_3$) δ 2.18 (4H, bs, N-CH_2), 4.40 (4H, bs, PCH_2P), 7.29 (24H, m, H (Ph_2P)), 7.85 (8H, m, H (Ph_2P)), 10.56 (8H, m, o-H (Ph_2 P)). μeff (Evans balance): 3.87 μ_B. Anal. Calcd. for $C_{52}H_{47}Cl_2FeN_2P_4S_2$: C, 61.55; H, 4.67; N, 2.76%. Found: C, 61.59; H, 4.78; N, 2.73%.

Synthesis of complex [$O_2N_2FeCl_2$] 7. The preparation of **7** (yielded as a very air-sensitive brown solid) and the obtainment of crystals were carried out using the same methods already described for **5**. **7** (73 mg, 80%).^{1}H (300 MHz, $CDCl_3$) δ 0.81 (4H, bs, N-CH_2), 1.18 (4H, bs, PCH_2P), 7.18 (40H, bs, (Ph_2P)). μeff (Evans balance): 4.03 μ_B. Anal. Calcd. for $C_{52}H_{47}Cl_2FeN_2O_2P_4$: C, 63.56; H, 4.82; N, 2.85%. Found: C, 63.61; H, 4.89; N, 2.79%.

Synthesis of complex [P_2N_2FeCl]BF_4 8. MeLi (140 µL, 0.222 mmol) was added to a suspension of ligand **2-(HCl)$_2$** (0.111 mmol) in THF (5 mL) cooled at −78 °C. The cold bath was removed and the solution allowed to warm to room temperature. Then, [$Fe(BF_4)_2MeCN_6$)] (53 mg, 0.111 mmol) was added and the solution turned immediately from colourless to yellow. After stirring 30 min at room temperature, THF was evaporated, the resulting solid was dissolved into CH_2Cl_2 (5 mL) to remove the insoluble lithium salts. After evacuation of solvents under vacuum, the obtained very air-sensitive yellow solid was washed with Et_2O (10 mL) and then dried. Crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a solution of **8** in dichloromethane at room temperature. **8** (77 mg, 69%).^{1}H (300 MHz, $CDCl_3$) δ 0.89 (4H, bs, N-CH_2), 4.65 (4H, bs, PCH_2P), 7.0–7.74 (40H, m, (Ph_2P). μeff (Evans balance): 4.17 μ_B. Anal. Calcd. for $C_{52}H_{48}BClF_4FeN_2P_4$: C, 62.27; H, 4.82; N, 2.79%. Found: C, 62.31; H, 4.85; N, 2.78%.

Synthesis of complex [$P_2N_2Fe(tBuNC)_2$](BF_4)$_2$ 9. MeLi (140 µL, 0.222 mmol) was added to a suspension of ligand **2-(HCl)$_2$** (0.111 mmol) in toluene (5 mL) cooled at −78 °C. The cold bath was removed and the solution allowed to warm to room temperature. After removal of the insoluble lithium salts from the colourless solution and evaporation of solvents under vacuum, acetonitrile (5mL) was added. Then, [$Fe(BF_4)_2MeCN_6$)] (53 mg, 0.111 mmol) was introduced, the solution turning immediately from colourless to purple. The immediate addition of tBuNC (0.026 mL, 0.222 mmol) induced a rapid colour change to orange. After stirring 30 min at room temperature, acetonitrile was evaporated and the resulting air stable orange solid was washed with Et_2O (10 mL) then dried. **9** (100 mg, 74%).^{31}P {^{1}H} (121.5 MHz, C_7D_8) δ 43.2 (vt, $^2J_{PP}$ = 14.5 Hz, $P^{(V)}$(N)), 65.2 (vt, $^2J_{PP}$ = 14.5 Hz, $P^{(III)}$). ^{1}H (300 MHz, C_7D_8) δ 0.99 (18H, s, $(CH_3)_3$-C), 3.02 (4H, bs, N-CH_2), 3.89 (4H, bs, PCH_2P), 7.00 (4H, m, p-H ($Ph_2P^{(III)}$)), 7.16 (8H, m, o,m-H ($Ph_2P^{(III)}$)), 7.33 (8H, m, o,m-H ($Ph_2P^{(III)}$)), 7.45 (8H, m, o,m-H ($Ph_2P^{(V)}$)), 7.56(4H, m, p-H ($Ph_2P^{(V)}$)), 7.61 (8H, m, o,m-H ($Ph_2P^{(V)}$)). ^{13}C {^{1}H} (75.5 MHz, C_7D_8) δ_C 29.5 (s, $(CH_3)_3$-C), 35.7 (d, $^1J_{CP}$ = 85.0 Hz), 51.6 (d, $^2J_{CP}$ = 13.0 Hz, NCH_2), 59.1 (C_{ipso}-$(CH_3)_3$), 127.6 (d, $^1J_{CP}$ = 87.0 Hz, C_{ipso}-($Ph_2P^{(III)}$)), 129.0 (t, J_{CP} = 5.0 Hz, CH-(Ph_2P)), 129.7 (d, J_{CP} = 12.0 Hz, CH-(Ph_2P)), 130.9 (d, J_{CP} = 10.0 Hz, CH-(Ph_2P)), 131.6 (s, CH-(Ph_2P)), 132.5 (d, J_{CP} = 11.0 Hz, CH-(Ph_2P)), 132.6 (t, J_{CP} = 5.0 Hz, CH-(Ph_2P)), 133.8 (dd, $^1J_{CP}$ = 26.0 Hz, $^4J_{CP}$ = 2.5 Hz, C_{ipso}-($Ph_2P^{(V)}$)), 133.9 (s, CH-(Ph_2P)), δ C_{ipso}-$(CH_3)_3$ not measurable. Anal. Calcd. for $C_{62}H_{66}B_2F_8FeN_4P_4$: C, 61.01; H, 5.45; N, 4.59%. Found: C, 61.09; H, 5.48; N, 4.62%.

