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Introduction

We have a long-standing interest in ferrocene-based chelate ligands other than the iconic 1,1'-bis(diphenylphosphino) ferrocene (dppf) and related standard diphosphines.¹ A substantial part of this work from our group has focused on diamido chelate complexes derived from secondary diamines of the type $fc(NHR)_2$ (fc = 1,1'-ferrocenylene). First examples of such compounds were reported in 2001 almost simultaneously by us^{1j} and by the groups of Arnold² and Gibson and Long.³ The chemistry of chelates containing the diamido ligand framework $[fc(NR)_2]^{2-}$ has flourished enormously since then, in particular through contributions in the area of f-block elements by the groups of Arnold,⁴ Eppinger⁵ and, in particular, Diaconescu.⁶ The heavier analogues of the ferrocene-based diamines mentioned above are secondary diphosphines of the type $fc(PHR)_2$. In this report we describe the synthesis of

Phosphido complexes derived from 1,1'ferrocenediyl-bridged secondary diphosphines † ‡

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This paper focuses on ferrocene-based secondary diphosphines of the type $[Fe{\{\eta^5-C_5H_4(PHR)\}_2}]$ with *P*-substituents of distinctly different steric and electronic properties, namely methyl, neopentyl (Np), *tert*butyl, phenyl and 3,5-bis(trifluoromethyl)phenyl (XyF). The reaction of $[Fe{\{\eta^5-C_5H_4(PHPh)\}_2}]$ (H₂**1a**) and $[Fe{\{\eta^5-C_5H_4(PHt-Bu)\}_2}]$ (H₂**1b**) with *n*-BuLi in the presence of TMEDA afforded lithium diphosphides of the type $[Li_2(\mu-1)(TMEDA)_2]$, which contain a cyclic non-planar Li_2P_2 core. The analogous reactions of $[Fe{\{\eta^5-C_5H_4(PHMe)\}_2}]$ (H₂**1c**) and $[Fe{\{\eta^5-C_5H_4(PHNp)\}_2}]$ (H₂**1d**) furnished dimeric aggregates exhibiting a ladder-type Li_4P_4 motif, *viz*. $[Li_4(\mu-1c)_2(TMEDA)_3]$ and $[Li_2(\mu-1d)(TMEDA)]_2$. H₂**1e** (R = XyF) did not afford a stable lithium diphosphide. A Brønsted metathesis with Zr(NMe₂)₄ was possible with the aryl-substituted compounds H₂**1a** and H₂**1e**, leading to products of the type $[{Zr(NMe_2)_3}_2(\mu-1)]$. In contrast, the alkyl-substituted congeners H₂**1b**-H₂**1d** were inert towards Zr(NMe₂)₄. The reaction of $[Fe{\{\eta^5-C_5H_4(PHR)\}_2}]$ with nickelocene afforded intractable mixtures of numerous products in the case of H₂**1c** and H₂**1e**. In the other three cases, compounds of the type $[(NiCp)_2(\mu-1)]$ were isolated. For H₂**1b** and H₂**1d** a two-stepped reaction *via* a phosphino–phosphido intermediate of the type [NiCp(H1)] was observed, which could be isolated and fully characterised in the case of [NiCp(H1b)].

various compounds of this class and their reactions affording corresponding phosphido complexes.

The phosphorus atom of a uninegative PR₂ unit contains two lone pairs of electrons. The coordination chemistry of these phosphido ligands is highly diverse, because both terminal and bridging coordination modes are possible. In the bridging mode, both lone pairs are occupied in metal-phosphorus bonds. In the terminal mode, the bonding environment of the phosphorus atom can be either trigonal pyramidal or trigonal planar.⁷ Only one lone pair on phosphorus is occupied in the trigonal pyramidal case. In the trigonal planar case, the second lone pair is engaged in π bonding to the metal centre, formally giving rise to a metal-phosphorus double bond. Terminal phosphido complexes are attracting considerable attention due to their relevance in important catalytic reactions such as phosphine dehydrocoupling and the hydrophosphination of alkenes and alkynes.8 The first structurally authenticated example was published in 1975.9,10 Phosphido-bridged complexes have been known for more than half a century¹¹ and continue to be of widespread interest.¹² For example, μ -PR₂ units are useful for the stabilisation of oligonuclear metal complexes and clusters,¹³ including even nanosized metalloid ones.14 First examples of complexes containing diphosphido ligands X(PR)₂²⁻ were published already in 1967.15 Surprisingly, just a single ferrocene-based ligand of this type is known to date, namely $fc(PPh)_2^{2-}$ (1a²⁻), which is present in the gold(I) complex $[Au_2(1a)]_n$ reported in

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[†] Dedicated to Prof. Evamarie Hey-Hawkins on the occasion of her 60th birthday. ‡ Electronic supplementary information (ESI) available: Plots of NMR spectra, crystal data and structure refinement details. CCDC 1536257–1536270. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c7dt00941k

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2010 by Glueck and co-workers as the only example so far of a complex containing this ligand.¹⁶ This diphosphido complex was synthesised by dehydrochlorination of its diphosphine precursor [(AuCl)₂(μ -H₂1a)]. Interestingly, the parent secondary diphosphine fc(PHPh)₂ (H₂1a) is commercially available, although its synthesis has not been described so far. Very recently, Pietschnig and co-workers published the only other 1,1'-ferrocenylene-bridged secondary diphosphine, namely fc (PH*t*-Bu)₂ (H₂1b).¹⁷ In a parallel study, this compound was investigated also in our group, together with several new homologues described below.

Results and discussion

Synthesis and characterisation of diphosphines

We have prepared three new 1,1'-ferrocenylene-bridged secondary diphosphines of the type $fc(PHR)_2$, *viz*. H_21c (R = methyl), H_21d [R = neopentyl (Np)] and H_21e [R = 3,5-bis(trifluoromethyl)phenyl (XyF)]. The synthesis of these compounds is outlined in Scheme 1. The phenyl congener H_21a is also included, because its preparation has not been reported to date. In addition, this scheme shows our synthesis of H_21b , since this differs from the recently reported route.¹⁷

The methyl-substituted compound H_21c was prepared in analogy to the published synthesis of the tert-butyl congener H_2 **1b**.¹⁷ The reaction of fc[PCl(NEt₂)]₂ (available in a twostepped reaction starting from 1,1'-dilithioferrocene)¹⁸ and methyllithium afforded fc[PMe(NEt₂)]₂ [(NEt₂)₂1c], which was subsequently transformed to fc(PMeCl)₂ (Cl₂1c) with HCl in diethyl ether. In the final step, Cl₂1c was reduced to H₂1c with lithium aluminium hydride. The yield of analytically pure H₂1c was 47% over three steps. All other diphosphines were more conveniently prepared by following a different synthetic approach for the intermediates of the type $fc[PR(NEt_2)]_2$, which is based on the reaction of 1,1'-dilithioferrocene with compounds of the type $PX(NEt_2)R$ (X = Cl, Br). The chloro compounds are readily available by published procedures for R = Ph,¹⁹ t-Bu,²⁰ and XyF.²¹ The neopentyl derivative PBr(NEt₂)Np was easily prepared from diethylamine and PBr₂Np, which was obtained in a routine way²² from PBr₃ and NpMgBr (the preparation of the Grignard reagent worked better in our hands with NpBr than with NpCl, and consequently PBr₃ was used instead of PCl₃ in order to avoid halide scrambling). The yield of analytically pure product obtained over three steps was 29% for H₂1a, 47% each for H₂1b and H₂1d and 44% for H₂1e.

The phosphorus atoms of 1,1'-ferrocenvlene-bridged secondary diphosphines of the type fc(PHR)₂ are chiral centres and rac and meso isomers are therefore expected for these compounds. In the case of the known compound H₂1b, the presence of two isomers is reflected by the observation of two doublets in the ³¹P NMR spectrum (δ –26.9 and –27.4 ppm in C_6D_6 solution).¹⁷ Likewise, two closely spaced doublets are present in the ³¹P NMR spectrum of the phenyl congener H₂1a $(\delta - 60.8 \text{ and } - 61.2 \text{ ppm in } C_6 D_6 \text{ solution})$ and the bis(trifluoromethyl)phenyl congener H₂1e (δ -61.2 and -61.5 ppm in C_6D_6 solution). The diastereometric ratio is 1:1 in each case. In contrast, the new alkyl-substituted congeners H_21c (R = Me) and H_2 1d (R = Np) each exhibit only a single doublet in the ³¹P NMR spectrum (C₆D₆), respectively located at -89.9 and -86.8 ppm. We surmise that in these cases the chemical shift difference of the rac and meso isomers is not sufficient for the detection of resolved individual signals. We have been able to determine the structures of rac-H₂1a, meso-H₂1b and meso-H₂1e by single-crystal X-ray diffraction (XRD) studies (Fig. 1–3). Pertinent metric parameters are collected in Table 1.

Crystalline *meso*-H₂**1b** and *meso*-H₂**1e** each exhibit crystallographically imposed inversion symmetry (molecular point group C_i), which leads to a staggered arrangement of the cyclopentadienyl rings with diametrically opposed phosphino substituents. Essentially the same structural motif is found for *rac*-H₂**1a**, which exhibits an approximately C_i symmetric fcP₂ core. The phosphorus bond lengths and angles compare well with those reported for the only two other examples of structurally characterised ferrocene-based secondary phosphines, *viz.* Fc-PH-*t*-Bu²³ and Fc-PH-Acn-P*i*-Pr₂ (Acn = acenaphthen-5,6diyl).²⁴

Synthesis and characterisation of lithium diphosphides

Secondary phosphines can be deprotonated with standard alkyllithium reagents. The resulting lithium phosphides LiPR₂ frequently form higher-order aggregates, which are insoluble



Scheme 1 Synthesis of H₂1a-H₂1e. Reagents and conditions: (a) PCl(NEt₂)R (for a, b, d and e), diethyl ether, 0 °C \rightarrow room temperature; (b) HCl in diethyl ether, room temperature; (c) MeLi, diethyl ether, -60 °C \rightarrow room temperature; (d) LiAlH₄, THF, room temperature, then H₂O.

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Fig. 1 Molecular structure of rac-H₂1a in the crystal. Only one enantiomer is shown.



