

# Synthesis and Crystal Structures of the *P,N*-Substituted Ferrocenes [Fe{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-P(S)Ph<sub>2</sub>}( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)] and [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)]

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The *P,N*-substituted ferrocene [Fe{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-P(S)Ph<sub>2</sub>}( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)] was prepared in six steps from the bromo derivative [Fe{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>}( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Br)]. Its reductive desulfurisation with Raney nickel afforded the corresponding phosphino-substituted derivative [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)]. Both compounds have been structurally characterised by single-crystal X-ray diffraction studies.

**Key words:** Crystal Structure, Ferrocene, Phosphine, *P,N*-Ligand, Thiophosphorane

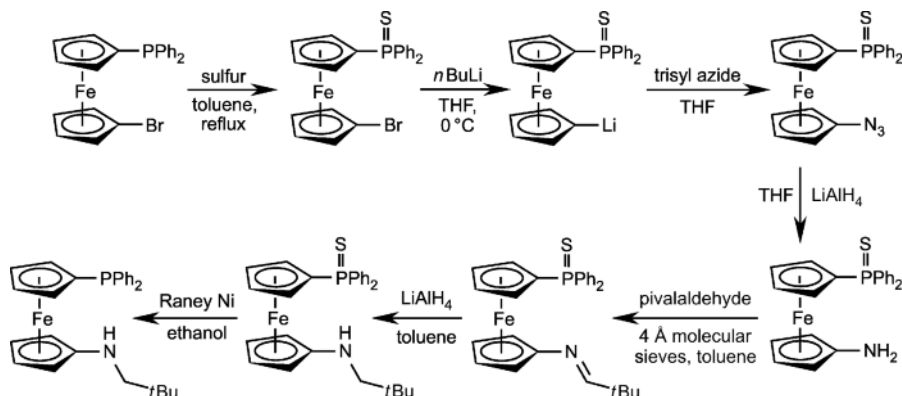
## Introduction

*P,N*-ligands are of great current interest. The combination of a soft *P*-donor site with a borderline to hard *N*-donor site has been utilised for applications in catalysis and supramolecular chemistry [1–7]. We have a long-standing interest in ferrocene-based bidentate ligands with a focus on symmetric *N,N*-ligands which contain a 1,1'-ferrocenylene (fc) backbone [8–18]. We recently expanded our work to related heteroditopic *P,N*-systems, since to date the majority of ferrocene-based *P,N*-ligands does not contain the fc backbone but rather have the *P*- and *N*-donor groups attached to the same cyclopentadienyl ring [19–23]. In this context we have been addressing mainly pyridylphosphine ligands such as, for example, [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-py)] (py = pyrid-2-yl) [24–26], which was found to give rise to seven-membered ring *P,N*-chelates with tetracoordinate metal centres like Zn<sup>II</sup> [25] and Pd<sup>II</sup> [26]. We are currently extending this project to ligands of the type [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NHR)], which contain an amine instead of an imine nitrogen atom. In contrast to the pyridylphosphine ligands just mentioned, the direct attachment of the N atom to the cyclopentadienyl ring is expected to give rise to six-membered ring chelates, which are known to be more stable than

larger chelate rings [27] and can be even more stable than five-membered ring chelates in the case of small metal centres [28]. In addition, the secondary amino group offers the scope for utilising such compounds as monoanionic phosphine-amido (*[P,N]*<sup>−</sup>) ligands of the type [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NR)]<sup>−</sup>. Bi- and oligodentate phosphine-amido ligands are highly popular in transition metal chemistry [29–33]. Simple bidentate *[P,N]*<sup>−</sup> ligands are mostly restricted to the *ortho*-phosphinoaniline system [34–37]. To the best of our knowledge, the only ferrocene-based *[P,N]*<sup>−</sup> ligand known to date is the 1,2-ferrocenylene-bridged [Fe{ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(PPh<sub>2</sub>)(CH<sub>2</sub>NTs)}( $\eta^5$ -Cp)]<sup>−</sup> anion (Ts = *p*-tosyl) recently introduced by Manoury [38].

## Results and Discussion

The obvious precursor for the target system [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NHR)] is [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-NH<sub>2</sub>)]. Butler and co-workers have shown that this amino-substituted ferrocene can be prepared in four steps [39, 40] starting from readily available 1,1'-dibromoferrocene [41, 42]. The crucial step of the “Butler sequence” [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Br)<sub>2</sub>] → [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Li)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Br)] → [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Br)] → [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Li)] → [Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)( $\eta^5$ -



Scheme 1. Synthesis of  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2\text{tBu})]$  (11% yield over all steps).

$\text{C}_5\text{H}_4\text{-NH}_2$ ]) is the final one, which involves the reaction of lithiated diphenylphosphinoferrrocene with *O*-benzylhydroxylamine. The yield reported by Butler is 15% with respect to  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{-Br})]$  [40]. In our hands the yield never exceeded 8%, which we ascribe to the cumbersome purification of the crude product. Consequently, we searched for a more efficient way of introducing the amino group and found that the azide-based sequence shown in Scheme 1 is more satisfactory. We were inspired by work of Gilbertson and Wang, whose synthesis of (dicyclohexylphosphino)serine involved the introduction of an azide group in the presence of a  $\text{PR}_2$  substituent [43]. The use of an organic azide requires protection of the phosphino group of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{-Br})]$  in order to prevent an unwanted Staudinger reaction [44]. This was easily achieved by thiophosphorane formation [45]. The method for electrophilic azide transfer utilising 2,4,6-trisopropylbenzenesulfonyl (trisyl) azide [46] had already been successfully applied in the synthesis of 1,1'-diazidoferrrocene [47]. The first six steps of the reaction sequence shown in Scheme 1 were conveniently telescoped (no work-up for intermediates apart from solvent change and filtration, if necessary), giving rise to  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2\text{tBu})]$  in 12% yield with respect to  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{-Br})]$ . The choice of pivalaldehyde for the condensation reaction with the primary amino group was based on our experience that the neopentyl substituent, which results after subsequent reduction of the imine, is beneficial for the crystallinity and solubility of 1,1'-diaminoferrrocene

derivatives [48–50]. The final reductive desulfurisation was achieved essentially quantitatively with Raney nickel [43, 51].

