Syntheses, structures, and reactivity of terminal phosphido complexes of iron(II) supported by a *β*-diketiminato ligand

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Abstract: We report the synthesis of the first series of terminal phosphido iron complexes supported by a *β*-diketiminato ligand (Dippnacnac) and their catalytic activity in the dehydrocoupling of secondary phosphines. Anionic and neutral mono- or diphosphido complexes were obtained from the reaction of [(Dippnacnac)$FeCl_2Li(dme)_2$] with the R_2PLi (R = *i*Pr, *t*Bu, Cy, Ph) phosphides by tuning the stoichiometric ratio, polarity of the solvent, and the bulkiness of the substituents at the P-atom. The structures of the synthesized compounds were determined by single-crystal X-ray diffraction, which revealed that the iron sites of the anionic complexes are four-coordinate, whereas those of the neutral complexes are three-coordinate with almost planar geometry. These phosphido iron complexes were also characterized by ^{1}H NMR and zero-field Mössbauer spectroscopy. The thermal stability and reactivity of selected complexes were studied. The catalytic properties of the phosphido complexes were confirmed by investigating the conversion of diphenylphosphine to symmetrical 1,1,2,2-teraphenyldiphosphane.

Introduction

One of the main research areas in the field of catalysis is primarily directed towards finding more efficient catalysts that are not based on rare, expensive metals such as ruthenium, palladium or platinum but rather on cheap, biologically benign, and earth abundant elements. Among the cheapest, non-toxic, and plentiful transition metals a special place is taken by iron - an element which is at the center of many biological processes including the well-known example of the bacterial dinitrogen fixation[1–3]. Due to its wide availability as well as the occurrence in a plethora of biological catalytic sites, iron has been viewed as an essential component of the next generation of sustainable catalysts[4–9].

The utility of synthetic iron complexes as catalysts is predicated on both: the redox properties of the central metal as well as the ability to stabilize, with appropriate ligand design, low coordination environments. Examples of ligands that support distinctive, low-coordinate environments include the N-containing *β*-diketiminates (e.g., nacnac)[10–13]. Depending on the N-atom substituents, the properties of *β*-diketiminates can vary considerably which, in turn, substantially influence the properties and reactivity of their complexes[14,15]. *β*-diketiminates with sterically demanding groups have been successfully employed in the synthesis of low-coordinate iron complexes. In contrast to a large number of heteroleptic *β*-diketiminato iron complexes with alkyl, aryl, vinyl, amido, and imido co-ligands[16–26], the chemistry of iron *β*-diketiminato complexes featuring phosphido co-ligands is largely unexplored[27]. Notably, the closest analogs of phosphido complexes reported by Holland and co-workers are iron complexes with NR_2 groups, which exhibit interesting structural properties and reactivity[20].

Metal complexes featuring phosphido ligands have attracted interest due to their great potential as effective catalysts, especially in promoting the formation of P-P[28–30] and P-C[31–40] bonds [41,42]. Moreover, these compounds are also catalytically active in the dehydrocoupling of amino- and phosphino-boranes, which are regarded as versatile processes for H_2 storage[43]. In this context, special attention should be given to terminal low-coordinated phosphido complexes with pyramidal or planar geometry[44–56]. In these cases, the phosphorus atom is connected only to one metal center and can exhibit either pyramidal geometry with one lone pair or planar geometry with the lone pair participating in *π* bonding[41,57–65]. It should be noted that, among the high number of bridged phosphido complexes[44,66–71], there are many reports of transition metal complexes featuring non-bridging, terminal phosphido ligands[44,46–55,72–79], including some supported by nacnac ligands[80–85]. However, only a handful of known terminal phosphido complexes[31,86–97] incorporate iron and, in most cases, these complexes are supported by carbonyl or cyclopentadienyl co-ligands.

Reports of the use of an iron(II) *β*-diketiminato pre-catalyst, [(Dippnacnac)$Fe(CH_2TMS)$], by Webster *et al.* [14,27,43,98–102] to carry out the hydrophosphination of unsaturated hydrocarbons and dehydrocoupling of primary and secondary phosphines, postulated the formation of an intermediate terminal phosphido complex. In the case of hydrophosphination, the authors proposed that the active catalyst is a monomeric phosphido complex; however, the active species was isolated as a bridging complex, [(Dippnacnac)$Fe(PRH(CH_2)_3CH{=}CH_2)]_2$[27]. Worth emphasizing is that this compound is not only the first *β*-diketiminate iron complex bridged by phosphido groups, but also a perfect example highlighting the catalytic potential of low-coordinate iron compounds. The hydrophosphination and dehydrocoupling processes are both ideally suited for the synthesis of novel P-containing compounds and their catalytic improvements will expand the access to

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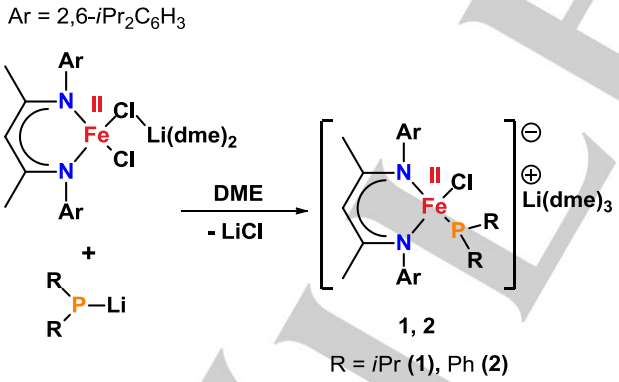
functionalized phosphines, diphosphanes, and other P-containing derivatives.

Recently, we have reported a new synthetic method to access iron(II) phosphanylphosphido complexes using as starting materials the *β*-diketiminato complex [(Dippnacnac)$FeCl_2Li(dme)_2$][103] and lithium salts of diphosphanes, R_2P-P($SiMe_3$)Li (R= *i*Pr, *t*Bu)[104]. Due to the propensity of the diphosphorus ligand to undergo P-P bond cleavage, these iron(II) phosphanylphosphido complexes have rather limited catalytic potential. Considering this limitation, we directed our attention to iron(II) complexes with phosphido R_2P ligands. In this paper, we detail the syntheses, structures, and spectroscopic characterization of the first series of terminal phosphido Fe(II) complexes stabilized by *β*-diketiminates. We also discuss their thermal stability and catalytic activity in promoting the dehydrocoupling of secondary phosphines.

Results and Discussion

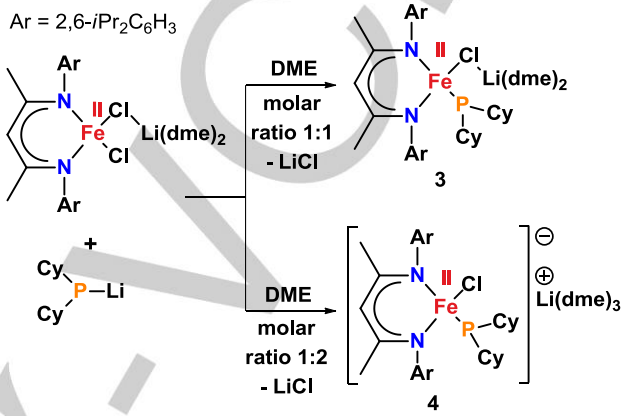
Syntheses

We have explored the reactivity of [(Dippnacnac)$FeCl_2Li(dme)_2$][103] towards phosphides R_2PLi (R= *i*Pr, *t*Bu, Cy, Ph). The outcome of the reaction between the iron(II) complex and R_2PLi is strongly influenced by the donor properties of the solvent. The main products of reactions performed with equimolar amounts of starting materials in DME are anionic, terminal phosphido complexes of iron(II) (**1**-**2**) (Scheme 1).



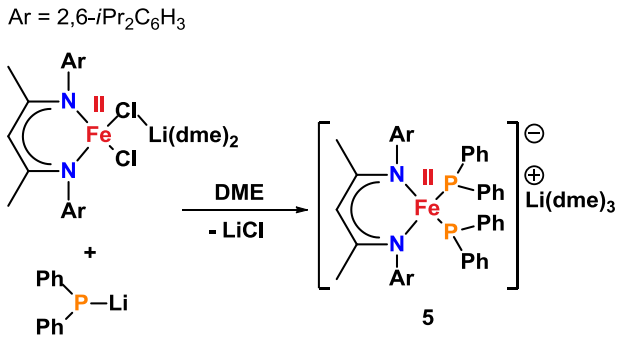
Scheme 1. Syntheses of anionic phosphido complexes **1** and **2**.

Compounds **1**-**2** were isolated from concentrated reaction mixtures at low temperature (first crop at +4 °C and second crop at -20 °C) as dark violet (**1**) or dark red (**2**) crystals. The yields of reactions were 46% and 29% for **1** and **2**, respectively. These species are solvent-separated ionic compounds where a Li cation is surrounded by three DME molecules and the anion is the Fe(II) complex bearing *β*-diketiminato, chlorido, and phosphido ligands. Reactions with *t*Bu_2PLi did not result in the formation of isolable anionic, terminal phosphido Fe(II) complex. Cy_2PLi yielded an isolable product, however, to our surprise, it was not the anticipated anionic complex but rather the contact ion pair **3**, where Li^+ is not separated by solvent molecules (Scheme 2). Reaction with two equivalents of Cy_2PLi produced only the anionic complex **4** (Scheme 2), which exhibits a structure analogous to those of **1** and **2**.