Fig. 2 Molecular structure of $meso-H_2$ 1b in the crystal.

in common organic solvents and thus difficult to crystallise and characterise.²⁵ This may be avoided by adduct formation with TMEDA, THF or similar Lewis basic donors. For example, the crystal structures of $[\text{Li}(\text{PPh}_2)(\text{Et}_2\text{O})]_n$,²⁶ $[\text{Li}(\text{PPh}_2)$ $(\text{DME})]_n$,²⁷ $[\text{Li}(\text{PPh}_2)(\text{THF})_2]_n$,²⁶ and $[\text{Li}(\text{PPh}_2)(\text{TMEDA})]_2$,²⁸ were reported already decades ago, whereas that of pristine lithium diphenylphosphide is still unknown. In the same vein, the crystal structure of the adduct $[\text{Li}_2{o-C_6H_4(\text{PPh})_2}(\text{TMEDA})_2]$ was published in 1987,²⁹ whereas that of the donor-free lithium diphosphide has not been reported to date.³⁰



Fig. 3 Molecular structure of meso-H₂1e in the crystal.

Table 1 Selected bond lengths (Å) and angles (°) in secondary diamines of the type fc(NHR)_2 $\,$

	P-C _{fc}	P-C _R	С-Р-С	Torsion angle ^a
<i>rac</i> -H ₂ 1a	1.804(3) 1.808(3)	1.834(3) 1.824(3)	102.9(1) 102.3(1)	178.0
$meso-H_2\mathbf{1b}$ $meso-H_2\mathbf{1e}^b$	1.816(3) 1.802(3)	1.878(3) 1.863(3)	103.3(1) 101.0(1)	180 180

 ${}^{a}C_{fc}$ -cg-cg-C_{fc} (cg = cyclopentadienyl ring centroid) torsion angle. b The structure was refined with disordered P atoms (two split positions with 65 and 35% probability). The data refer to the most probable atom positions.

Pietschnig and co-workers recently described the formation of the lithium diphosphide Li₂1**b** by reaction of H₂1**b** with *n*-BuLi in the presence of TMEDA (two equivalents each).¹⁷ ³¹P and ⁷Li NMR data indicate that the two phosphorus atoms are associated symmetrically with the two lithium atoms in hydrocarbon solution. Interestingly, the phosphine-to-phosphide transformation, which occurs by lithiation of H₂1**b**, has a negligible effect on the chemical shift of the ³¹P NMR signal.³¹ We have isolated the TMEDA adduct [Li₂(μ -1**b**)(TMEDA)₂] from this reaction in *n*-hexane as orange-red crystals in 79% yield (Scheme 2).

Its molecular structure in the solid state reveals a symmetrically bridging arrangement of the lithium and phosphorus atoms, which form a non-planar Li₂P₂ ring (see below). This compound exhibits a surprisingly high solubility in benzene. Consequently, good quality ¹H, ⁷Li, ¹³C and ³¹P NMR spectra could be obtained from C₆D₆ solutions. Our ⁷Li (δ 1.9 ppm; t, ¹J_{PLi} = 51 Hz) and ³¹P NMR spectroscopic data (δ –26.9 ppm; sept, ¹J_{PLi} = 51 Hz) (Table 2) are similar to those reported by Pietschnig and co-workers for Li₂1b in C₆D₆.



Scheme 2 Lithiation of H₂**1a**-H₂**1d** with *n*-BuLi in the presence of TMEDA afforded compounds of structure type A (R = Ph, t-Bu) or B (R = Me, Np; in the latter case the Li atoms marked with a surrounding square are tricoordinate, while in the former case these Li atoms are probably bridged by a TMEDA ligand and are tetracoordinate). Attempts to lithiate H₂**1e** afforded only intractable material. Reagents and conditions: (a) *n*-BuLi, TMEDA, *n*-hexane, room temperature.

Table 2 31 P NMR spectroscopic data of the diphosphines H₂1a-H₂1d and the corresponding lithium diphosphide TMEDA adducts

	C_6D_6	THF- d_8	$\Delta \delta^a$
H ₂ 1a [$\text{Li}_2(\mu$ -1a)(TMEDA) ₂]	-60.8, -61.2 -66.9 (br.) -26.9 -27.4	-62.0 (br.)	-6
$\begin{bmatrix} \text{Li}_2(\mu-1\mathbf{b})(\text{TMEDA})_2 \end{bmatrix}$	-26.9, $-27.4-26.9 (sept, {}^{1}J_{PLi} = 51 Hz)$	-26.6 (br.)	0
$\begin{bmatrix} \text{Li}_4(\mu-\mathbf{1c})_2(\text{TMEDA})_3 \end{bmatrix}$ H-1d	-86.8	-125.7 (br.)	-36
$[\text{Li}_2(\mu-1d)(\text{TMEDA})]_2$	b	-118.9 (br.)	-32
^{<i>a</i> ³¹P NMR signal sh solubility.}	ift caused by lithiation of	H_2 1 . ^b Insuff	icient

Note that a significantly larger ${}^{1}J_{PLi}$ value of 80 Hz was reported by Lappert and co-workers for the donor-free lithium phosphide dimer [LiP{CH(SiMe₃)₂}₂]₂ in C₆D₆.³² The use of the donor solvent THF- d_8 leads to the observation of a respective broad signal in the ⁷Li (δ 4.0 ppm) and ³¹P NMR spectrum $(\delta$ –26.6 ppm) instead of the well-resolved ⁷Li triplet and ³¹P septet detected for $[Li_2(\mu-1b)(TMEDA)_2]$ in C₆D₆ solution. The absence of ¹J_{PLi} coupling in solution NMR spectra of lithium phosphides has been ascribed to lithium exchange processes which are rapid on the NMR time scale and/or to the formation of solvated lithium cations and phosphide anions in strong donor solvents like THF.33 For example, lithium diphenylphosphide forms a dimeric aggregate at low temperatures in Et₂O solution,³⁴ which exhibits a triplet in the ⁷Li and a septet in the ³¹P NMR spectrum at 202 K (${}^{1}J_{PLi}$ = 44 Hz) or below, ^{31*b*,34,35} but no such coupling is observed in THF solution even at 155 K.^{33a} The lithiation of the other ferrocenebased diphosphines was also investigated by us and revealed the formation of two structure types, viz. monomer A and dimeric aggregate B in Scheme 2, depending on the substituents R. Due to the only moderate solubility of the phenyl congener H₂1a in n-hexane, this compound was reacted with n-BuLi and TMEDA (two equivalents each) in a mixture of toluene and n-hexane (3:1), which afforded the TMEDA adduct $[Li_2(\mu-1a)(TMEDA)_2]$ as orange-red crystals in 80% yield. The molecular structure in the solid state is similar to

that observed for $[Li_2(\mu-1b)(TMEDA)_2]$ (see below). In comparison to the tert-butyl congener, lithiation has a non-negligible effect on the chemical shift of the ³¹P NMR signal in this case (upfield shift, $\Delta \delta \approx -6$ ppm in C₆D₆; see Table 2). No ¹J_{PLi} coupling is observed, since the respective ⁷Li and ³¹P NMR signal is fairly broad both for C_6D_6 and for THF- d_8 solutions. The analogous reaction of the methyl congener H_21c in *n*-hexane furnished the product as an amorphous red solid. Crystals suitable for an XRD study could not be obtained in this case, despite many attempts with various solvents. The ¹H NMR spectrum indicates a 2:3 ratio of 1c and TMEDA in this product, which therefore may be plausibly represented as $[Li_4(1c)_2(TMEDA)_3]$ (76% yield). Unfortunately, the result of the CHN analysis is not in satisfactory agreement with this composition, because the value determined for nitrogen is too low by 2.4%. We note, however, that we have observed an almost identical deviation from the calculated value for nitrogen in the case of the structurally characterised compounds [Li₂(µ-1a) $(TMEDA)_2$ and $[Li_2(\mu-1b)(TMEDA)_2]$. This indicates that the quantity of TMEDA was lower in the samples used for CHN analysis than in the samples used for NMR spectroscopy and XRD (very likely because the samples used for CHN analysis were routinely subjected to oil pump vacuum for prolonged periods of time, which removed some of the reasonably volatile TMEDA). The solubility of $[Li_4(1c)_2(TMEDA)_3]$ was sufficient for NMR spectroscopic purposes only in THF-d₈. Two broad signals are observed in the ⁷Li spectrum (δ 11.3 and 6.2 ppm) and the ³¹P NMR spectrum exhibits a single, fairly broad signal (δ –125.7 ppm). In comparison to the *tert*-butyl and phenyl congeners, lithiation has a pronounced effect on the chemical shift of the ³¹P NMR signal in this case, causing an upfield shift of $\Delta \delta \approx -36$ ppm (see Table 2). A similarly pronounced upfield shift was observed upon lithiation of the neopentyl congener H₂1d ($\Delta \delta \approx -32$ ppm; see Table 2), which furnished $[Li_2(\mu-1d)(TMEDA)]_2$ as orange-red crystals in 71% yield under our standard conditions (two equivalents each of *n*-BuLi and TMEDA in *n*-hexane solution). In the solid state, two types of lithium atoms are present in the structure (see below). A broad ⁷Li NMR signal is observed for this compound in THF- d_8 solution (δ 3.4 ppm). This signal is not symmetrical and apparently exhibits a shoulder. Similar to the methyl congener $[\text{Li}_4(\mathbf{1c})_2(\text{TMEDA})_3]$, the solubility of $[\text{Li}_2(\mu-\mathbf{1d})(\text{TMEDA})]_2$ in C_6D_6 was not sufficient for NMR purposes and THF- d_8 was used throughout. The ³¹P NMR spectrum contains a single, fairly broad signal (δ –118.9 ppm). The ¹H and ¹³C NMR spectra are compatible with symmetrical structures in solution, which exhibit equivalent PR units in both cases (R = Me, Np). The lithiation of H_2 **1e** afforded a product which unfortunately resisted characterisation. A pale orange precipitate resulted under our standard conditions, which immediately turned black upon contact with standard organic solvents, including C₆D₆ and THF-d₈. When the lithiation was performed in toluene or THF solution at -90 °C, a colour change from orange to red was observed, compatible with the formation of the target phosphide. However, upon warming to ca. -40 °C, the colour rapidly turned brown and a dark precipitate

formed. We surmise that this behaviour is due to the comparatively high CH acidity of the aryl groups caused by the CF₃ substituents. Note, for example, that 1,3-bis(trifluoromethyl) benzene is readily lithiated with *n*-BuLi in the presence³⁶ or absence of TMEDA.³⁷

The structures of $[Li_2(\mu-1a)(TMEDA)_2]$, $[Li_2(\mu-1b)(TMEDA)_2]$ and $[Li_2(\mu-1d)(TMEDA)]_2$, were determined by single-crystal XRD analyses (Fig. 4–6). Pertinent metric parameters are collected in Table 3.