General procedure for the transfer hydrogenation of acetophenone

A Schlenk was charged under nitrogen atmosphere with the iron complex (0.01 mmol, 9.5 mg for **5**, 10.2 mg for **6**, 9.8 mg for **7**, 10.0 mg for **8**) and sodium isopropanolate (32.8 mg, 0.4 mmol). Isopropanol (5 mL) and acetophenone (1.15 mL, 10 mmol) were then added and the reaction mixture was vigorously stirred under isopropanol reflux (82 °C). The progress of the reaction was monitored by ^{1}H NMR. At the appropriate time, an aliquot was taken from the reaction mixture, dried under vacuum, flushed on a short silica column with $CDCl_3$ to remove the iron complexes, and then analysed by ^{1}H NMR.

Table 2 Crystal data and structural refinement details for **5**, **6**, **7** and **8**

Compound	$P_2N_2FeCl_2$ **5**	$S_2N_2FeCl_2$ **6**	$O_2N_2FeCl_2$ **7**	$[P_2N_2FeCl]BF_4$ **8**
Crystal size/mm	0.40 × 0.24 × 0.18	0.30 × 0.20 × 0.10	0.22 × 0.16 × 0.14	0.38 × 0.36 × 0.26
Crystal habit	Pale yellow block	Pale yellow block	Pale yellow block	Pale yellow block
Empirical formula	$C_{52}H_{48}Cl_2FeN_2P_4$, 1.5 C_4H_8O, CH_2Cl_2	$C_{52}H_{46}Cl_2FeN_2P_4S_2$, 3 CH_2Cl_2	$C_{52}H_{48}ClFeN_2O_2P_4$,Cl, CH_2Cl_2	$C_{52}H_{48}ClFeN_2P_4$,CH_2Cl_2, BF_4
Molecular mass	1144.64	1268.44	1153.41	1087.84
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	36.269(1)	13.700(1)	11.611(1)	10.868(1)
b/Å	15.077(1)	15.476(1)	20.231(1)	13.934(1)
c/Å	19.211(1)	15.866(1)	25.508(1)	18.166(1)
α/°	90.00	91.952(1)	108.182(1)	100.819(1)
β/°	90.424(1)	114.158(1)	102.266(1)	101.043(1)
γ/°	90.00(1)	103.426(1)	92.630(1)	102.516(1)
V/Å^3	10504.8(9)	2953.7(3)	5522.0(6)	2559.3(3)
Z	8	2	4	2
Calcd density/g cm^{-3}	1.447	1.426	1.387	1.412
Abs. coefficient/cm^{-1}	0.659	0.834	0.721	0.630
θ_{max}/°	28.70	30.03	27.47	30.02
T/K	150.0(1)	150.0(1)	150.0(1)	150.0(1)
F(000)	4768	1300	2376	1120
Index ranges	–48–38; –20–18; –25–22	–19–19; –21–21; –22–22	–15–14; –26–24; 0–33	–15–15; –18–19; –25–25
Refl. collected/independant	34140/13547	39926/17238	24439/24439	29603/14716
Refl. used	9652	12502	17218	11542
(R_{int})	0.0337	0.0285	0.0364	0.0247
Abs. corr.	0.7786 min., 0.8907 max.	0.7879 min., 0.9212 max.	0.8575 min, 0.9058 max	0.7959 min., 0.8534 max.
Parameters refined	573	649	1142	613
Reflection/parameter	16	19	15	14
Final R_1/w$R2$ [I>2σI)]	0.0552/0.1840	0.0486/0.1422	0.0545/0.1608	0.0394/0.7764
Goodness-of-fit on F^2	1.100	1.066	1.092	1.062
Difference peak/hole/e Å^{-3}	1.499/–0.642	1.451/–0.917	0.820/–0.765	0.816/–0.809

General procedure for the hydrogenation of acetophenone

The reaction was performed in a magnetically stirred 120 mL stainless steel autoclave, equipped with a pressure gauge. A solution of the iron complex (0.01 mmol, 9.5 mg for **5**, 10.0 mg for **8**) and acetophenone (1.15 mL, 10 mmol) in toluene (20 mL) was introduced in the reactor under nitrogen atmosphere. The reactor was then charged with H_2 (20 bar) and brought to the working temperature (80 °C). After 24 h, the autoclave was allowed to cool down to room temperature then depressurized. The reaction mixture was dried up under vacuum, flushed on a short silica column with $CDCl_3$ to remove the iron products, then analysed by ^{1}H NMR.

X-Ray crystallography

Data were collected on a Nonius Kappa CCD diffractometer using a Mo-Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 2. Electronic supplementary information contains the supplementary crystallographic data for this paper (CIF files for complexes **5**, **6**, **7** and **8**). CCDC reference numbers 702897–702900. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b816439h. The crystal structure was solved using SIR 97[20] and SHELXL-97.[21] ORTEP drawings were made using ORTEP III[22] for Windows.

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