Scheme 2. Syntheses of complexes **3** and **4**.

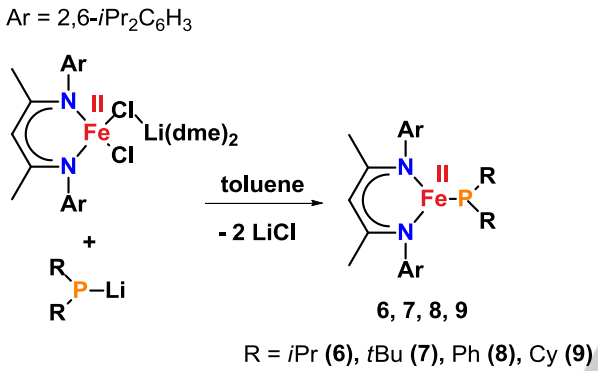
Attempts to obtain a Fe(II) complex bearing two terminal phosphido ligands were successful only when Ph_2PLi was employed. Reaction of [(Dippnacnac)$FeCl_2Li(dme)_2$] with Ph_2PLi in DME in 1:2 molar ratio gave a mixture of mono- (**2**) and diphosphido (**5**) complexes. Exclusive formation of **5** was achieved only for a threefold excess of Ph_2PLi (Scheme 3). Excess of Ph_2PLi is noticeable in the $^{31}P\{^1H\}$ NMR spectra of reaction mixtures and this excess of phosphide accelerates the second stage of the reaction leading to product **5.** Complete conversion of the monophosphido derivative **2** to the diphosphido derivative **5** was reached by keeping the reaction mixture at room temperature for several days. Dark brown crystals of **5** were isolated from concentrated reaction mixtures at low temperature with a 37% yield.



Scheme 3. Synthesis of complex **5**.

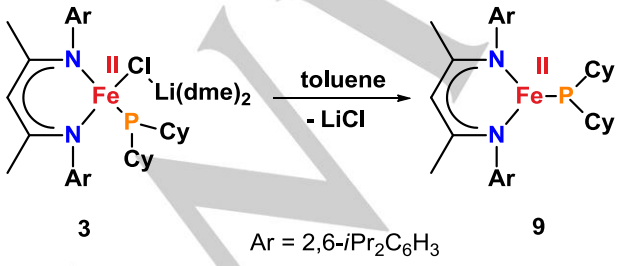
The addition of 12-crown-4 to the DME solutions of either **1** or **5** led to the complexation of lithium cations by the crown ether, which resulted in the isolation of crystalline complexes [(Dippnacnac)FeCl(P*i*Pr$_2$)][Li(12-crown-4)$_2$] (**1'**) and [(Dippnacnac)Fe(PPh$_2$)$_2$]$_2$[Li(12-crown-4)(dme)][Li(dme)$_3$] (**5'**).

The nature of the solvent exerted a strong influence on the outcomes of reactions between [(Dippnacnac)FeCl$_2$Li(dme)$_2$] and R$_2$PLi (R= *i*Pr, *t*Bu, Cy, Ph). In contrast to the reactions run in DME, we observed that reactions in toluene at a 1:1 molar ratio proceeded with the exclusive formation of neutral terminal phosphido complexes (**6**-**9**) (Scheme 4).



Scheme 4. Syntheses of neutral phosphido complexes **6**, **7**, **8** and **9**.

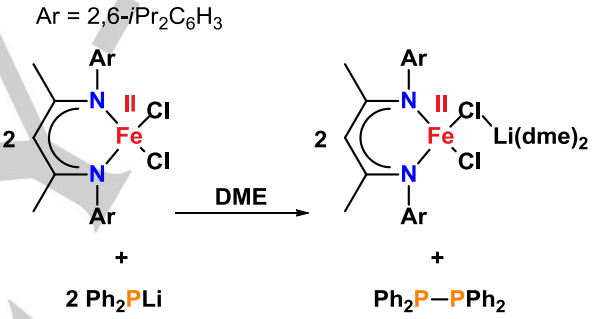
Reactions carried out in toluene gave isolable products in moderate yields (28-55% for **7**-**9**), with the exception of **6** isolated in low yield (5%). Dark green (**6**, **8**-**9**) and dark violet (**7**) crystals of the neutral complexes were obtained via crystallization in pentane at low-temperatures (first crop at +4 °C and second crop at -20 °C). The neutral phosphido complexes can be also obtained from the corresponding anionic complexes (Scheme 5). For example, dissolution of crystalline **3** in toluene led to the formation of the corresponding neutral complex **9**. However, the direct syntheses of neutral complexes from [(Dippnacnac)FeCl$_2$Li(dme)$_2$] and R$_2$PLi in toluene were more effective.



Scheme 5. Synthesis of neutral phosphido complex **9** from complex **3**.

We note that all terminal phosphido complexes (**1**-**9**) are extremely moisture and oxygen sensitive and were handled with great care to prevent their decomposition. In contact with air, for example, dark red, dark violet or dark green hydrocarbon solutions of **1**-**9**, underwent a color change to dark brown within seconds. Moreover, crystals of **1**-**9** disintegrate within minutes into yellow powders when exposed to air. Notably, the most air-sensitive compounds of the whole series of terminal phosphido complexes are those bearing *i*Pr$_2$P groups (**1**, **6**), due to the smallest steric protection compared to other isolated compounds with R$_2$P ligands.

During our studies on Fe(II) *β*-diketiminato complexes we observed that addition of phosphides to the Fe(III) complex [(Dippnanac)Fe^{III}Cl$_2$] leads to the formation of Fe(II) complexes and compounds containing P-P bond. An example of such reactivity is the reaction of [(Dippnanac)Fe^{III}Cl$_2$] with Ph$_2$PLi in either DME or toluene leading to the formation of Ph$_2$P-PPh$_2$ and the corresponding Fe(II) complex (Scheme 6).



Scheme 6. Reaction of [(Dippnanac)FeCl$_2$] with Ph$_2$PLi.

[(Dippnacnac)Fe^{II}Cl$_2$Li(dme)$_2$] was isolated in crystalline form when the reaction was performed in DME, whereas in toluene a possibly dimeric complex [(Dippnacnac)Fe^{II}Cl]$_2$ might form. Because of this oxidative dimerization of phosphides, it was not possible to obtain the *β*-diketiminato phosphido complexes of Fe(III) in this direct way.

Crystal Structures

The monophoshido anionic complexes **1**, **1'**, **2**, **4** and contact ion pair **3** exhibit similar structural features and are discussed together. The solid-state structures of anions of **1**-**4** are presented in Figure 1, whereas the structure of **1'** is shown in Figure S1 (ESI). The Fe-site geometry of these compounds is distorted pseudotetrahedral with a coordination sphere composed of two N atoms of the *β*-diketiminato ligand, one P atom of phosphido ligand and one chlorido ligand. The Fe center is located out of the plane of the Dippnacnac ligand. The phosphido ligand is situated opposite to the *β*-diketiminato ligand, whereas the Fe-Cl bond is perpendicular to the Dippnacnac plane. The N1-Fe1-

N2 bite angles and N-Fe1 bond lengths in complexes **1**-**4** are typical for low-coordinated Fe-diketiminato compounds (Table 1)[20]. The Fe1-P1 bond distances are in the range 2.371(1)-2.407(1) Å, longer than those observed for tetrahedral phosphanylphosphido complex [(Dippnacnac)Fe(η^2-*i*Pr$_2$P-P-SiMe$_3$)] (2.3638(9)Å)[104]. The elongation of the Fe1-P1 bonds together with the pyramidal geometry around P1 atoms (Table 1) indicate a single-bond character for the Fe1-P1 bonds in **1**-**4**.

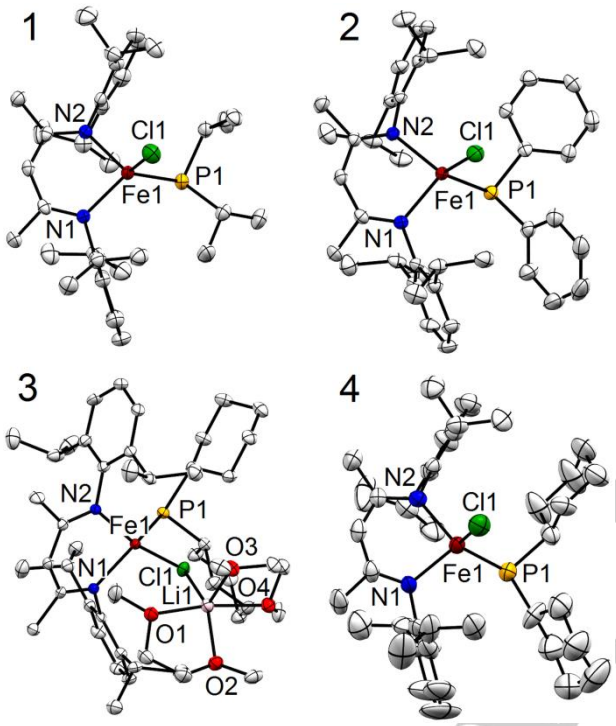


Figure 1. X-ray structures of complex anions **1**, **2**, **4**, and of the neutral complex **3** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity.