The structural motif found for $[Li_2(\mu-1a)(TMEDA)_2]$ and $[Li_2(\mu-1b)(TMEDA)_2]$ (structure type A in Scheme 2) closely resembles that of the monomeric bis(diorganophosphide) $[Li_2{o-C_6H_4(PPh)_2}(TMEDA)_2]^{29}$ as well as that of the dimeric diorganophosphides [LiPt-Bu₂(DME)]₂²⁷ and [Li(PPh₂) (TMEDA)]₂.²⁸ The lithium and phosphorus atoms form a fourmembered ring, which is not planar. The dihedral angle between the two Li₂P planes is 45.9° in the case of $[Li_2(\mu-1a)]$ $(TMEDA)_2$ and 41.5° for the $[Li_2(\mu-1b)(TMEDA)_2]$ molecule shown in Fig. 5. For comparison, this angle is 38.5° in the case of [Li₂{o-C₆H₄(PPh)₂}(TMEDA)₂].²⁹ The Li-P distances are indistinguishable within experimental error in each case and are typical for lithium diorganophosphides containing fourcoordinate lithium.²⁵ The dimeric aggregate $[Li_2(\mu-1d)]$ (TMEDA)]₂ exhibits quite a different structural motif (structure type B in Scheme 2). The lithium and phosphorus atoms form a four-rung ladder, which is strongly reminiscent of the arrangement found for $[Li_2(\mu_3-Pt-Bu_2)(\mu_2-Pt-Bu_2)(THF)]_2$.³⁸ In both structures two types of lithium and phosphorus atoms



Fig. 4 Molecular structure of $[Li_2(\mu-1a)(TMEDA)_2]$ in the crystal. TMEDA carbon atoms are shown as smaller circles without hydrogen atoms for clarity.



Fig. 5 Molecular structure of $[Li_2(\mu\text{-}1b)(TMEDA)_2]$ in the crystal. The asymmetric unit contains two independent molecules, one of which exhibits a disorder in a TMEDA unit. Only the non-disordered molecule is shown. TMEDA carbon atoms are shown as smaller circles without hydrogen atoms for clarity.



Fig. 6 Molecular structure of $[Li_2(\mu-1d)(TMEDA)]_2$ in the crystal. TMEDA and neopentyl carbon atoms are shown as smaller circles without hydrogen atoms for clarity. The Li…Fe contact of 2.610(6) Å is indicated by a broken line.

are each present, which differ in their number of Li–P bonds (either two or three). Each lithium atom bonded to only two phosphorus atoms is additionally coordinated by a donor molecule. In the case of $[\text{Li}_2(\mu_3\text{-Pt-Bu}_2)(\mu_2\text{-Pt-Bu}_2)(\text{THF})]_2$, all lithium atoms are in a tricoordinate bonding environment

Table 3 Selected bond lengths (Å) and angles (°) for the lithium diphosphide TMEDA adducts derived from H_21a, H_21b and H_21d

	Average Li-P	Li-P-Li	P-Li-P	C-P-C
$[Li_2(\mu-1a)(TMEDA)_2]$	2.59	89.3(2) 88.8(2)	82.0(2) 82.1(2)	103.7(2) 101.7(2)
$[\mathrm{Li}_2(\mu\text{-}\mathbf{1b})(\mathrm{TMEDA})_2]$	2.57	88.8(3) 88.8(3)	84.2(3) 83.5(3)	98.9(3) 99.8(3)
$[\mathrm{Li}_2(\mu\text{-}\mathbf{1d})(\mathrm{TMEDA})]_2$	2.49^{a} 2.59^{b}	$84.4(2)^{c}$ $80.3(2)^{d}$	$99.0(2)^a$ 117.8(2) ^a	103.5(2) 98.3(2)
		$62.2(2)^d$ $132.4(2)^d$	$125.8(2)^a$ 94.3(2) ^b	
^{<i>a</i>} Tricoordinate Li ato	ms. ^b Tetracoord	linate Li atoi	ns. ^c u ₂ -P. ^d u	ı₂-P.

(either P_3 or P_2O), because THF is a monodentate donor. In the case of $[Li_2(\mu-1d)(TMEDA)]_2$, the bidentate donor TMEDA causes a four-coordinate P2N2 environment for two of the lithium atoms, while the other two are in a tricoordinate P₃ environment. Due to crystallographically imposed inversion symmetry (molecular point group C_i), the central Li₂P₂ ring of $[Li_2(\mu-1d)(TMEDA)]_2$ is exactly planar, whereas the outer Li_2P_2 rings each exhibit a dihedral angle between the two Li₂P planes of 14.1°. On average, the Li-P distances of the tricoordinate lithium atoms are 0.1 Å shorter than those of the fourcoordinate ones, which is in accord with previous observations.25 Each tricoordinate lithium atom exhibits an additional short contact to the iron atom of its fcP2 unit. The Li-Fe distance of 2.610(6) Å is almost identical with the sum of the covalent radii (Li 1.28 Å, low-spin Fe 1.32 Å).39 We have observed a similarly short Li…Fe contact of 2.62 Å for the closely related ferrocene-based lithium amide [Li₂fc(NMes)₂], where we came to the conclusion that the proximity of the two metal atoms very likely does not reflect intermetallic bonding, but is primarily due to steric effects.⁴⁰ In contrast to [Li₂(µ-1a) $(TMEDA)_2$ and $[Li_2(\mu-1b)(TMEDA)_2]$, the N-substituents of each fc(PR)₂ moiety are in a cis orientation in the case of $[Li_2(\mu-1d)(TMEDA)]_2$. Steric repulsion between these neopentyl groups is indicated by a cyclopentadienyl ring tilt angle of 11.1°, which is significantly larger than the corresponding angles of 4.1° and 1.6° determined for $[Li_2(\mu-1a)(TMEDA)_2]$ and $[Li_2(\mu-1b)(TMEDA)_2]$, respectively. We surmise that in the case of $[Li_4(1c)_2(TMEDA)_3]$ the small methyl groups allow the coordination of an additional TMEDA ligand, which probably bridges the two lithium atoms that are in a P₃ environment (Scheme 2).

Reaction of the diphosphines with $Zr(NMe_2)_4$

In our work with the secondary diamines $fc(NHPh)_2$ and $fc(NHTipp)_2$ (Tipp = 2,4,6-triisopropylphenyl) we found that these compounds cleanly react with $Zr(NMe_2)_4$ at room temperature, respectively affording $[Zr{fc(NPh)_2}(NMe_2)_2(NHMe_2)]$ and $[Zr{fc(NTipp)_2}(NMe_2)_2]$.^{1g,j} Phosphines are generally more acidic than the corresponding amines.⁴¹ We therefore expected an analogous Brønsted metathesis reaction for the secondary diphosphines of the type H₂1, similar to that reported by Winston and Bercaw for the bis(diarylphosphine) py[o $C_6H_4(PHPh)]_2$ (py = pyridine-2,6-diyl), which furnished the PNP pincer complex [$Zr{py[o-C_6H_4(PPh)]_2-\kappa^3N,P,P'}(NMe_2)_2$].⁴² Indeed, the two aryl-substituted congeners H_21a and H_21e each reacted smoothly and swiftly with $Zr(NMe_2)_4$ under mild conditions (room temperature, 1 h), respectively affording [${Zr(NMe_2)_3}_2(\mu-1a)$] and [${Zr(NMe_2)_3}_2(\mu-1e)$] (Scheme 3).

The yield was quantitative, when two equivalents of Zr(NMe₂)₄ were used. In contrast, the alkyl-substituted compounds H₂1b-H₂1d turned out to be inert even under rather forcing conditions (toluene- d_8 , 100 °C, several days), which is in line with an analogous observation reported by Hayes and co-workers for the bis(dialkylphosphine) m-C₆H₄(CH₂PHt- Bu_{2}^{30a} Very likely, the acidity of the secondary phosphines is not sufficient in the alkyl-substituted cases for a Brønsted metathesis with $Zr(NMe_2)_4$. $[{Zr(NMe_2)_3}_2(\mu-1a)]$ and $[{Zr(NMe_2)_3}_2(\mu-1e)]$ each exhibit a fairly broad singlet in the ³¹P NMR spectrum, respectively located at -32.8 and -30.9 ppm. These values correspond to a low-field shift of ca. 30 ppm in comparison to the corresponding diphosphine, which is similar to the effect observed by Winston and Bercaw upon going from $py[o-C_6H_4(PHPh)]_2$ to $[Zr{py[o-C_6H_4(PPh)]_2}]_2$ $\kappa^{3}N, P, P'$ (NMe₂)₂ ($\Delta \delta \approx 44 \text{ ppm}$).⁴²

Single-crystal XRD studies were performed for $[{Zr(NMe_2)_3}_2(\mu-1a)]$ and $[{Zr(NMe_2)_3}_2(\mu-1e)]$, which revealed that, similar to $[Zr{py[o-C_6H_4(PPh)]}(NMe_2)_2]$,⁴² the zirconium atoms are in a five-coordinate P_2N_3 bonding environment in these compounds (Fig. 7 and 8). Pertinent metric parameters are collected in Table 4.

The zirconium and phosphorus atoms in $[{Zr(NMe_2)_3}_2(\mu-1a)]$ and $[{Zr(NMe_2)_3}_2(\mu-1f)]$ form a four-membered ring, which is not planar. The dihedral angle between the two Zr₂P planes is 57.9° and 58.5° for the two independent molecules of the former and 58.4° for the latter compound. The deviation from planarity is more pronounced than in the case of the lithium diphosphides, where a dihedral angle of at most 45.9° was observed (see above). The zirconium coordination environment in $[{Zr(NMe_2)_3}_2(\mu-1a)]$ and $[{Zr(NMe_2)_3}_2(\mu-1f)]$ may be described as distorted trigonal bipyramidal. In each case, the axial positions are occupied by one amido and one phosphido ligand and both zirconium atoms share the same phosphorus atom in axial position. The corresponding Naxial-Zr-Paxial bond angles deviate strongly from linearity (ca. 150°). The Zr-N and Zr-P bond lengths each vary only marginally, and the same holds true for the P-Zr-P and Zr-P-Zr bond angles. The difference between the average Zr-N and Zr-P bond lengths is



Scheme 3 Reaction of H₂1a and H₂1e with $Zr(NMe_2)_4$. Reagents and conditions: (a) $Zr(NMe_2)_4$, THF (for a) or toluene (for e), room temperature.