The diphosphido anionic complexes **5** and **5'** possess similar structural features as their monophosphido counterparts **1**-**4**. The molecular structures of **5** and **5'** are shown in Figure 2 and Figure S2 (ESI), respectively. The Fe1-P2 bond in both diphosphido complexes **5** and **5'** is situated perpendicular to the plane of Dippnacnac ligand – similarly to the Fe1-Cl bond in **1**-**4** – and is significantly longer than Fe1-P1 bond (Fe1-P1/Fe1-P2 = 2.366(1)/2.473(1) for **5** and 2.375(2)/2.454(2) for **5**'). Moreover, the geometries of both phosphorus atoms in **5** and **5'** exhibit a higher degree of planarity than the P atoms in **1**-**4** (Table 1).

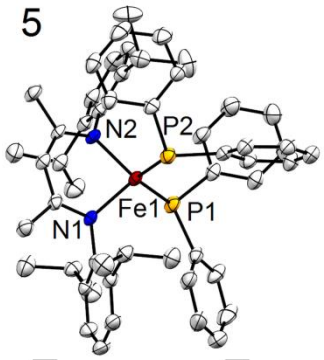


Figure 2. X-ray structure of complex anion **5**. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity.

Table 1. Selected bond lengths and geometries around iron and phosphorus atoms for compound **1**-**9**.

Complex	Fe1-P1 Fe1-P2 (Å)	Fe1-N1 Fe1-N2 (Å)	Fe1-Cl Fe1-O1 (Å)	ΣFe1[a] (°)	ΣP1 ΣP2 (°)
1	2.4054(8)	2.073(2) 2.070(2)	2.3623(8)	322.36	316.50
1'	2.371(1)	2.064(3) 2.057(3)	2.361(1)	320.32	321.49
2	2.3827(6)	2.042(1) 2.045(2)	2.3012(5)	320.84	322.13
3	2.3771(9)	2.026(2) 2.041(2)	2.377(1)	326.23	320.94
4	2.407(1)	2.062(4) 2.064(3)	2.345(1)	325.22	323.06
5	2.366(1) 2.473(1)	2.072(4) 2.038(4)		315.74	338.85 337.44
5'	2.375(2) 2.454(2)	2.047(4) 2.088(4)		314.51	332.36 333.88
6	2.372(1)	1.989(3) 2.011(3)		357.08	333.73
7	2.366	2.001 2.001		359.25	345.34
8	2.3663(6)	2.026(2) 2.024(2)	2.129(2)	334.50	325.75
9	2.328(2)	1.990(5) 1.988(5)		358.39	327.68

[a]Sum of angles: N1-Fe1-N2, N2-Fe1-P1, P1-Fe1-N2

The X-ray structures of compounds **6**, **7**, and **9** are shown in Figure 3. These neutral phosphido complexes differ in many aspects from **1**-**4**. The geometry around the Fe center is trigonal planar with two N atoms and one P atom coordinated to the metal atom. In contrast to **1**-**4**, the Fe atom is located in the Dippnacnac plane. Similar spatial alignment of the iron atom was observed for terminal amido complexes supported by nacnac ligands[20]. When we compared the anionic and neutral complexes possessing the same R_2P groups we noticed that the Fe-P distances are shorter in case of neutral complexes (Table 1). Compound **8** stands out from the series of neutral phosphido complexes. Its X-ray

structure, shown in Figure 3, indicates additional coordination of the O atom of the DME molecule to the metal center. Because of this, the structural features of **8** resemble a greater degree than those observed for the anionic complexes **1**-**4**.

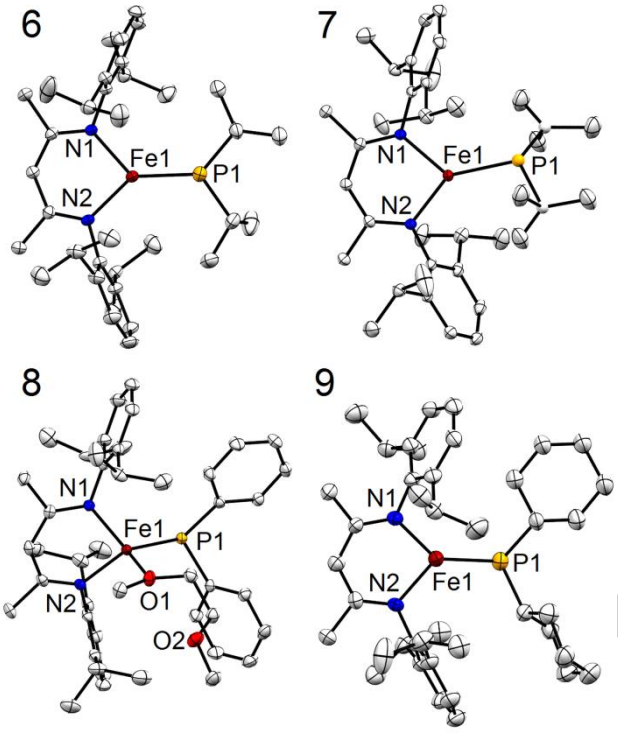


Figure 3. X-ray structures of **6**-**9** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity.

The coordination geometry of Fe in **8** can be described as distorted pseudotetrahedral with the coordination sphere completed by N1, N2, O1 and P1 atom of Ph_2P ligand. However, the angles N1-Fe1-N2, N2-Fe-P1, P1-Fe1-N1 are somewhat widened in **8** (ΣFe1 = 334.50° omitting the Fe1-O1 bond) in comparison to anionic complex **2** (ΣFe1 = 320.84° omitting the Fe1-Cl1 bond) bearing the same phosphido ligand. Similarly to **1**-**4**, the Fe atom in complex **8** is out of the plane of Dippnacnac ligand. As indicated by microanalysis of crystals of **8**, the DME ligand can be effectively removed from the metal center coordination sphere by keeping crystals of **8** under vacuum (10^{-3} Torr) for several hours.

^{1}H NMR Spectroscopy

Solutions of the anionic, **1**-**5**, and neutral, **7**-**9**, terminal phosphido Fe(II) complexes were studied using ^{1}H NMR spectroscopy. Despite of their paramagnetic character, many Fe(II) *β*-diketiminato complexes can be successfully characterized by ^{1}H NMR spectroscopy[15,26]. However, due to the broadness and overlap of many of the observed resonances, the spectra recorded for the anionic tetrahedral complexes **1**-**5** were difficult to interpret. In contrast, the resonances observed for the neutral species **7**-**9** (Figures S3-S8, ESI) were separated and discernible from one another, which allowed us to rationalize these spectra. These spectra exhibit resonances within a wide range of chemical shifts extending from +105.78 to -112.70 ppm. A comparable wide range of chemical shifts was observed for *β*-diketiminate-supported Fe(II)-amido[20] and Fe(II)-phosphanylphosphido complexes[104]. The chemical shifts observed for **7**-**9** depend strongly on the position of the respective protons relative to the Dippnacnac plane. Protons located in the plane of the *β*-diketiminato ligand are shifted downfield, whereas those normal to the plane resonate at higher fields. Spectral integration was necessary to unequivocally assign the observed peaks. The spectra obtained for the phosphido complexes **7** and **8** exhibit many similarities to those observed for the planar, trigonal amido complexes synthesized by Holland group[20]. Thus, the signals of the four isopropyl groups of the Dippnacnac ligand, as well as those of the two methyl groups of the nacnac backbone, and accordingly aromatic *para* and *meta* protons are equivalent. Moreover, the signals assigned to the *t*Bu and Ph groups of **7** and **8**, respectively, are also equivalent. This observation suggests that in solution compounds **7** and **8** adopt a C_{2v} point group symmetry. Furthermore, the solution-based ^{1}H NMR spectra of **8** do not exhibit signals that can be associated with a DME molecule, which in the solid-state X-ray structure was found to be coordinated to the iron atom. This observation, together with the high symmetry of **8** in solution, indicates that the DME molecule was removed upon exposure of crystals to vacuum prior to the preparation of the NMR sample. Most likely, the loss of the crystal-bound DME molecule results in a trigonal planar geometry at the metal center. In contrast to the ^{1}H NMR spectra recorded for **7**-**8,** the spectrum of **9** exhibits many more signals. Incorporating the Cy groups in the phosphido ligand of **9** leads not only to non-equivalent Cy groups but also to a loss of molecular symmetry and thus to a splitting of the Dippnacnac ligand resonances.

^{57}Fe Mössbauer Spectroscopy

To assess the oxidation state of the iron sites we have recorded a series of 4.2 K, zero-field Mössbauer spectra. The four-coordinate complexes **1**, **2**, **4**, and **5** exhibit well-defined quadrupole doublets (Figure 4). These spectra are characterized by isomer shifts δ = 0.69-0.78 mm/s and quadrupole splittings ΔE_Q = 2.52-2.67 mm/s, values that are typical of high-spin iron(II) sites[105]. In contrast, the 4.2 K spectrum of the three-coordinate complex **9** (not shown) exhibits magnetic hyperfine splitting, which collapses into a broad quadrupole doublet at 100 K. This behavior demonstrates that the ground state of **9** consists of a quasi-doublet with a vanishing zero-field splitting[106]. For three-coordinate complexes supported by *β*-diketiminato ligands such as **9**, this behavior originates from the presence of

a {z^2/yz} orbital degeneracy[107]. The zero-field Mössbauer parameters of **9** determined at 100 K are very similar to those observed for **7** and **8** at 4.2 K for which we observe well-defined quadrupole doublets even at low-temperature.

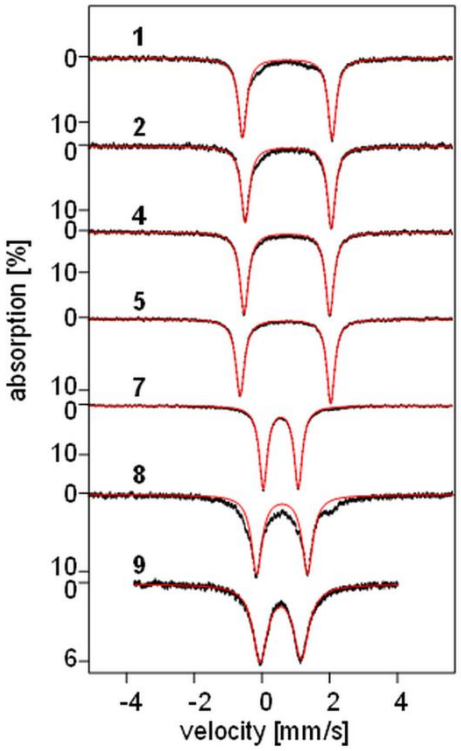


Figure 4. Zero-field ^{57}Fe Mössbauer spectra recorded at 4.2 K for **1**, **2**, **4**, **5**, **7**, **8** and at 100 K for **9**. The solid red lines are simulations obtained using the parameters listed in Table 2.

The decrease in the isomer shift values δ = 0.54-0.58 mm/s is consistent with the decrease in the coordination number and is concomitant with a sizable drop in the quadrupole splitting to ΔE_Q = 1.0-1.5 (Table 2). The spectrum recorded for **8** was obtained after exposing the sample to high-vacuum at room-temperature for several days. Unlike for all other samples for which the major spectral component (theoretical simulation shown in red) accounts for more than 95% of the iron present in the sample, the major component in the spectrum of **8** accounts for only 75% of the iron. The remaining amount can be represented by a quadrupole doublet with parameters analogous to those of the four-coordinate complexes studied here. This observation suggests that upon exposure to vacuum **8** loses the DME solvent molecule incorporated in the crystal leading to a three-coordinate iron site. Finally, the zero-field Mössbauer parameters of **7**-**9** are similar to those of other three-coordinate ferrous ions supported by *β*-diketiminato complexes[108].

Table 2. Zero-field Mössbauer parameters.

Complex	CN	δ [mm/s]	ΔE_Q [mm/s]	$\Gamma_{L/R}$ [mm/s]
1	4	0.746(4)	2.644(3)	0.31/0.29
2	4	0.778(3)	2.532(3)	0.34/0.30
4	4	0.735(4)	2.526(4)	0.31/0.30
5	4	0.690(4)	2.676(3)	0.31/0.28
7	3	0.552(5)	1.033(3)	0.29/0.29
8[a]	3	0.575(6)	1.497(5)	0.40/0.42
9[b]	3	0.54(2)	1.21(2)	0.51/0.53

[a]spectrum recorded for a sample exposed to high-vacuum

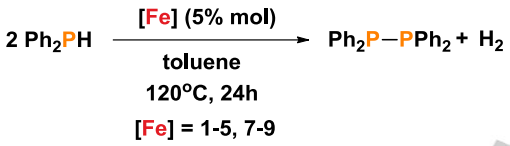
[b] parameters determined at 100 K

Reactivity studies

It was previously postulated that transient terminal phosphido complexes play a crucial role in the catalytic dehydrocoupling (DHC) of secondary phosphines[98]. Having access to multigram quantities of this class of compounds allowed us to test this hypothesis. In order to get a boarder and deeper insight into the forms of catalysts under dehydrocoupling conditions, we studied the thermal stability of a toluene solutions of phosphido complexes **1, 2, 4, 5, 7, 8** and **9**. Heating these solutions to 120°C for 24 hours leads to the decomposition of the title compounds. The various diamagnetic decay products were identified using ^{31}P NMR spectroscopy (for details see ESI). Complexes **2**, **5** and **8**, which incorporate Ph_2P co-ligands, decomposed with the formation of Ph_2P(*p*-tol) and diphosphane, Ph_2P-PPh_2. Symmetrical diphosphanes $i Pr_2P$-$Pi Pr_2$ (together with $i Pr_2PH$) and Cy_2P-PCy_2 were also obtained by heating toluene solutions of **1** ($i Pr_2P$ co-ligand) and **4** and **9** (Cy_2P co-ligand), respectively. For a solution of complex **7** ($t Bu_2P$ co-ligand) only a strong signal of $t Bu_2PH$ was observed. It is worth mentioning that, albeit much slower, the decomposition of the phosphido complexes also takes place at room temperature, with the same phosphorus-based products being identified. These results suggest that the phosphido complexes can act as sources of phosphanyl radicals. Whereas the Ph_2P(*p*-tol), $i Pr_2PH$, and $t Bu_2PH$ can be viewed as products of the reaction of $R_2P\cdot$ radicals with the solvent (toluene), the symmetrical diphosphanes are formed by the coupling of phosphanyl radicals. We anticipate that in solution the coupling of radicals to be far less likely than the reaction of those radicals with the solvent. The amount of symmetrical diphosphanes identified in these reaction mixtures is surprisingly large and can be explained only if the coupling of the phosphanyl radicals takes place in the inner coordination sphere of the iron atoms. We anticipate that the starting phosphido complex **8** dimerizes yielding a short-lived intermediate two-core iron complex possessing bridging phosphido ligands. This complex can further eliminate Ph_2P-PPh_2 to form a dinuclear Fe(I) complex. Very important in this context is the comparison of thermal reactions of **5** and **8**. For **5** in the reaction solution only Ph_2P(*p*-tol) is visible. Because of its structural features, **5** has no tendency to dimerization

and a symmetrical diphosphane is not formed at all. Similarly, in the case of decomposition of complex **7** containing more crowded phosphido ligand tBu$_2$P, a steric interaction prevented the formation of dimeric Fe intermediates, whereas tBu$_2$P radical is released into solution and reacts only with the solvent yielding tBu$_2$PH.

We investigated the catalytic activity of phosphido iron(II) complexes possessing different geometries, anionic or neutral character, and diverse R$_2$P ligands (**1**-**5**, **7**-**9**). We have tested the scope and the extent of the DHC for the following secondary phosphines: Ph$_2$PH, tBuPhPH, tBu$_2$PH, Cy$_2$PH, and (iPr$_2$N)$_2$PH. All runs were carried out under the same reaction conditions: 5 mol% of phosphido complex in toluene heated at 120°C in a closed Schlenk tube for 24 h. The reaction progress was monitored by ^{31}P NMR spectroscopy. We have identified the formation of diphosphane R$_2$P-PR$_2$ only in runs involving Ph$_2$PH. A similar reactivity was observed recently in the dehydrocoupling[98] and hydrophosphination[31] reactions catalyzed by Fe(II) complexes, which were also limited to the aromatic derivatives of phosphines. Catalytic activity in the dehydrocoupling of Ph$_2$PH (Scheme 7) was observed for all tested Fe(II) complexes.



Scheme 7. Dehydrocoupling (DHC) of Ph$_2$PH.

Table 3. The extent of conversion of Ph$_2$PH using Fe(II) phosphido complexes.

Run	Complex [Fe]	Conversion of Ph$_2$PH to Ph$_2$PPPh$_2$ (%)
1	**1**	89
2	**2**	88
3	**3**	86
4	**4**	90
5	**5**	88
6	**7**	98
7	**8**	89
8	**9**	86
9	**8** (after heating)	90
10	[(Dippnacnac)FeCl$_2$Li(dme)$_2$]	0

We observed a high conversion of Ph$_2$PH to Ph$_2$P-PPh$_2$ (86-98%) for all runs involving phosphido complexes (run entries *1-8* in Table 3). It is worth mentioning that small amounts of Ph$_2$P(p-tol) (5-8 mol%) were also detected in all DHC experiments catalyzed by phosphido complexes (run entries *1-9*), which is the most probable product of a side reaction of Ph$_2$P· radicals with the solvent. Moreover, for the reaction of complex **8** and Ph$_2$PH, we have also tested the effect of varying the dilutions of the reaction mixture on the conversion of secondary phosphines to symmetrical diphosphanes. We observed that the two- and four-fold dilution of the reaction mixture reduced the conversion rate from 89% to 64% and 44%, respectively (Figure S18, ESI).

Furthermore, we have also tested the catalytic activity of the toluene solution of **8** after heating this solution at 120°C for 24 hours. Despite decomposition of **8** (with the formation of Ph$_2$P(p-tol), diphosphane Ph$_2$P-PPh$_2$ and probably diiron complexes) this solution exhibited high DHC catalytic conversion of Ph$_2$PH (Table 3, run *9*, 90%). This behavior together with the lack of catalytic activity of investigated complexes at room temperature, suggests that the diiron complexes could play an important role in DHC of Ph$_2$PH. Additionally, we tested this reaction with catalytic amounts of [(Dippnacnac)FeCl$_2$Li(dme)$_2$] (Table 3, run *10*), the starting material for the syntheses of all phosphido complexes. However, this compound exhibits no catalytic activity in DHC of secondary phosphines.