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Fig. 7 Molecular structure of $[{Zr(NMe_2)_3}_2(\mu-1a)]$ in the crystal. Only one of the two independent molecules present in the asymmetric unit is shown. Methyl carbon atoms are shown as smaller circles without hydrogen atoms for clarity.

0.78 Å, which is much larger than the covalent radii difference of nitrogen and phosphorus ($\Delta d_{\rm cov}$ 0.36 Å).³⁹ In conjunction with the trigonal planar bonding environment of the nitrogen atoms, this indicates partial double bond character for the zirconium-nitrogen bonds due to a significant degree of π -bonding. Each phosphorus atom in [{Zr(NMe₂)₃}₂(μ -1a)] and $[{Zr(NMe_2)_3}_2(\mu-1e)]$ bridges two zirconium atoms and is tetracoordinate. Consequently, the average Zr-P bond length of 2.83 Å is significantly longer than that of Bercaw's pincer complex $[Zr{py[o-C_6H_4(PPh)]_2-\kappa^3N, P, P'}(NMe_2)_2]$ (2.69 Å), which contains tricoordinate phosphorus atoms. In fact, the Zr-P_{phosphido} bond lengths in our complexes are essentially identical to the Zr-Pphosphine bond length of 2.824(1) Å reported by Ballmann and co-workers for the trisamidophosphine complex $[Zr{P[o-C_6H_4(CH_2NXyl)]_3-\kappa^4N, N', N'', P}(NMe_2)]$ (Xyl = 3.5-dimethylphenyl).⁴³

Reaction of the diphosphines with nickelocene

According to sporadic reports in the literature, secondary phosphines may undergo Brønsted metathesis reactions with nickelocene, which prompted us to investigate compounds H_2 **1a**- H_2 **1e** in this context. For example, Stone and co-workers described the reaction between the rather acidic bis(trifluoro-methyl)phosphine⁴⁴ and nickelocene, which afforded the phosphide-bridged dimeric complex [NiCp{ μ -P(CF₃)₂]₂.⁴⁵



Fig. 8 Molecular structure of $[{Zr(NMe_2)_3}_2(\mu-1e)]$ in the crystal. Methyl carbon atoms are shown as smaller circles without hydrogen atoms for clarity.

Interestingly, an analogous reaction was reported by Heinicke and Jux for the secondary 2-phosphinophenol HPAr^{OH}Et $(Ar^{OH} = 2 - OH - 3 - MeC_6H_3)$, leading to $[NiCp(\mu - PAr^{OH}Et)]_2$.⁴⁶ The Brønsted acidity of this secondary (alkyl)(aryl)phosphine is certainly lower than that of the phenolic OH group present in the Ar^{OH} group. Nevertheless, the reaction with nickelocene leads to the phosphido, and not to the phenolato, complex. We note in this context that phenolato complexes of the type $[NiCp(\mu-OAr)]_2$ are not unprecedented even for bulky cyclopentadienyl and aryl groups.⁴⁷ The preference for the formation of the phosphido complex may be rationalised in terms of Pearson's HSAB principle.48 Complexes of the type [NiCp(µ-PR₂)]₂ are surprisingly scarce, and only two structurally characterised example have been reported to date, namely $[NiCp(\mu-PPh_2)]_2^{49}$ (obtained from the reaction of Ph₂P-PPh₂ and $[NiCp(\mu-CO)]_2$ in boiling toluene)⁵⁰ and [NiCp $(\mu$ -PMeMes)]₂ (prepared from $[NiCp(\mu$ -HPMes)]₂ by a repetitive lithiation/methylation sequence using *n*-BuLi and MeI).⁵¹

All five compounds H_21a-H_21e showed a reaction with nickelocene, which was monitored by ³¹P NMR spectroscopy. In the case of the methyl congener H_21c and the 3,5-bis(trifluoromethyl)phenyl congener H_21e , only intractable mixtures of numerous products were obtained, which resisted further ana-

	Average Zr–N	Average Zr-P	P–Zr–P	Zr-P-Zr	C-P-C
$[\{\operatorname{Zr}(\operatorname{NMe}_2)_3\}_2(\mu\text{-}\mathbf{1a})]^a$	2.05	2.82	66.12(2)	103.35(3)	105.9(1)
			65.92(2)	102.68(3)	103.5(1)
	2.05	2.84	65.04(2)	103.89(3)	101.8(2)
			65.28(2)	103.67(3)	100.8(1)
$[\{Zr(NMe_2)_3\}_2(\mu\text{-}\mathbf{1e})]$	2.05	2.83	64.96(7)	104.87(8)	101.3(4)
			64.50(7)	103.81(8)	103.7(4)
^a Two independent molecul	es		64.50(7)	103.81(8)	

Table 4Selected bond lengths (Å) and angles (°) for the zirconium chelates of the type $[{Zr(NMe_2)_3}_2(\mu-1)]$

lysis. The formation of insoluble material and the observation of increasingly broad ³¹P NMR signals during the course of these reactions suggest the formation of oligomeric or polymeric and/or paramagnetic species. In contrast, the *tert*-butyl substituted congener H_2 **1b** was particularly well-behaved in this context (Scheme 4).

Its reaction with two equivalents of nickelocene in THF for two days cleanly afforded the expected bis(diorganophosphido) chelate $[(NiCp)_2(\mu-1b)]$ in 83% isolated yield. The phosphorus atoms in this compound are equivalent and give rise to a singlet in the ³¹P NMR spectrum (δ –47.4 ppm in C₆D₆ solution). ³¹P NMR spectroscopy revealed the presence of a single intermediate during this reaction, which was assumed to be the phosphino-phosphido chelate [NiCp(H1b)] due to the presence of characteristic signals in the ³¹P NMR spectrum, located at 69.8 (dd, ${}^{1}J_{PH}$ = 365 Hz, ${}^{2}J_{PP}$ = 89 Hz) and 63.0 ppm (d, ${}^{2}J_{PP}$ = 89 Hz) for the phosphino and the phosphido P atom, respectively.52 Our hypothesis could be verified by the preparation of [NiCp(H1b)] through a rational synthesis. This compound was afforded in 76% isolated yield by the reaction of H₂1b with only one equivalent of nickelocene at room temperature. According to a ³¹P NMR spectroscopic analysis, the neopentyl congener H21d also reacts with nickelocene in a two-stepped manner, leading to [(NiCp)₂(µ-1d)] via [NiCp (H1d)] in an almost quantitative process (90% isolated yield). The ³¹P NMR spectroscopic signatures of these two complexes are analogous to those of the respective tert-butyl congener. A singlet is observed in the ³¹P NMR spectrum (δ –109.2 ppm in C_6D_6 solution) of [(NiCp)₂(μ -1d)] due to the equivalent phosphorus atoms. The presence of a phosphino P atom in [NiCp



Scheme 4 Reaction of H₂1a, H₂1b and H₂1d with nickelocene. Reagents and conditions: (a) Nickelocene, THF, room temperature. [NiCp(H1a)] is plausibly assumed as an intermediate in the reaction affording [(NiCp)₂(μ -1a)].

(H1d)] is revealed by a doublet located at -3.2 ppm (${}^{1}J_{PH} = 283$ Hz), which collapses to a singlet in the ${}^{31}P{}^{1}H$ NMR spectrum. The phosphido P atom causes a singlet at -12.3 ppm. In contrast to the tert-butyl congener [NiCp(H1b)], no coupling is observed between the two inequivalent phosphorus atoms. The reaction of H₂1d with one equivalent of nickelocene was less specific than that of H₂1b and afforded mixtures of unreacted starting material, [(NiCp)₂(µ-1d)] and [NiCp(H1d)], whose similar solubilities severely hampered purification of the latter compound by recrystallization. Regrettably, therefore, [NiCp(H1d)] could not be obtained in pure form. The reaction of the phenyl congener H₂1a with two equivalents of nickelocene in THF for two days afforded $[(NiCp)_2(\mu-1a)]$ in 84% isolated yield. In this case, several intermediates are involved according to the results of our ³¹P NMR spectroscopic monitoring of the reaction. It has not been possible to elucidate their nature.

The bis(diorganophosphido) chelates $[(NiCp)_2(\mu-1a)]$ and $[(NiCp)_2(\mu-1b)]$ were structurally characterised by XRD (Fig. 9 and 10). The structure of the phosphino–phosphido complex [NiCp(H1b)] was also determined (Fig. 11). We have not been



Fig. 9 Molecular structure of [(NiCp)₂(μ-1a)] in the crystal.



Fig. 10 Molecular structure of [(NiCp)₂(μ -1b)] in the co-crystal with [Ni(μ_2 -OH){NiCp(μ_2 -1b)}]₂.



Fig. 11 Molecular structure of [NiCp(H1b)] in the crystal.

able to grow suitable single crystals of $[(NiCp)_2(\mu-1b)]$, despite many attempts. Finally, a co-crystal composed of a 1:1 mixture of $[(NiCp)_2(\mu-1b)]$ and $[Ni(\mu_2-OH)\{NiCp(\mu_2-1b)\}]_2$ (see Fig. S1 in the ESI[‡]) was serendipitously obtained, which was used for the structural study. The hydroxido complex was probably formed from $[(NiCp)_2(\mu-1b)]$ and adventitious moisture during our numerous crystallisation experiments, which in addition furnished a single crystal of a further unexpected compound, namely $[\{Ni[NiCp(\mu_2-1b)]\}_2 \{\mu_2-\eta^5;\eta^5-(C_5H_4)_2\}]$ (see Fig. S2 in the ESI[‡]). From a formal point of view, this unusual fulvalenide-bridged complex⁵³ is the result of an oxidative coupling of $[(NiCp)_2(\mu-1b)]$. In the same vein, our crystallisation experiments with $[(NiCp)_2(\mu-1a)]$ and [NiCp(H1b)] respectively afforded single crystals of $[Ni{\mu-[NiCp(\mu-1a)]}_2]$ and $[Ni (H1b)_2]$ (see Fig. S3 and S4 in the ESI[‡]) by serendipity. We refrain from speculating about the formation pathway of these unexpected complexes. Table 5 contains pertinent metric parameters of the nickel complexes of this study which were obtained by rational synthesis (see Table S2 in the ESI[‡] for the other nickel complexes).