For previously reported dehydrocoupling of secondary phosphanes with Zr-catalysts, a mechanism of σ-bond metathesis was postulated[30]. However, in contrast to the Fe(II) catalysts, the Zr-catalyzed reactions proceed both with aryl and alkyl substituted phosphines. Moreover, our reactivity studies of phoshido Fe(II) complexes indicates that they also act as a source of phosphanyl radicals. This observation suggests a radical-mediated mechanism for dehydrocoupling reactions involving Fe(II) complexes. Our DFT calculations also support a radical-based mechanism. Thus, it was found that the stability of phosphanyl radicals is strongly dependent on the size and type of the P-substituent and decreases such that: Ph$_2$P·> tBuPhP· > (iPr$_2$N)$_2$P· > tBu$_2$P· (for details see ESI). The Ph$_2$P· radical exhibits the highest degree of spin density delocalization due to the presence of aromatic rings. Furthermore, it has the highest value of radical stabilization energy (RSE)[109] of the entire series of studied radicals. These results can explain the lack of reactivity of alkyl- and amino- substituted secondary phosphines in our DHC experiments.

It is important to stress that the monomeric complex **8** is not stable under our reaction conditions (see stability studies) and the most plausible explanation for its observed catalytic activity is the formation of a dimeric species in the catalytic cycle. The perfect examples confirming this hypothesis are the visible-light and thermal driven catalytic reactions employing the commercially available diiron compound [CpFe(CO)$_2$]$_2$ (Cp = η^5-C$_5$H$_5$) as precatalyst recently reported by Waterman and co-workers[110,111]. Moreover, the Fe(I)-Fe(I) dimers play crucial roles in biologically important systems including [Fe-Fe] hydrogenases. Such moieties are electron rich and favor oxidative additions in catalytic cycles [112]. The low oxidation state in the postulated Fe(I) dimers strongly suggests the formation of a Fe-Fe bond. Isolated complexes of iron with unsupported Fe-Fe bond not involving CO ligands are, however, extremely rare[113].

Conclusions

We found that a series of terminal phosphido complexes of Fe(II) supported by a *β*-diketiminato ligand can be straightforwardly synthesized via the reaction of [(Dippnacnac)$FeCl_2Li(dme)_2$] with phosphides R_2PLi (R= *i*Pr, *t*Bu, Cy, Ph). The nature of the reaction products is dictated by solvent and reaction stoichiometry. This new series of terminal phosphido complexes includes neutral trigonal planar complexes, which are coordinatively unsaturated; anionic tetrahedral complexes; and species featuring two phosphido ligands. The reactivity studies of selected terminal phosphido Fe(II) complexes revealed that such compounds can act as sources of phosphanyl radicals. A preliminary investigation of the catalytic activity of these phosphido complexes showed that they are good catalysts for dehydrocoupling of phosphines. We proposed that the DHC of Ph_2PH undergoes through a radical-mediated mechanism. Additional studies on the reactivity of terminal phosphido complexes of Fe(II) are in progress and will be published in due course.

Experimental Section

Materials and methods

All manipulations were performed under an Ar atmosphere in flame-dried Schlenk-type glassware on a vacuum line or in a dry box. Solvents 1,2-dimethoxyethane (DME) and toluene were dried over K/benzophenone and distilled under argon. Pentane was dried over Na/benzophenone/diglyme and distilled under argon, while petroleum ether was dried over sodium-potassium alloy and also distilled under argon. $^{31}P\{^1H\}$ NMR (external standard 85% H_3PO_4), ^1H (internal standard Me_4Si) spectra were recorded on a Bruker AV400 MHz spectrometer at room and low temperature. ^{31}P NMR and $^{31}P\{^1H\}$ NMR spectra used for quantitative integration were recorded at 25 °C using an inverse-gated decoupling pulse sequence in case of $^{31}P\{^1H\}$ NMR spectra, with 64 scans, using a -250 to 150 ppm spectral width, 16 K data points, with a relaxation delay of 80 s. Data were processed using Bruker's Topspin 3.5 software. The accuracy of the method was determined by integration of ^{31}P NMR and $^{31}P\{^1H\}$ NMR spectra of reference samples containing Ph_2PH, Ph_3P, and Ph_2P-PPh_2, where the biggest error was 2%. Ph_2PH, Cy_2PH, and *t*-Bu_2PH were purchased from Aldrich and used as received. Literature methods were used to prepare *i*-Pr_2PH[114] and [(Dippnacnac)$FeCl_2Li(dme)_2$][103]. All obtained compounds are very moisture and air-sensitive.

Diffraction data of complexes **1'**, **2**, **3**, **5**, **5'**, **6**, **7**, **8**, and **9** were collected on diffractometer equipped with a STOE image plate detector using Mo*K*α radiation with graphite monochromatization (λ = 0.71073 Å). The experimental diffraction data of **1** and **4** were collected with a KM4CCD kappa-geometry diffractometer equipped with a Sapphire2 CCD detector using Mo*K*α radiation source with a graphite monochromator (λ = 0.71073 Å). Determination of the unit cells and data collection was carried out at 120 K for **5**, **6**, **7**, **8** and **9**, at 130 K for **2** and **3**, at 150 K for **1**, **1'** and **5'** and at 298K for **4**. The structures were solved by direct methods and refined against F^2 using the Shelxs-97 and Shelxl-97 programs[115] run under WinGX[116]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed to be 1.5 times U_{eq} of C atoms for $-CH_3$ or 1.2 times U_{eq} for $-CH$, $-CH_2$ groups and aromatic H. The crystallographic details together with ORTEP drawings of obtained compounds are placed in ESI. For the structure of **7**, the P atom and *tert*-buthyl groups were refined as positional disordered over two positions (special position for the mentioned atoms, glade plane) by using the PART -1 command (in this model the occupancies were refined to 0.5 and 0.5). The anisotropic displacement parameters of the methyl carbon atoms (c17 c18 c19 c21 c22 c23) were each constrained to be identical. The two carbon atoms P1, c16 and c20 were refined isotopically, by using ISOR command. All bond distances C-C and P-C in the disordered sections were restrained to be the same within a standard deviation of 0.002 Å.

Crystallographic data for the structures of **1**, **1'**, **2**, **3**, **4**, **5**, **5'**, **6**, **7**, **8**, and **9** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1560588-1560598. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk). For more crystallographic details see ESI.

The temperature-dependent, zero-field ^{57}Fe Mössbauer spectra were recorded using a spectrometer operated in a constant acceleration mode. The instrument was fitted with a flow-type cryostat cooled with liquid helium. The source consisted of 100 mCi ^{57}Co dispersed in rhodium foil. The isomer shifts are reported against the centroid of a spectrum of α-iron metal foil recorded at room temperature.

Synthetic procedures

General procedure for the synthesis of phosphides: 5 mol% excess of *n*BuLi (2.5 M in hexane) or *t*BuLi (1.7 M in pentane) was added dropwise to a solution of R_2PH in petroleum ether at -30°C. The resulting reaction mixture was then slowly allowed to warm to RT and stirred overnight at this temperature. Afterwards, obtained precipitation of R_2PLi, with the yield higher than 90%, was filtered off in an inert atmosphere.

General procedure for the synthesis of anionic phosphido iron complexes supported by *β*-diketiminates: To the stirred suspension of [(Dippnacnac)$FeCl_2Li(dme)_2$] in DME, the solution of R_2PLi in DME at -30°C was added. The temperature of the reaction was maintained at -30°C to -20°C for half hour. A color change from light yellow to almost black was observed. The reaction mixture was stirred overnight at RT. Afterwards, the resulting solution was concentrated to the half of volume and the precipitated LiCl was filtered off. First of all, the solution was stored at +4°C to yield dark crystals, which was isolated, washed with cold pentane at -50°C and dried *in vacuo*. Cooling to -20°C of the mother liquor gave an additional crop.

[(Dippnacnac)FeCl(P*i*Pr_2)][Li(dme)$_3$]·dme (1): Reaction of 0.732 g (1 mmol) of [(Dippnacnac)$FeCl_2Li(dme)_2$] in 5 mL of DME with 0.124 g (1 mmol) of *i*Pr_2PLi in 3 mL of DME yielded 0.415 g (0.459 mmol, 46%) dark violet crystals. Crystals were dried under high vacuum resulting in the removal of non-coordinated DME. Elemental Analysis (Found: C, 62.31; H, 9.006; N, 3.41. Calc for $C_{47}H_{85}ClFeLiN_2O_6P$: C, 62.49; H, 9.484; N, 3.10%).

[(Dippnacnac)FeCl(PPh_2)][Li(dme)$_3$] (2): Reaction of 0.366 g (0.5 mmol) [(Dippnacnac)$FeCl_2Li(dme)_2$] in 2.5 mL of DME with 0.096 g (0.5 mmol) Ph_2PLi in 1.5 mL of DME yielded 0.140 g (0.144 mmol, 29%) dark red crystals. Elemental Analysis (Found: C, 65.02; H,

8.000; N, 3.29. Calc. for $C_{53}H_{81}ClFeLiN_2O_6P$: C, 65.53; H, 8.404; N, 2.88%).

[(Dippnacnac)FeCl(PCy$_2$)Li(dme)$_2$]·(dme) (3): Reaction of 0.732 g (1 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 5 mL of DME with 0.204 g (1 mmol) Cy$_2$PLi in 3 mL of DME yielded 0.517 g (0.526 mmol, 53%) dark crystals. Elemental Analysis (Found: C, 64.42; H, 9.309; N, 3.09. Calc for $C_{53}H_{93}ClFeLiN_2O_6P$: C, 64.72; H, 9.531; N, 2.84%).