The nickel complexes which contain bridging bis(diorganophosphido) ligands exhibit four-membered Ni₂P₂ rings, which are not planar. The dihedral angles between the two Ni₂P planes range from 43.6° for $[(NiCp)_2(\mu-1a)]$ to 56.6° for $[Ni{[NiCp(\mu_2-1a)]}_2]$, which is in between the corresponding Li_2P (41.5 and 45.9°) and Zr_2P dihedral angles (ca. 58°) observed in this study (see above). We note that the Ni_2P_2 core of [NiCp(µ-PPh₂)]₂ is perfectly planar (dihedral angle 0°),⁴⁹ whereas that of [NiCp(µ-PMeMes)]₂ exhibits a large dihedral angle of 60.1° for the Ni₂P planes.⁵¹ The structurally characterised nickel complexes of our study have rather similar Ni-P bond lengths. These range from 2.1426(7) Å in $[(NiCp)_2(\mu-1a)]$ to 2.220(4) Å in $[Ni{[NiCp(\mu_2-1a)]}_2]$ and thus compare well with values reported for closely related nickel(II) compounds such as, for example, the bis(diorganophosphine) complexes $[NiX_2(HPCy_2)_2]$ (X = Cl, Br, Cy = cyclohexyl),⁵⁴ the phosphinophosphido complex [NiCp{HP(SiFTipp2)}(PPh3)]55 and the bis(diorganophosphido) complexes $[NiCp(\mu-PPh_2)]_2^{49}$ and $[NiCp(\mu-PMeMes)]_2$.⁵¹ We note that the Ni–P bond lengths of 2.1446(6) Å determined for the homoleptic nickel(0) diorganophosphine complex $[Ni(HPPh_2)_4]$ also lie in this range.⁵⁶ If the Cp ligand is viewed as occupying one coordination site, all complexes except [Ni(H1b)₂] contain three-coordinate nickel atoms. In addition, $[Ni(\mu_2-OH){NiCp(\mu_2-1b)}]_2$ and $[Ni{[NiCp}]$ (μ_2-1a)]₂ also contain four-coordinate ones, which are in a distorted square-planar coordination environment. This is in contrast to the tetrahedral coordination of the nickel atom in $[Ni(H1b)_2]$, a structure associated with paramagnetic behaviour for Ni^{II.57} It is tempting to surmise that the broad ³¹P NMR signals observed in the case of the reactions of H₂1c and H₂1e with nickelocene are at least in part due to paramagnetic species of this type.

	Average Ni-P	Ni-P-Ni	P-Ni-P	С-Р-С
[(NiCp) ₂ (µ-1a)]	2.15	98.29(3) 98.20(3)	75.03(2) 74.64(2)	107.2(1) 105.6(1)
$[(NiCp)_2(\mu-1b)]^a$	2.17	96.93(3)	74.58(3)	101.3(1)
[NiCp(H 1b)] ^b	2.19		85.76(7)	100.2(3) 100.6(3)

^{*a*} Molecular C_{2v} symmetry. ^{*b*} Approximate C_s symmetry of the [Ni(H1b)] fragment, because the phosphino and phosphido P atom could not be distinguished from one another experimentally.

Summary and conclusion

We have investigated 1,1'-ferrocenylene-bridged secondary diphosphines of the type $fc(PHR)_2$ (H₂1) with various P-substituents, ranging from alkyl groups of distinctly different steric bulk (Me < Np < t-Bu) to comparatively electron-withdrawing aryl groups (Ph < XyF). The reaction of these compounds with n-BuLi in the presence of TMEDA cleanly afforded the corresponding lithium diphosphide TMEDA adducts, except in the case of R = XyF, where only intractable material was obtained. Monomeric compounds of the type $[Li_2(\mu-1)(TMEDA)_2]$ with a cyclic non-planar P_2Li_2 core were isolated in the case of R = Ph and t-Bu. In contrast, dimeric aggregates exhibiting a ladder-type Li₄P₄ motif were afforded with primary alkyl substituents Me and Np, the viz. $[\text{Li}_4(\mu-\mathbf{1c})_2(\text{TMEDA})_3]$ and $[\text{Li}_2(\mu-\mathbf{1d})(\text{TMEDA})]_2$. A Brønsted metathesis with $Zr(NMe_2)_4$ was possible only with the arylsubstituted compounds H_2 1a (R = Ph) and H_2 1e (R = XyF), leading to products of the type [$\{Zr(NMe_2)_3\}_2(\mu-1)$]. The inertness of the alkyl-substituted congeners suggests that their acidity is not sufficient for this reaction. All secondary diphosphines of our study underwent a reaction with nickelocene. Intractable mixtures of numerous products were obtained with the methyl congener H₂1c and the 3,5-bis(trifluoromethyl)phenyl congener H_2 1e. In the other cases, compounds of the type $[(NiCp)_2(\mu-1)]$ were isolated. For R = *t*-Bu and Np a two-stepped reaction *via* a phosphino-phosphido intermediate of the type [NiCp(H1)] was observed. The lithium, zirconium and nickel compounds prepared in our study clearly demonstrate the propensity of the diphosphido system 1^{2-} to act as a "bridging chelate ligand", leading to cyclic non-planar M2P2 units. In view of the rather diverse nature of the metals used so far, namely an early and a late transition metal as well as an s-block metal, our results augur well for the development of a rich coordination chemistry with ferrocene-based diphosphido ligands of this type. Our future work will particularly address the functionality of the redox-active ligand backbone, which renders these ligands non-innocent. Note that the exploration of phosphorus-containing redox-active ligands has been mostly confined to metallocene-based phosphines akin to the iconic dppf,⁵⁸ with anionic phosphorus ligands being particularly scarce in this context.^{58a,c} The diphosphido system 1^{2-} represents a promising platform for systematic studies in this direction.

Experimental

General considerations

All reactions were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. PCl(NEt₂)Ph,¹⁹ PCl(NEt₂)*t*-Bu,²⁰ PCl(NEt₂)XyF,²¹ [(fcLi₂)₃(TMEDA)₂]⁵⁹ and fc [PCl(NEt₂)]₂¹⁸ were synthesised by following adapted versions of published procedures. PBr(NEt₂)Np was prepared from di-

ethylamine and PBr₂Np, which was obtained from the reaction of PBr₃ with NpMgBr. NMR spectra were recorded with Varian NMRS-500 and MR-400 spectrometers operating at 499.7 and 399.9 MHz, respectively, for ¹H. Where necessary, signal assignments were made with the help of 2D NMR experiments, in particular HSQC, HMBC and HH-COSY. High-resolution ESI mass spectra were obtained with a micrOTOF time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) using an ApolloTM "ion funnel" ESI source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry, University of Kassel, Germany.

Preparative work

H₂1a

Synthesis of (NEt₂)₂1a. A solution of PCl(NEt₂)Ph (29.40 g, 136.3 mmol) in diethyl ether (60 mL) was added dropwise to a stirred suspension of [(fcLi₂)₃(TMEDA)₂] (18.77 g, 22.7 mmol) in diethyl ether (140 mL) cooled with an ice bath. Stirring was continued at room temperature for 2 d. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (2×40 mL). The filtrate and washings were combined and volatile components removed in vacuo. The residue was triturated with n-hexane (150 mL). Insoluble material was removed by filtration through a Celite pad and washed with *n*-hexane (3 \times 15 mL). The filtrate and washings were combined and volatile components removed in vacuo, leaving (NEt₂)₂1a as a yellow solid. Yield 37.07 g (100%). NMR spectroscopic data are in agreement with those published by Mizuta and co-workers, who obtained this compound via a different route as an orange liquid.18a

Synthesis of Cl_21a . A solution of HCl in diethyl ether (27.2 mL, 5.0 M, 136 mmol) was added dropwise to a stirred solution of (NEt₂)₂1a (18.51 g, 34.0 mmol) in diethyl ether (150 mL) cooled to -80 °C. The cooling bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (5 × 20 mL). The volume of the combined filtrate and washings was reduced to approximately one half *in vacuo*. Storing of the solution at -40 °C afforded Cl₂1a as an orange, microcrystalline solid, which was isolated by filtration and dried *in vacuo*. Yield 7.21 g (45%). NMR spectroscopic data are in agreement with those published by Mizuta and co-workers, who obtained this compound by using PCl₃ instead of HCl in diethyl ether.^{18a}

Synthesis of H_2 **1a** (1:1 mixture of diastereomers). Finely powdered lithium aluminium hydride (1.45 g, 38.2 mmol) was added to a stirred solution of Cl₂**1a** (7.21 g, 15.3 mmol) in THF (100 mL). After 14 h the mixture was cooled with an ice bath and water (2.76 mL, 153.2 mmol) was slowly added dropwise. The ice bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with THF (4 × 20 mL). The filtrate and washings were combined and volatile components removed *in vacuo*. The residue was subjected to purification by column chromatography (silica gel, toluene). Remaining minor impurities were subsequently removed by Soxhlet extraction of the product adsorbed on silica gel with *n*-hexane. Yield 4.02 (65%; 29% over all steps). ¹H NMR (C₆D₆): δ 7.42 (m, 4H, Ph), 7.03 (m, 6H, Ph), 5.15 (d, 2H, PH, ¹J_{PH} = 219 Hz); 4.25, 4.21 (2 m, 2 × 1H, C₅H₄); 4.17–4.01 (m, 6H, C₅H₄). ¹³C{¹H} NMR (C₆D₆): δ 137.4, 133.0, 128.6, 128.2 (4 m, Ph); 76.8, 76.4, 75.9, 75.8, 72.6, 72.4, 70.0, 69.4 (8 m, C₅H₄). ³¹P NMR (C₆D₆): δ –60.8, –61.2 (2 d, ¹J_{PH} = 218 Hz). HRMS/ESI(+): *m*/z 508.9423 [M + Ag]⁺, 508.9441 calc. for [C₂₂H₂₀AgFeP₂]⁺. Calc. for C₂₂H₂₀FeP₂ (402.2): C, 65.7; H, 5.0. Found: C, 66.1; H, 5.4.