[(Dippnacnac)FeCl(PCy$_2$)][Li(dme)$_3$](dme)$_{1.5}$ (4): Reaction of 0.732 g (1 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 5 mL of DME and 0.408 g (2 mmol) Cy$_2$PLi in 6 mL of DME yielded 0.560 g (0.521 mmol, 52%) dark crystals. Drying under high vacuum resulted in the removal of non-coordinated DME. Elemental Analysis (Found: C, 63.28; H, 9.228; N, 2.53 Calc for $C_{57}H_{103}ClFeLiN_2O_8P$: C, 63.76; H, 9.670; N, 2.61%).

[(Dippnacnac)Fe(PPh$_2$)$_2$][Li(dme)$_3$] (5): Reaction of 0.366 g (0.5 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 2.5 mL of DME and 0.288 g (1.5 mmol) Ph$_2$PLi in 4.5 mL of DME yielded 0.217 g (0.186 mmol, 37%) dark brown crystals (co-crystallization with LiCl in ratio 1:1). To achieve full conversion in this reaction, the mixture was allowed to react for a few days at room temperature. Elemental Analysis (Found: C, 67.40; H, 7.825; N, 2.63. Calc. for $C_{65}H_{91}FeLiN_2O_6P_2$ + LiCl: C, 67.10; H, 7.883; N, 2.41%).

General procedure for the synthesis of neutral phosphido iron complexes supported by *β*-diketiminates: To the stirred suspension of [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in toluene, the suspension of R$_2$PLi in toluene at -30°C was added. The temperature of the reaction was maintained at -30°C to -20°C for half hour. A color change from light yellow to almost black occurred. The reaction mixture was stirred overnight at RT. Afterwards, the solvent was evaporated under vacuum and the residue was washed with pentane (20 mL). The solution was concentrated to the half of volume and LiCl was filtered off. The solution was then stored at +4°C to yield dark crystals, which were isolated, washed with cold pentane at -50°C and dried *in vacuo*. Cooling to -20°C of the mother liquor gave an additional crop.

[(Dippnacnac)Fe(P*i*Pr$_2$)] (6): Reaction of 0.366 g (0.5 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 2.5 mL of toluene and 0.062 g (0.5 mmol) *i*-Pr$_2$PLi in 3 mL of toluene yielded 0.015 g (0.025 mmol, 5%) dark green crystals.

[(Dippnacnac)Fe(P*t*Bu$_2$)] (7): Reaction of 0.732 g (1 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 5 mL of toluene and 0.152 g (1 mmol) *t*-Bu$_2$PLi in 6 mL of toluene yielded 0.337 g (0.545 mmol, 55%) dark violet crystals. Elemental Analysis (Found: C, 71.69; H, 9.630; N, 4.76. Calc for $C_{37}H_{59}FeN_2P$: C, 71.83; H, 9.612; N, 4.53%).

^{1}H NMR (400 MHz; toluene-d$_8$; Me$_4$Si; 25°C): *δ* = 57.28 (6H, Me nacnac), 50.78 (18H, *t*Bu$_2$P), 48.02 (1H, CH nacnac), 9.99 (4H, *m*-H), 1.66 (12H, *i*Pr methyl), -46.02 (12H, *i*Pr methyl), -46.52 (4H, *i*Pr methine), -112.42 (2H, *p*-H) ppm.

[(Dippnacnac)Fe(PPh$_2$)(dme)] (8): Reaction of 0.732 g (1 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 5 mL of toluene and 0.192 g (1 mmol) Ph$_2$PLi in 6 mL of toluene yielded 0.256 g (0.365 mmol, 37%) dark green needle-shape crystals (co-crystallization with LiCl in 1:1 ratio). Drying under high vacuum resulted in the removal of the DME molecule. Elemental Analysis (Found: C, 70.22; H, 7.357; N, 3.99. Calc for $C_{41}H_{51}FeN_2P$ + LiCl: C, 70.24; H, 7.332; N, 3.99%).

^{1}H NMR (400 MHz; toluene-d$_8$; Me$_4$Si, 25°C): *δ* = 79.69 (1H, CH nacnac), 35.52 (8H, Ph$_2$P), 34.77 (2H, Ph$_2$P), 33.02 (6H, Me nacnac), -11.96 (12H, *i*Pr methyl), -12.10 (4H, *m*-H), -74.02 (2H, *p*-H), -94.92 (12H, *i*Pr methyl), -99.68 (4H, *i*Pr methine) ppm.

[(Dippnacnac)Fe(PCy$_2$)] (9): Reaction of 0.732 g (1 mmol) [(Dippnacnac)FeCl$_2$Li(dme)$_2$] in 5 mL of toluene and 0.204 g (1 mmol) Cy$_2$PLi in 6 mL of toluene yielded 0.187 g (0.279 mmol, 28%) dark green crystals. Elemental Analysis (Found: C, 73.42; H, 9.563; N, 4.24. Calc for $C_{41}H_{63}FeN_2P$: C, 73.41; H, 9.467; N, 4.18%).

^{1}H NMR (400 MHz; toluene-d$_8$; Me$_4$Si; 25°C): *δ* = 105.78 (2H, Cy$_2$P), 77.22 (4H, Cy$_2$P), 58.12 (1H, Cy$_2$P), 50.33 (1H, Cy$_2$P), 35.50 (3H, Me nacnac), 31.74 (2H, Cy$_2$P), 20.90 (3H, Me nacnac), 19.67 (2H, *m*-H), 10.41 (2H, *m*-H), 6.45 (6H, *i*Pr methyl), 1.33 (4H + 4H, broad signal, Cy$_2$P), -9.51 (6H + 6H, broad signal, Me nacnac), -1.33 (4H, Cy$_2$P) - 45.04 (2H, broad signal, *i*Pr methine), -59.31 (1H, *p*-H), -75.35 (1H, *p*-H), -88.88 (6H, *i*Pr methyl), -99.89 (2H, broad signal, *i*Pr methine) ppm. The resonance of methine proton of the Dippnacnac ligand was not observed.

General procedure for the dehydrocoupling of phosphines: To the solutions containing 5 mol% of selected phosphido iron complexes stabilized by *β*-diketiminato co-ligand in 0.35 mL of toluene, the phosphine Ph$_2$PH was added dropwise at room temperature. The reaction mixture was stirred at 120 °C for 24 h. Conversion of Ph$_2$PH to Ph$_2$P-PPh$_2$ was confirmed by signal integration in the ^{31}P and ^{31}P{^{1}H} NMR spectra.

In the case of run entry *9*, a solution of complex **8** (0.021 g, 0.03 mmol) in 0.35 mL of toluene was stirred at 120°C for 24h. After this time, the solution was cooled to RT and Ph$_2$PH (0.111 g, 0.6 mmol) was added dropwise. The reaction mixture was stirred again at 120°C for 24 h. Conversion of Ph$_2$PH to Ph$_2$P-PPh$_2$ was confirmed by signal integration in the ^{31}P and ^{31}P{^{1}H} NMR spectra.

Ph$_2$PH: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -40.6 ppm

Ph$_2$P-PPh$_2$: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -14.9 ppm[117]

Table 4. Experimental details for the dehydrocoupling of phosphines catalyzed by phosphido iron complexes.

Run #	Complex	Mass of iron complex catalyst (g)	Mass of Ph$_2$PH (g)	Conversion of Ph$_2$PH to Ph$_2$P-PPh$_2$ (%)
1	**1**	0.027	0.111	89
2	**2**	0.026	0.100	88
3	**3**	0.027	0.101	86
4	**4**	0.028	0.098	90
5	**5**	0.030	0.096	88
6	**7**	0.018	0.107	98
7	**8**	0.020	0.106	89
8	**9**	0.019	0.107	86
9	**8** (after heating)	0.021	0.111	90
10	[LFeCl$_2$Li(dme)$_2$][a]	0.018	0.093	Not observed

[a]L = Dippnacnac

General procedure for the thermal stability investigation of phosphido complexes supported by *β*-diketiminates: In the case of all discussed complexes, two solutions were prepared as the result of the dilution of the pure crystals (0.025 mmol) in 0.35 mL. Part of them was stirred at room temperature for 24 h, while the other part was heated to 120°C and stirred at that temperature for 24 h. Reaction progress was monitored by ^{31}P and ^{31}P{^{1}H} NMR spectroscopy.

*i*Pr$_2$PH: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -15.0 ppm

*t*Bu$_2$PH: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = 19.6 ppm

*i*Pr$_2$P-P*i*Pr$_2$: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -12.1 ppm[118]

Ph$_2$P-PPh$_2$: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -14.9 ppm[117]

Cy$_2$P-PCy$_2$: ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -21.7 ppm[117]

PPh$_2$(*p*-tol): ^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, H$_3$PO$_4$, 25°C): *δ* = -5.3 ppm[119]

Table 5. Experimental details for the thermal stability investigations of phosphido iron complexes.