$H_2 1b$

Synthesis of $(NEt_2)_2$ **1b**. A solution of PCl(NEt_2)*t*-Bu (10.91 g, 55.8 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of $[(fcLi_2)_3(TMEDA)_2]$ (7.68 g, 9.3 mmol) in diethyl ether (150 mL) cooled with an ice bath. Stirring was continued at room temperature for 2 d. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (4 × 15 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, leaving (NEt₂)₂**1b** as an amorphous orange solid that was sufficiently pure for the next step. Yield 14.07 g (100%). NMR spectroscopic data are in agreement with those published by Mizuta and co-workers, who obtained this compound *via* a different route as a dark orange liquid.^{18a}

Synthesis of Cl_2 **1b**. A solution of HCl in diethyl ether (22.2 mL, 5.0 M, 111 mmol) was added dropwise to a stirred solution of $(NEt_2)_2$ **1b** (14.07 g, 27.9 mmol) in diethyl ether (150 mL) cooled to -80 °C. The cooling bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (5 × 20 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, affording Cl₂**1b** as an orange, microcrystalline solid that was sufficiently pure for the next step. Yield 11.21 g (93%). NMR spectroscopic data are in agreement with those published by Mizuta and co-workers, who obtained this compound by using PCl₃ instead of HCl in diethyl ether.^{18a}

Synthesis of H₂1b. Finely powdered lithium aluminium hydride (2.47 g, 65.1 mmol) was added to a stirred solution of Cl₂1b (11.21 g, 26.0 mmol) in THF (250 mL). After 14 h the mixture was cooled with an ice bath and water (4.68 mL, 259.8 mmol) was slowly added dropwise. The ice bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with THF (4 \times 25 mL). The filtrate and washings were combined and volatile components removed in vacuo. The residue was subjected to purification by column chromatography (silica gel, n-hexane). Remaining minor impurities were subsequently removed by triturating the product with cold *n*-hexane (100 mL) and removing insoluble material by filtration. The filtrate was reduced to dryness in vacuo, affording the product as orange crystals. Yield 4.71 g (50%; 47% over all steps). NMR spectroscopic data are in agreement with those published by Pietschnig and co-workers.¹⁷ HRMS/ESI(+): m/z 385.0908 $[M + Na]^+$, 385.0913 calc. for $[C_{18}H_{28}FeNaP_2]^+$. Calc. for $C_{18}H_{28}FeP_2$ (362.2): C, 59.7; H, 7.8. Found: C, 59.7; H, 8.2. **H₂1c**

Synthesis of $(NEt_2)_2 \mathbf{1c}$. A solution of MeLi in diethyl ether (33.1 mL, 1.60 M, 53.0 mmol) was added dropwise to a stirred solution of fc[PCl(NEt₂)]₂ (12.21 g, 26.5 mmol) in diethyl ether (250 mL) cooled to -60 °C. Stirring was continued at room temperature for 14 h. Volatile components were removed in vacuo. The residue was triturated with n-hexane (60 mL). Insoluble material was removed by filtration through a Celite pad and washed with *n*-hexane $(4 \times 15 \text{ mL})$. The filtrate and washings were combined and volatile components removed *in vacuo*, leaving $(NEt_2)_2$ **1c** as an orange oil that was sufficiently pure for the next step. Yield 11.13 g (100%). ¹H NMR (C_6D_6): δ 4.28, 4.16, 4.13, 4.05 (4 br., 4 × 2H, C₅H₄); 2.81 (m, 8H, CH_2CH_3), 1.39 (m, 6H, PMe), 0.87 (t, ${}^{3}J_{HH}$ = 7.0 Hz, 12H, CH_2CH_3). ¹³C{¹H} NMR (C₆D₆): δ 81.2, 75.4, 75.1, 72.1, 70.7, 68.9 (6 m, C₅H₄); 43.5 (m, CH₂CH₃), 15.4 (m, PCH₃), 12.9 (m, CH_2CH_3). ³¹P NMR (C₆D₆): δ 34.2.

Synthesis of $Cl_2\mathbf{1}c$. A solution of HCl in diethyl ether (21.2 mL, 5.0 M, 106 mmol) was added dropwise to a stirred solution of $(NEt_2)_2\mathbf{1}c$ (11.13 g, 26.5 mmol) in diethyl ether (200 mL) cooled to -60 °C. The cooling bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (3 × 15 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, affording $Cl_2\mathbf{1}c$ as an orange oil that was sufficiently pure for the next step. Yield 5.65 g (62%). ¹H NMR (C_6D_6): δ 4.28 (br., 1H, C_5H_4), 4.16 (br., 2H, C_5H_4), 4.04 (br., 1H, C_5H_4), 3.96 (br., 4H, C_5H_4), 1.54 (m, 6H, Me). ¹³C{¹H} NMR (C_6D_6): δ 74.8, 73.5, 72.5, 71.9, 70.0, 69.6 (6 m, C_5H_4); 19.4 (m, Me). ³¹P NMR (C_6D_6): δ 82.0.

Synthesis of H₂1c. Finely powdered lithium aluminium hydride (1.53 g, 40.3 mmol) was added to a stirred solution of Cl₂1c (5.65 g, 26.0 mmol) in THF (100 mL). After 14 h the mixture was cooled with an ice bath and water (2.91 mL, 161.5 mmol) was slowly added dropwise. The ice bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with THF (3 \times 20 mL). The filtrate and washings were combined and volatile components removed in vacuo. The residue was triturated with n-hexane (50 mL). Insoluble material was removed by filtration and washed with *n*-hexane $(2 \times 10 \text{ mL})$. The filtrate and washings were combined and volatile components removed in vacuo, affording the product as an orange oil. Yield 3.47 g (77%; 47% over all steps). ¹H NMR (C₆D₆): δ 4.10 (d, ¹*J*_{PH} = 204 Hz, 2H, PH), 4.09 (m, 8H, C₅H₄), 1.08 (m, 6H, Me). ${}^{13}C{}^{1}H$ NMR (C₆D₆): δ 75.2, 75.1, 74.1, 74.0, 71.9, 71.5 (6 m, C_5H_4); 7.1 (m, Me). ³¹P NMR (C_6D_6): δ –89.9 (d, ${}^{1}J_{PH}$ = 204 Hz). Calc. for C₁₂H₁₆FeP₂ (278.0): C, 51.8; H, 5.8. Found: C, 52.4; H, 5.7.

H_21d

Synthesis of $(NEt_2)_2$ 1d (1:1 mixture of diastereomers). A solution of PBr(NEt₂)Np (13.50 g, 53.1 mmol) in diethyl ether (50 mL) was added dropwise to a stirred suspension of $[(fcLi_2)_3(TMEDA)_2]$ (7.31 g, 8.8 mmol) in diethyl ether (50 mL)

cooled with an ice bath. Stirring was continued at room temperature for 1 d. Volatile components were removed *in vacuo*. The residue was triturated with *n*-hexane (30 mL). Insoluble material was removed by filtration through a Celite pad and washed with *n*-hexane (2 × 10 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, leaving (NEt₂)₂1d as a brownish-orange oil that was sufficiently pure for the next step. Yield 14.09 g (100%). ³¹P NMR (C₆D₆): δ 38.3, 37.0.

Synthesis of $Cl_2 \mathbf{1d}$ (1:1 mixture of diastereomers). A solution of HCl in diethyl ether (32.0 mL, 5.0 M, 160 mmol) was added dropwise to a stirred solution of $(NEt_2)_2 \mathbf{1c}$ (14.09 g, 26.5 mmol) in diethyl ether (100 mL) cooled to -80 °C. The cooling bath was removed and stirring was continued for 14 h. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (3 × 15 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, affording $Cl_2 \mathbf{1d}$ as a yellow solid that was sufficiently pure for the next step. Yield 10.03 g (83%). ³¹P NMR (C₆D₆): δ 89.6, 88.1.

Synthesis of H₂1d. Finely powdered lithium aluminium hydride (2.07 g, 54.5 mmol) was added to a stirred solution of Cl₂1d (10.03 g, 21.8 mmol) in THF (100 mL). After 14 h the mixture was cooled with an ice bath and water (3.93 mL, 218.2 mmol) was slowly added dropwise. The ice bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with THF (4 \times 20 mL). The filtrate and washings were combined and volatile components removed in vacuo. The residue was triturated with n-hexane (50 mL). Insoluble material was removed by filtration and washed with *n*-hexane (2×10 mL). The filtrate and washings were combined and volatile components removed in vacuo, affording the product as an orange oil, which crystallised upon standing. Yield 4.82 g (57%; 47% over all steps). ¹H NMR (C_6D_6): δ 4.23 (m, 2H, C_5H_4), 4.14 (m, 6H, C₅H₄), 4.07 (d, ${}^{1}J_{PH}$ = 208 Hz, 2H, PH); 1.99, 1.48 (2 m, 2 × 2H, CH₂); 0.99 (m, 18H, Me). ${}^{13}C{}^{1}H$ NMR (C₆D₆): δ 75.9, 75.6, 75.4, 75.3, 72.0, 71.7 (6 m, C₅H₄), 40.5 (m, CH₂), 31.2 (m, *C*Me₃), 30.6 (m, Me). ³¹P NMR (C₆D₆): δ -86.8 (d, ¹*J*_{PH} = 208 Hz). HRMS/ESI(+): m/z 413.1232 [M + Na]⁺, 413.1226 calc. for $[C_{20}H_{32}FeNaP_2]^+$. Calc. for $C_{20}H_{32}FeP_2$ (390.3): C, 61.55; H, 8.3. Found: C, 61.4; H, 8.6.

H_21e

Synthesis of $(NEt_2)_2$ **1e** (1:1 mixture of diastereomers). A solution of PCl(NEt₂)XyF (15.53 g, 44.2 mmol) in diethyl ether (40 mL) was added dropwise to a stirred suspension of $[(\text{fcLi}_2)_3(\text{TMEDA})_2]$ (6.08 g, 7.4 mmol) in diethyl ether (50 mL) cooled with an ice bath. Stirring was continued at room temperature for 14 h. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (2 × 15 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, leaving (NEt₂)₂**1e** as an orangebrown solid that was sufficiently pure for the next step. Yield 17.96 g (100%). ¹H NMR (C₆D₆): δ 8.33, 8.18, 7.75 (3 m, 3 × 2H, XyF); 4.49 (m, 1H, C₅H₄); 4.39, 4.29 (2 m, 2 × 2H, C₅H₄); 4.17, 3.88, 3.83 (3 m, 3 × 1H, C₅H₄); 2.78 (m, 8H, CH₂), 0.81 (m,

12H, Me). ¹³C{¹H} NMR (C₆D₆): δ 147.1, 146.7, 131.5, 131.3, 130.8, 124.3, 121.4 (7 m, XyF); 79.0, 78.8, 74.5, 73.7, 72.9, 72.7, 72.2, 71.6, 71.1, 70.2, 69.5 (11 m, C₅H₄) 44.6 (m, CH₂), 14.5 (m, Me). ³¹P NMR (C₆D₆): δ 53.2, 51.7.