Iron complex	Mass of iron complex (g)	Identified products
1	0.023	*i*Pr$_2$P-P*i*Pr$_2$ *i*Pr$_2$PH
2	0.022	Ph$_2$P-PPh$_2$ PPh$_2$(*p*-tol)
4	0.027	Cy$_2$P-PCy$_2$
5	0.030	PPh$_2$(*p*-tol)
7	0.016	*t*Bu$_2$PH
8	0.018	Ph$_2$P-PPh$_2$ PPh$_2$(*p*-tol)
9	0.017	Cy$_2$P-PCy$_2$

Reaction of [(Dippnacnac)FeCl$_2$] with Ph$_2$PLi: To the suspension of [(Dippnacnac)FeCl$_2$] (0.272 g, 0.5 mmol) in 2.5 mL of solvent (toluene or DME) was added the suspension of Ph$_2$PLi (0.096 g, 0.5 mmola) in 4 mL of toluene or 2 mL of DME at room temperature. The reaction mixture was stirred overnight and then analyzed by ^{31}P{^{1}H} NMR spectroscopy. From concentrated DME solution at -20°C orange crystals of [(Dippnacnac)FeCl$_2$Li(dme)$_2$] were formed (0.083 g, 0.113 mmol, 23%).

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[1] B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983–3012.
[2] R. R. Eady, *Chem. Rev.* **1996**, *96*, 3013–3030.
[3] S. E. Creutz, J. C. Peters, *Chem. Sci.* **2017**, *8*, 2321–2328.
[4] C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254.
[5] K. Gopalaiah, *Chem. Rev.* **2013**, *113*, 3248–3296.
[6] K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Chem. Rev.* **2014**, *114*, 5215–5272.
[7] I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 3170–3387.
[8] L. C. Misal Castro, H. Li, J.-B. Sortais, C. Darcel, *Green Chem.* **2015**, *17*, 2283–2303.
[9] A. Fürstner, *ACS Cent. Sci.* **2016**, *2*, 778–789.
[10] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3065.
[11] D. J. Mindiola, *Angew. Chem. Int. Ed.* **2009**, *48*, 6198–6200.
[12] Y.-C. Tsai, *Coord. Chem. Rev.* **2012**, *256*, 722–758.
[13] C. Chen, S. M. Bellows, P. L. Holland, *Dalt. Trans.* **2015**, *44*, 16654–16670.
[14] R. L. Webster, *Dalt. Trans.* **2017**, *46*, 4483–4498.
[15] F. Spitzer, C. Graßl, G. Balázs, E. M. Zolnhofer, K. Meyer, M. Scheer, *Angew. Chemie Int. Ed.* **2016**, *55*, 4340–4344.
[16] P. L. Holland, T. R. Cundari, L. L. Perez, N. A. Eckert, R. J. Lachicotte, *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424.
[17] J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela, P. L. Holland, *J. Am. Chem. Soc.* **2006**, *128*, 756–769.
[18] J. Vela, S. Vaddadi, T. R. Cundari, J. M. Smith, E. A. Gregory, R. J. Lachicotte, C. J. Flaschenriem, P. L. Holland, *Organometallics* **2004**, *23*, 5226–5239.
[19] J. M. Smith, R. J. Lachicotte, P. L. Holland, *Organometallics* **2002**, *21*, 4808–4814.
[20] N. A. Eckert, J. M. Smith, R. J. Lachicotte, P. L. Holland, *Inorg. Chem.* **2004**, *43*, 3306–3321.
[21] J. Vela, S. Stoian, C. J. Flaschenriem, E. Münck, P. L. Holland, *J. Am. Chem. Soc.* **2004**, *126*, 4522–4523.
[22] N. A. Eckert, S. Stoian, J. M. Smith, E. L. Bominaar, E. Münck, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 9344–9345.
[23] J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857–7870.
[24] Y. Yu, W. W. Brennessel, P. L. Holland, *Organometallics* **2007**, *26*, 3217–3226.
[25] Y. Yu, A. R. Sadique, J. M. Smith, T. R. Dugan, R. E. Cowley, W. W. Brennessel, C. J. Flaschenriem, E. Bill, T. R. Cundari, P. L. Holland, *J. Am. Chem. Soc.* **2008**, *130*, 6624–6638.
[26] P. L. Holland, *Acc. Chem. Res.* **2008**, *41*, 905–914.
[27] M. Espinal-Viguri, A. K. King, J. P. Lowe, M. F. Mahon, R. L. Webster, *ACS Catal.* **2016**, *6*, 7892–7897.
[28] C. A. Jaska, A. Bartole-Scott, I. Manners, *Dalt. Trans.* **2003**, 4015–4021.
[29] E. M. Leitao, T. Jurca, I. Manners, *Nat. Chem.* **2013**, *5*, 817–829.
[30] R. Waterman, *Chem. Soc. Rev.* **2013**, *42*, 5629–5641.
[31] M. Itazaki, S. Katsube, M. Kamitani, H. Nakazawa, *Chem. Commun.* **2016**, *52*, 3163–3166.
[32] V. Koshti, S. Gaikwad, S. H. Chikkali, *Coord. Chem. Rev.* **2014**, *265*, 52–73.
[33] L. Rosenberg, *ACS Catal.* **2013**, *3*, 2845–2855.
[34] D. S. Glueck, *Top. Organomet. Chem.* **2010**, *31*, 65–100.
[35] R. Waterman, *Dalt. Trans.* **2009**, 18–26.
[36] D. S. Glueck, *Chem. Eur. J.* **2008**, *14*, 7108–7117.
[37] D. S. Glueck, *Dalt. Trans.* **2008**, 5276–5286.
[38] M. Kamitani, M. Itazaki, C. Tamiya, H. Nakazawa, *J. Am. Chem. Soc.* **2012**, *134*, 11932–11935.
[39] C. A. Bange, R. Waterman, *Chem. - A Eur. J.* **2016**, *22*, 12598–12605.
[40] J. Sugiura, T. Kakizawa, H. Hashimoto, H. Tobita, H. Ogino, *Organometallics* **2005**, *24*, 1099–1104.
[41] P. E. Sues, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2014**,

136, 4746–4760.

[42] A. M. Geer, Á. L. Serrano, B. De Bruin, M. A. Ciriano, C. Tejel, *Angew. Chemie Int. Ed.* **2015**, *54*, 472–475.

[43] N. T. Coles, M. F. Mahon, R. L. Webster, *Organometallics* **2017**, *36*, 2262–2268.

[44] L. Rosenberg, *Coord. Chem. Rev.* **2012**, *256*, 606–626.

[45] D. Weber, E. Fluck, H. G. von Schnering, K. Peters, *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.* **1982**, *37*, 594–600.

[46] D. G. Dick, D. W. Stephan, *Organometallics* **1991**, *10*, 2811–2816.

[47] D. Fenske, A. Grissinger, E. Hey-Hawkins, J. Magull, *Zeitschrift fur Anorg. und Allg. Chemie* **1991**, *595*, 57–66.

[48] W. E. Buhro, M. H. Chisholm, K. Folting, J. C. Huffman, J. D. Martin, E. Streib, *J. Am. Chem. Soc.* **1992**, *114*, 557–570.

[49] J. G. Planas, F. Hampel, J. A. Gladysz, *Chem. Eur. J.* **2005**, *11*, 1402–1416.

[50] R. T. Baker, J. F. Whitney, S. S. Wreford, *Organometallics* **1983**, *2*, 1049–1051.

[51] W. E. Buhro, B. D. Zwick, S. Georgiou, J. P. Hutchinson, J. A. Gladysz, *J. Am. Chem. Soc.* **1988**, *110*, 2427–2439.

[52] G. Boni, O. Blacque, P. Sauvageot, N. Poujaud, C. Moïse, M. M. Kubicki, *Polyhedron* **2002**, *21*, 371–379.

[53] P. Mastrorilli, *Eur. J. Inorg. Chem.* **2008**, 4835–4850.

[54] A. T. Normand, C. G. Daniliuc, B. Wibbeling, G. Kehr, P. Le Gendre, G. Erker, *J. Am. Chem. Soc.* **2015**, *137*, 10796–10808.

[55] M. J. Tylor, M. P. Coles, J. R. Fulton, *Aust. J. Chem.* **2015**, *68*, 635–640.

[56] E. Hey-Hawkins, *Chem. Rev.* **1994**, *94*, 1661–1717.

[57] M. D. Fryzuk, K. Bhangu, *J. Am. Chem. Soc.* **1988**, *110*, 961–963.

[58] Y. Gloaguen, W. Jacobs, B. de Bruin, M. Lutz, J. I. van der Vlugt, *Inorg. Chem* **2013**, *52*, 1682–1684.

[59] M. A. M. Hoyle, D. A. Pantazis, H. M. Burton, R. McDonald, L. Rosenberg, *Organometallics* **2011**, *30*, 6458–6465.

[60] D. S. Glueck, *Synlett.* **2007**, 2627–2634.

[61] C. Scriban, D. S. Glueck, L. N. Zakharov, W. S. Kassel, A. G. DiPasquale, J. A. Golen, A. L. Reinhold, *Organometallics* **2006**, *25*, 5757–5767.

[62] C. Scriban, I. Kovacik, D. S. Glueck, *Organometallics* **2005**, *24*, 4871–4874.

[63] I. Kovacik, C. Scriban, D. S. Glueck, *Organometallics* **2006**, *25*, 536–539.

[64] E. J. Derrah, D. A. Pantazis, R. McDonald, L. Rosenberg, *Organometallics* **2007**, *26*, 1473–1482.

[65] A. Takaoka, A. Mendiratta, J. C. Peters, *Organometallics* **2009**, *28*, 3744–3753.

[66] A. J. Carty, S. A. MacLaughlin, D. Nucciarone, *Methods Stereochem. Anal.* **1987**, *8*, 559–619.