Synthesis of Cl_21e (1 : 1 mixture of diastereomers). A solution of HCl in diethyl ether (17.2 mL, 5.0 M, 86 mmol) was added dropwise to a stirred solution of $(NEt_2)_212$ (17.96 g, 22.0 mmol) in diethyl ether (200 mL) cooled to -70 °C. The cooling bath was removed and stirring was continued for 14 h. Insoluble material was removed by filtration through a Celite pad and washed with diethyl ether (4 × 25 mL). The filtrate and washings were combined and volatile components removed *in vacuo*, affording Cl_21e as an orange solid that was sufficiently pure for the next step. Yield 13.82 (84%). ¹H NMR (C_6D_6): δ 8.00 (m, 4H, XyF), 7.68 (s, 2H, XyF); 4.23, 4.08, 4.00 (3 m, 3 × 2H, C_5H_4); 3.85, 3.80 (2 m, 2 × 1H, C_5H_4). ¹³C{¹H} NMR (C_6D_6): δ 143.6, 143.2, 132.1, 131.3, 124.1 (5 m, XyF); 123.5 (q, ¹ $_{JCF}$ = 273 Hz, CF₃); 78.8, 78.5, 74.0, 72.3 (4 m, C_5H_4). ³¹P NMR (C_6D_6): δ 72.8, 72.7.

Synthesis of H_2 **1e** (1:1 mixture of diastereomers). Finely powdered lithium aluminium hydride (1.76 g, 46.5 mmol) was added to a stirred solution of Cl₂1e (13.82 g, 19.6 mmol) in THF (250 mL). After 14 h the mixture was cooled with an ice bath and water (3.35 mL, 186.0 mmol) was slowly added dropwise. The ice bath was removed and stirring was continued for 2 h. Insoluble material was removed by filtration through a Celite pad and washed with THF (3×25 mL). The filtrate and washings were combined and volatile components removed in vacuo. The residue was subjected to purification by column chromatography (silica gel, n-hexane), which afforded the product as an orange, microcrystalline solid. Yield 6.50 g (52%; 44% over all steps). ¹H NMR (C_6D_6): δ 7.68 (m, 4H, XyF), 7.59 (s, 2H, XyF), 4.84 (d, ${}^{1}J_{PH}$ = 223 Hz, 2H, PH); 4.08, 4.05 $(2 \text{ m}, 2 \times 1\text{H}, C_5\text{H}_4)$; 4.00 (m, 4H, C₅H₄); 3.87, 3.84 (2 m, 2 × 1H, C₅H₄). ¹³C{¹H} NMR (C₆D₆): δ 141.8, 141.6, 132.0, 131.7 (4 m, XyF); 123.8 (q, ${}^{1}J_{CF}$ = 273 Hz, CF₃), 121.9 (m, XyF); 77.1, 76.8, 75.5, 75.4, 73.3, 73.1 (6 m, C_5H_4). ³¹P NMR (C_6D_6): δ -61.2, -61.5 (2 d, ¹J_{PH} = 223 Hz). HRMS/ESI(+): *m*/*z* 674.9958 $[M + H]^+$, 674.9963 calc. for $[C_{26}H_{17}F_{12}FeP_2]^+$. Calc. for C₂₆H₁₆F₁₂FeP₂ (674.2): C, 46.3; H, 2.4. Found: C, 46.5; H, 3.0.

 $[Li_2(\mu-1a)(TMEDA)_2]$. A solution of *n*-BuLi in *n*-hexane (0.69 mL, 1.60 M, 1.10 mmol) was added with shaking to a solution of H_2 1a (201 mg, 0.50 mmol) and TMEDA (128 mg, 1.10 mmol) in a mixture of toluene (21 mL) and n-hexane (7 mL). The volume of the mixture was reduced to ca. 5 mL in vacuo, affording the product as orange-red crystals, which were isolated by filtration and dried in vacuo. Yield 259 mg (80%). ¹H NMR (THF- d_8): δ 6.96, 6.59 (2 br., 2 × 4H, P); 6.23 (br., 2H, Ph); 4.01, 3.84 (2 br., $2 \times 4H$, C_5H_4), 2.30 (br., 8H, CH₂), 2.15 (br., 24H, Me). ¹H NMR (C₆D₆): δ 7.33 (br., 4H, Ph), 7.10 (m, 4H, Ph), 6.77 (m, 2H, Ph), 4.45 (s, 4H, C₅H₄), 4.27 (s, 4H, C₅H₄), 2.12 (s, 24H, Me), 1.75 (br., 8H, CH₂). ¹³C{¹H} NMR (THF- d_8): δ 163.2, 127.6, 126.8, 116.4 (4 br., Ph); 85.0, 78.9, 68.6 (3 br., C_5H_4); 58.9 (CH₂), 46.3 (Me). ¹³C{¹H} NMR (C_6D_6): δ 127.6, 127.3 (2 m, Ph); 118.7 (Ph), 79.7 (br., C₅H₄), 78.7 (m, C₅H₄), 69.9 (C₅H₄), 57.0 (br., CH₂), 46.8 (Me). ³¹P NMR

(THF- d_8): δ –62.0 (br.). ³¹P NMR (C₆D₆): δ –66.9 (br.). ⁷Li NMR (THF- d_8): δ 2.9 (br.). ⁷Li NMR (C₆D₆): δ 2.4 (br.). Calc. for C₃₄H₅₀N₄FeLi₂P₂ (646.5): C, 63.2; H, 7.8; N, 8.7. Found: C, 63.7; H, 8.2; N, 6.4. Although the result for nitrogen is outside the range viewed as establishing analytical purity, these data are provided to illustrate the best values obtained to date. The data suggest partial loss of TMEDA and agree more with [Li₂(µ-1a)(TMEDA)_{1.5}] [calc. for C₃₁H₄₂N₃FeLi₂P₂ (588.4): C, 63.3; H, 7.2; N, 7.1].

 $[Li_2(\mu-1b)(TMEDA)_2]$. A solution of *n*-BuLi in *n*-hexane (0.39 mL, 1.60 M, 0.62 mmol) was added with shaking to a solution of H₂1b (101 mg, 0.28 mmol) and TMEDA (73 mg, 0.63 mmol) in n-hexane (10 mL). Orange-red crystals of the product formed almost immediately, which were isolated by filtration and dried in vacuo. Yield 131 mg (79%). ¹H NMR (THF- d_8): δ 3.90, 3.78 (2 m, 2 × 4H, C₅H₄); 2.31 (m, 8H, CH₂), 2.16 (m, 24H, NMe₂), 1.02 (m, 18H, CMe₃). ¹H NMR (C₆D₆): δ 4.36, 4.17 (2 s, 2 × 4H, C₅H₄), 2.27 (s, 24H, NMe₂), 1.95 (s, 8H, CH₂), 1.44 (s, 18H, CMe₃). ¹³C{¹H} NMR (THF- d_8): δ 83.1, 80.8 (2 m, C₅H₄); 68.2 (C₅H₄), 58.9 (CH₂), 46.3 (NMe₂), 35.5 (t, $^{2}J_{PC}$ = 7 Hz, CMe₃), 28.7 (m, CMe₃). $^{13}C{^{1}H}$ NMR (C₆D₆): δ 82.3 (m, C₅H₄); 80.6, 68.7 (2 s, C₅H₄); 57.4 (CH₂), 47.7 (NMe₂), 35.8 (m, CMe₃), 29.1 (br., CMe₃). ³¹P NMR (THF- d_8): δ –26.6 (br.). ³¹P NMR (C₆D₆): δ –26.9 (sept, ¹J_{PLi} = 51 Hz). ⁷Li NMR (THF- d_8): δ 4.0 (br.). ⁷Li NMR (C₆D₆): δ 1.9 (t, ¹ J_{PLi} = 51 Hz). Calc. for C30H58N4FeLi2P2 (606.5): C, 59.4; H, 9.6; N, 9.2. Found: C, 59.5; H, 9.5; N, 6.8. Although the result for nitrogen is outside the range viewed as establishing analytical purity, these data are provided to illustrate the best values obtained to date. The data suggest partial loss of TMEDA and agree more with $[Li_2(\mu-1b)(TMEDA)_{1.5}]$ [calc. for $C_{27}H_{50}N_3FeLi_2P_2$ (548.4): C, 59.1; H, 9.2; N, 7.7].

 $[Li_4(\mu-1c)_2(TMEDA)_3]$. A solution of *n*-BuLi in *n*-hexane (0.74 mL, 1.60 M, 1.18 mmol) was added with shaking to a solution of H₂1c (150 mg, 0.54 mmol) and TMEDA (137 mg, 1.18 mmol) in n-hexane (10 mL). The product precipitated almost immediately as an amorphous red solid, which was isolated by filtration and dried *in vacuo*. Yield 190 mg (76%). ¹H NMR (THF- d_8): δ 3.69, 3.50 (2 s, 2 × 8H, C₅H₄); 2.29 (s, 12H, CH₂), 2.15 (s, 36H, NMe₂), 1.35 (s, 12H, PMe). ¹³C{¹H} NMR (THF-d₈): δ 69.7, 68.2, 64.8 (3 m, C₅H₄); 58.9 (CH₂), 46.3 (NMe₂), 6.6 (m, CH₃). ³¹P NMR (THF- d_8): δ -125.7 (br.). ⁷Li NMR (THF- d_8): δ 11.3, 6.2 (2 × br.). Calc. for C₄₂H₇₆N₆Fe₂Li₄P₄ (928.4): C, 54.3; H, 8.25; N, 9.05. Found: C, 53.7; H, 8.7; N, 6.65. Although the result for nitrogen is outside the range viewed as establishing analytical purity, these data are provided to illustrate the best values obtained to date. The data suggest partial loss of TMEDA and agree more with $[Li_2(\mu-1c)]$ (TMEDA)] [calc. for C₁₈H₃₀N₂FeLi₂P₂ (406.1): C, 53.2; H, 7.4; N, 6.9].