[67] W. Wang, P. J. Low, A. J. Carty, E. Sappa, G. Gervasio, C. Mealli, A. Ienco, E. Perez-Carreño, *Inorg. Chem.* **2000**, *39*, 998–1005.

[68] H. Werner, *Inorg. Chem.* **1990**, *10*, 267–295.

[69] P. Coburger, S. Demeshko, C. Rödl, E. Hey-Hawkins, R. Wolf, *Angew. Chemie Int. Ed.* **2017**, *56*, 15871–15875.

[70] C. M. Alvarez, M. E. García, M. A. Ruiz, N. G. Connelly, *Organometallics* **2004**, *23*, 4750–4758.

[71] F. Lindenberg, T. Shribman, J. Sieler, E. Hey-Hawkins, M. S. Eisen, *J. Organomet. Chem.* **1996**, *515*, 19–25.

[72] W. Clegg, *Inorg. Chem* **1976**, *15*, 2928–2931.

[73] R. E. Ginsburg, J. M. Berg, R. K. Rothrock, J. P. Collman, K. O. Hodgson, L. F. Dahl, *J. Am. Chem. Soc.* **1979**, *101*, 7218–7231.

[74] R. T. Baker, J. C. Calabrese, P. J. Krusic, M. J. Therien, W. C. Trogler, *J. Am. Chem. Soc.* **1988**, *110*, 8392–8412.

[75] N. J. Grist, G. Hogarth, S. A. R. Knox, B. R. Lloyd, D. A. V. Morton, A. G. Orpen, *J. Chem. Soc., Chem. Commun.* **1988**, 673–675.

[76] B. Walther, H. Hartung, J. Reinhold, P. G. Jones, H.-C. Böttcher, U. Baumeister, A. Krug, *Chem. Ber.* **1992**, *125*, 1379–1382.

[77] M. R. Adams, J. Galluci, A. Wojcicki, G. J. Long, *Inorg. Chem* **1992**, *31*, 2–4.

[78] V. Kumar, D. W. Lee, M. G. Newton, R. B. King, *J. Organomet. Chem.* **1996**, *512*, 1–9.

[79] R. Melenkivitz, D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2002**, *124*, 3846–3847.

[80] S. Yao, S. Block, M. Brym, M. Driess, *Chem. Commun.* **2007**, 3844–3846.

[81] A. Seifert, D. Scheid, G. Linti, T. Zessin, *Chem. Eur. J.* **2009**, *15*, 12114–12120.

[82] Y. Yang, N. Zhao, Y. Wu, H. Zhu, H. W. Roesky, *Inorg. Chem.* **2012**, *51*, 2425–2431.

[83] E. C. Y. Tam, N. A. Maynard, D. C. Apperley, J. D. Smith, M. P. Coles, J. R. Fulton, *Inorg. Chem.* **2012**, *51*, 9403–9415.

[84] E. C. Y. Tam, L. M. Harris, E. S. Borren, J. D. Smith, M. Lein, M. P. Coles, J. R. Fulton, *Chem. Commun.* **2013**, *49*, 10278–10280.

[85] J. Zhou, T. Li, L. Maron, X. Leng, Y. Chen, *Organometallics* **2015**, *34*, 470–476.

[86] M. J. Barrow, G. A. Sim, *J. Chem. Soc., Dalt. Trans.* **1975**, 291–295.

[87] W. Malisch, W. Angerer, A. H. Cowley, N. C. Norman, *J. Chem. Soc., Chem. Commun.* **1985**, 1811–1812.

[88] L. Weber, K. Reizig, R. Boese, *Chem. Ber.* **1985**, *118*, 1193–1203.

[89] L. Weber, U. Sonnenberg, H. G. Stammler, B. Neumann, *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.* **1991**, *46*, 714–718.

[90] L. Weber, R. Kirchoff, H. G. Stammler, B. Neumann, *Chem. Ber.* **1992**, *125*, 1553–1557.

[91] L. Weber, M. Frebel, R. Boese, *Zeitschrift fur Anorg. und Allg. Chemie* **1992**, *607*, 139–145.

[92] L. Weber, I. Schumann, H.-G. Stammler, B. Neumann, *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.* **1992**, *47*, 1134–1140.

[93] L. Weber, O. Kaminski, H. G. Stammler, B. Neumann, V. D. Romanenko, *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.* **1993**, *48*, 1784–1794.

[94] L. Weber, H. Misiak, H. G. Stammler, B. Neumann, *Zeitschrift fur Anorg. und Allg. Chemie* **1994**, *620*, 1730–1735.

[95] W. Petz, F. Weller, *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.* **1996**, *51*, 715–721.

[96] M. Okazaki, T. Yoshitomi, J. Naito, A. Sato, T. Komuro, H.

Tobita, *J. Am. Chem. Soc.* **2008**, *130*, 17674–17675.

[97] A. K. Hickey, S. B. Muñoz, S. A. Lutz, M. Pink, C.-H. Chen, J. M. Smith, *Chem. Commun.* **2017**, *53*, 412–415.

[98] A. K. King, A. Buchard, M. F. Mahon, R. L. Webster, *Chem. Eur. J.* **2015**, *21*, 15960–15963.

[99] A. K. King, K. J. Gallagher, M. F. Mahon, R. L. Webster, *Chem. Eur. J.* **2017**, *23*, 9039–9043.

[100] M. Espinal-Viguri, M. F. Mahon, S. N. G. Tyler, R. L. Webster, *Tetrahedron* **2017**, *73*, 64–69.

[101] M. Espinal-Viguri, C. R. Woof, R. L. Webster, *Chem. Eur. J.* **2016**, *22*, 11605–11608.

[102] K. J. Gallagher, M. Espinal-Viguri, M. F. Mahon, R. L. Webster, *Adv. Synth. Catal.* **2016**, *358*, 2460–2468.

[103] R. Grubba, Ł. Ponikiewski, Ł. Tomorowicz, J. Pikies, *Acta Crystallogr. Sect. E Struct. Reports Online* **2010**, *66*, m77.

[104] R. Grubba, K. Kaniewska, Ł. Ponikiewski, B. Cristóvão, W. Ferenc, A. Dragulescu-Andrasi, J. Krzystek, S. A. Stoian, J. Pikies, *Inorg. Chem.* **2017**, *56*, 11030–11042.

[105] P. Gütlich, E. Bill, A. X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications*, Springer-Verlag, Berlin, **2011**.

[106] K. K. Surerus, M. P. Hendrich, P. D. Christie, D. Rottgardt, W. H. Orme-Johnson, E. Münck, *J. Am. Chem. Soc.* **1992**, *114*, 8579–8590.

[107] H. Andres, E. L. Bominaar, J. M. Smith, N. A. Eckert, P. L. Holland, E. Münck, *J. Am. Chem. Soc.* **2002**, *124*, 3012–3025.

[108] S. F. McWilliams, E. Brennan-Wydra, K. Cory MacLeod, P. L. Holland, *ACS Omega* **2017**, *2*, 2594–2606.

[109] H. Zipse, in *Radicals Synth. I*, Springer-Verlag, Berlin/Heidelberg, **2006**.

[110] J. K. Pagano, C. A. Bange, S. E. Farmiloe, R. Waterman, *Organometallics* **2017**, *36*, 3891–3895.

[111] B. J. Ackley, J. K. Pagano, R. Waterman, *Chem. Commun.* **2018**, *54*, 2774–2776.

[112] P. A. Lindahl, *J. Inorg. Biochem.* **2012**, *106*, 172–178.

[113] C. R. Hess, T. Weyhermüller, E. Bill, K. Wieghardt, *Angew. Chemie Int. Ed.* **2009**, *48*, 3703–3706.

[114] K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13044–13053.

[115] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2007**, *64*, 112–122.

[116] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[117] D. L. Dodds, M. F. Haddow, A. G. Orpen, P. G. Pringle, G. Woodward, *Organometallics* **2006**, *25*, 5937–5945.

[118] S. Aime, R. K. Harris, E. M. McVicker, M. Fild, *J. Chem. Soc., Dalt. Trans.* **1976**, 2144–2153.

[119] M. Sun, H. Y. Zhang, Q. Han, K. Yang, S. D. Yang, *Chem. - A Eur. J.* **2011**, *17*, 9566–9570.

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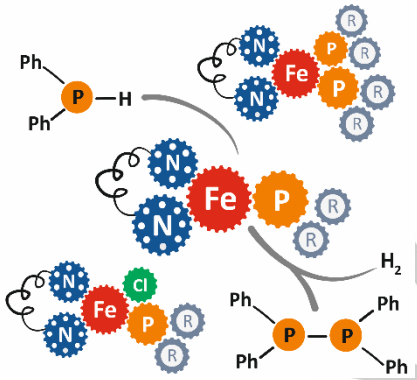
Layout 1:

FULL PAPER

The facile synthesis of a novel family of iron(II) complexes supported by terminal phosphido ligands is presented. The structures of the terminal phosphido complexes described here could be easily tuned by a judicious choice of solvent and by a change in the stoichiometry of the reaction. A preliminary investigation of the catalytic activity of these phosphido complexes showed that they exhibit good catalytic activity in the dehydrocoupling of phosphines.



Phosphido complexes

Kinga Kaniewska, Alina Dragulescu-Andrasi, Łukasz Ponikiewski, Jerzy Pikies, Sebastian A. Stoian and Rafał Grubba**

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Syntheses, structures and reactivity of terminal phosphido complexes of iron(II) supported by a *β*-diketiminato ligand