[Li₂(μ -1d)(TMEDA)]₂. A solution of *n*-BuLi in *n*-hexane (0.80 mL, 1.60 M, 1.28 mmol) was added with shaking to a solution of H₂1d (200 mg, 0.51 mmol) and TMEDA (149 mg, 1.28 mmol) in *n*-hexane (10 mL). Orange-red crystals of the product formed almost immediately, which were isolated by filtration and dried *in vacuo*. Yield 187 mg (71%). ¹H NMR

(THF- d_8): δ 3.78, 3.74 (2 s, 2 × 4H, C₅H₄), 2.32 (s, 4H, C H_2 NMe₂), 2.17 (s, 12H, NMe₂), 1.82 (s, 4H, C H_2 CMe₃), 0.86 (s, 18H, CMe₃). ¹³C{¹H} NMR (THF- d_8): δ 75.9 (br., C₅H₄), 69.7 (m, C₅H₄), 66.8 (C₅H₄), 58.8 (CH₂NMe₂), 46.3 (s, NMe₂), 43.5 (m, CH₂CMe₃), 33.5 (br., CMe₃), 31.3 (CMe₃). ³¹P NMR (THF- d_8): δ –118.9 (br.). ⁷Li NMR (THF- d_8): δ 3.4 (br., sh.). Calc. for C₅₂H₉₂N₄Fe₂Li₄P₄ (1036.7): C, 60.25; H, 8.95; N, 5.4. Found: C, 60.3; H, 9.3; N, 5.5.

[{**Zr**(**NMe**₂)₃}₂(**μ**-1**a**)]. THF (20 mL) was added to H₂1**a** (302 mg, 0.75 mmol) and Zr(NMe₂)₄ (399 mg, 1.49 mmol). The mixture was stirred for 1 h. Volatile components were removed *in vacuo*, leaving the product as a yellow, microcrystalline solid. Yield 632 mg (100%). ¹H NMR (C₆D₆): δ 7.40, 7.12, 6.96 (3 m, 10H, Ph); 4.42, 4.31 (2 s, 2 × 4H, C₅H₄): 3.00 (s, 36H, Me). ¹³C {¹H} NMR (C₆D₆): δ 145.1, 133.0, 130.7 (3 m, Ph); 125.1 (Ph); 78.5, 73.0, 68.0 (3 m, C₅H₄); 43.1 (m, Me). ³¹P NMR (C₆D₆): δ -32.8 (br.). C₃₄H₅₄N₆FeP₂Zr₂ (847.1): C, 48.2; H, 6.4; N, 9.9. Found: C, 48.0; H, 6.7; N, 9.0.

[{**Zr**(**NMe**₂)₃}₂(**μ**-1e)]. Toluene (15 mL) was added to H₂1e (297 mg, 0.44 mmol) and Zr(NMe₂)₄ (235 mg, 0.88 mmol). The mixture was stirred for 1 h. Volatile components were removed *in vacuo*, leaving the product as a yellow, microcrystalline solid. Yield 492 mg (100%). ¹H NMR (C₆D₆): δ 7.87 (br. s, 4H, XyF), 7.58 (s, 2H, XyF); 4.25, 4.17 (2 s, 2 × 4H, C₅H₄); 2.84 (s, 36H, Me). ¹³C{¹H} NMR (C₆D₆): δ 150.3, 131.0, 130.1 (3 m, XyF); 124.3 (q, ¹J_{CF} = 273 Hz, CF₃), 118.7 (m, XyF); 78.2, 74.0, 65.4 (3 m, C₅H₄); 42.5 (br., Me). ³¹P NMR (C₆D₆): δ -30.9 (br.). C₃₈H₅₀N₆F₁₂FeP₂Zr₂ (1119.1): C, 40.8; H, 4.5; N, 7.5. Found: C, 39.9; H, 4.8; N, 6.7.

[(NiCp)₂(µ-1a)]. THF (10 mL) was added to H₂1a (302 mg, 0.75 mmol) and nickelocene (282 mg, 1.49 mmol). The mixture was stirred for 2 d. Volatile components were removed *in vacuo*. The residue was triturated with toluene (10 mL). A small amount of insoluble material was removed by filtration through a Celite pad and washed with toluene (2×5 mL). The filtrate and washings were combined and reduced to dryness *in vacuo*, affording the product as a black, microcrystalline solid. Yield 410 mg (84%). ¹H NMR (C₆D₆): δ 7.59 (m, 4H, Ph), 7.00 (m, 6H, Ph), 5.09 (m, 4H, C₅H₄), 4.95 (s, 10H, Cp), 4.28 (m, 4H, C₅H₄). ¹³C{¹H} NMR (C₆D₆): δ 143.3 (br., Ph); 131.1, 127.9 (2 m, Ph); 127.4 (Ph), 89.8 (Cp); 84.4, 80.7 (2 m, C₅H₄); 70.5 (br., C₅H₄). ³¹P NMR (C₆D₆): δ –96.9. HRMS/ESI(+): *m/z* 645.9708 [M]⁺, 645.9723 calc. for [C₃₂H₂₈FeNi₂P₂]⁺. Calc. for C₃₂H₂₈FeNi₂P₂ (647.7): C, 59.3; H, 4.4. Found: C, 59.3; H, 5.15.

[(NiCp)₂(µ-1b)]. THF (10 mL) was added to H₂1b (311 mg, 0.86 mmol) and nickelocene (325 mg, 1.72 mmol). The mixture was stirred for 2 d. Volatile components were removed *in vacuo*. The residue was triturated with *n*-hexane (10 mL). A small amount of insoluble material was removed by filtration through a Celite pad and washed with *n*-hexane (2 × 5 mL). The filtrate and washings were combined and reduced to dryness *in vacuo*, affording the product as a brown, microcrystalline solid. Yield 432 mg (83%). ¹H NMR (C₆D₆): δ 5.31 (s, 10H, Cp); 4.89, 4.14 (2 s, 2 × 4H, C₅H₄), 0.87 (m, 18H, Me). ¹³C {¹H} NMR (C₆D₆): δ 88.9 (Cp); 84.0, 80.1 (2 m, C₅H₄); 70.2 (C₅H₄), 30.1 (*C*Me₃), 28.8 (m, *CMe*₃). ³¹P NMR (C₆D₆): δ -47.4.

HRMS/ESI(+): m/z 606.0323 [M]⁺, 606.0349 calc. for $[C_{28}H_{36}FeNi_2P_2]^+$. Calc. for $C_{28}H_{36}FeNi_2P_2$ (607.8): C, 55.3; H, 6.0. Found: C, 55.45; H, 6.1.

 $[(NiCp)_2(\mu-1d)]$. THF (10 mL) was added to H₂1d (301 mg, 0.77 mmol) and nickelocene (291 mg, 1.54 mmol). The mixture was stirred for 2 d. Volatile components were removed in vacuo. The residue was triturated with n-hexane (10 mL). A small amount of insoluble material was removed by filtration through a Celite pad and washed with *n*-hexane $(2 \times 5 \text{ mL})$. The filtrate and washings were combined and reduced to dryness in vacuo, affording the product as a brown, amorphous solid. Yield 436 mg (90%). ¹H NMR (C_6D_6): δ 5.26 (s, 10H, Cp), 5.04 (br., 4H, C₅H₄), 4.10 (m, 4H, C₅H₄), 1.73 (m, 4H, CH₂), 0.85 (s, 18H, Me). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): δ 90.0 (Cp); 80.2, 69.7, 69.2 (3 m, C₅H₄); 49.9 (m, CH₂), 33.0 (CMe₃), 31.3 (m, CMe₃). ³¹P NMR (C₆D₆): δ -109.2. HRMS/ESI(+): m/z 634.0645 [M]⁺, 634.0662 calc. for $[C_{30}H_{40}FeNi_2P_2]^+$. The compound was reasonably pure according to ¹H NMR spectroscopy (see Fig. S53 in the ESI;[†] the spectrum shows a number of minor impurities in addition to silicon grease, which was contained already in the NMR solvent due to its storage in a stoppered Schlenk flask). Satisfactory microanalytical data could not be obtained.

[NiCp(H1b)]. H₂**1b** (340 mg, 0.94 mmol) and nickelocene (177 mg, 0.94 mmol) were dissolved in diethyl ether (20 mL). Storing of the solution for14 h afforded the product as black needles, which were isolated by filtration and dried *in vacuo*. Yield 346 mg (76%). ¹H NMR (C₆D₆): δ 5.49 (s, 5H, Cp), 4.83 (dd, 1H, PH, ¹*J*_{PH} = 365 Hz, ³*J*_{PH} = 18 Hz); 4.52, 4.29, 4.21, 4.17, 3.90, 3.86 (6 m, 8H, C₅H₄); 1.27, 0.81 (2 d, ³*J*_{PH} = 14.1 Hz, 2 × 9H, Me). ¹³C{¹H} NMR (C₆D₆): δ 87.8 (Cp); 77.8, 77.5, 77.3 (3 m, C₅H₄); 74.6, 73.6, 73.5 (3 s, C₅H₄); 71.4, 71.2, 67.6, 66.6 (4 m, C₅H₄); 30.6 (m, *C*Me₃), 29.5 (m, *C*Me₃), 27.0 (m, *CMe₃*), 26.7 (m, *CMe₃*). ³¹P NMR (C₆D₆): δ 69.8 (dd, PH*t*-Bu, ¹*J*_{PH} = 365 Hz, ²*J*_{PP} = 89 Hz), 63.0 (d, *Pt*-Bu, ²*J*_{PP} = 89 Hz). HRMS/ESI(+): *m*/*z* 485.0734 [M + H]⁺, 485.0760 calc. for [C₂₃H₃₃FeNiP₂]⁺. Calc. for C₂₃H₃₂FeNiP₂ (485.0): C, 57.0; H, 6.65. Found: C, 57.8; H, 7.6.

X-ray crystal structure determinations

For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collections were carried out using Mo-K α radiation (λ = 0.71073 Å) on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector except for $[{Zr(NMe_2)_3}_2(\mu-1e)]$, for which the diffraction experiment was done using a Stoe StadiVari diffractometer equipped with a 200 K Dectris Pilatus detector. The data sets were corrected for absorption (by integration), Lorentz and polarisation effects. The structures were solved by direct methods (SIR 2008)⁶⁰ and refined using alternating cycles of least-squares refinements against F^2 (SHELXL2014/7).⁶¹ For [Li₂(μ -1a) (TMEDA)₂] a disordered solvent molecule was removed from the dataset using the SQUEEZE routine from PLATON.⁶² H atoms were included to the models in calculated positions with the 1.2 fold isotropic displacement parameter of their

bonding partner. Experimental details for each diffraction experiment are given in Table S1 (ESI[‡]). Data for all compounds have been deposited with the Cambridge Crystallographic Database.

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