We have been able to perform single-crystal X-ray structure analyses for  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2\text{tBu})]$  and  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2\text{tBu})]$ . The molecular structures are shown in Figs. 1 and 2.

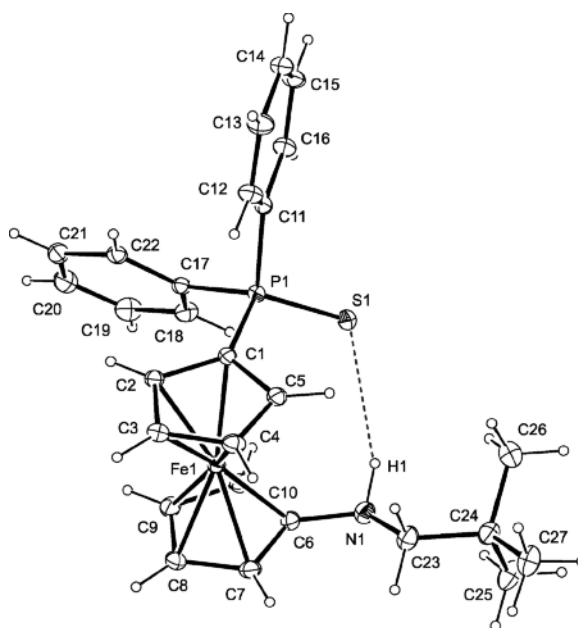


Fig. 1. Molecular structure of  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2\text{tBu})]$  in the crystal. The intramolecular N-H...S contact is indicated by a dotted line.

Table 1. Selected phosphorus bond lengths (Å) and angles (deg) for  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$  and  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$  and two related phosphane/thiophosphorane pairs, with estimated standard deviations in parentheses.

	P–C <sub>ferrocenyl</sub>	P–C <sub>phenyl</sub>	C–P–C <sup>a</sup>	P–S	
$[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$	1.825(4)	1.865(3)	101.2		this work
$[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$	1.783(3)	1.811(3)	105.5	1.9542(13)	this work
$\text{fc}(\text{PPh}_2)_2$	1.819(5)	1.836(4)	102.1		ref. [55]
$\text{fc}[\text{P(S)Ph}_2]_2$	1.796(3)	1.818(3)	105.4	1.938(2)	ref. [56]
		1.815(4)			
	1.794(4)	1.815(3)	105.0	1.944(3)	ref. [57]
		1.825(3)			
$\text{fcBr}(\text{PPh}_2)$	1.813(4)	1.833(4)	101.3		ref. [58]
	1.839(4)				
$\text{fcBr}[\text{P(S)Ph}_2]^b$	1.809(9)	1.806(8)	105.2	1.947(3)	ref. [45]
		1.181(9)			
	1.792(8)	1.815(8)	104.9	1.946(3)	
		1.820(8)			

<sup>a</sup> Average value; <sup>b</sup> two independent molecules.

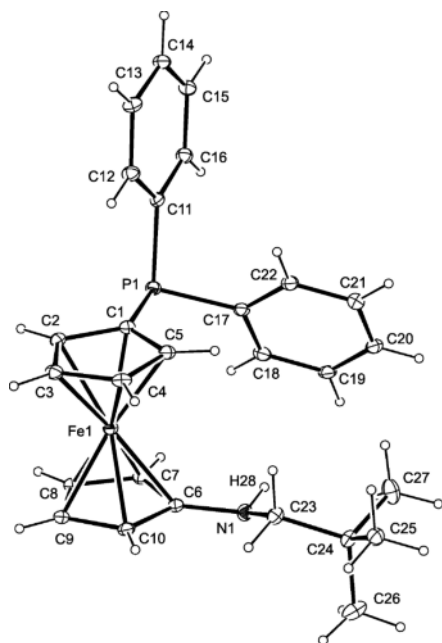


Fig. 2. Molecular structure of  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$  in the crystal.

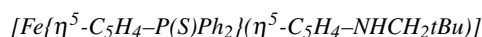
The cyclopentadienyl rings are in an eclipsed synclinal conformation in both cases. An intramolecular N–H⋯S contact is observed for  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$ . The metric param-

eters (H⋯S 2.73 Å, N⋯S 3.64 Å,  $\angle\text{N-H}\cdots\text{S}$  154.7°) are compatible with a weak hydrogen bond [52]. In particular, the H⋯S distance is significantly below the sum of the van der Waals radii of H and S (3.09 Å [53]). Intramolecular N–H⋯S hydrogen bonds involving a thiophosphorane unit have been reported before by Woollins and co-workers for *P*-monodentate complexes of  $\text{Ph}_2\text{PNH-}o\text{-C}_6\text{H}_4\text{-P(S)Ph}_2$  (L) such as, for example  $[\text{IrCl}_2\text{Cp}^*(\kappa\text{P-L})]$  (H⋯S 2.60 Å, N⋯S 3.42 Å,  $\angle\text{N-H}\cdots\text{S}$  142°) [54]. In contrast, the  $\text{NHCH}_2t\text{Bu}$  unit of the  $\text{PPh}_2$  derivative is not involved in hydrogen bond interactions. A comparison of the phosphorus bond lengths and angles of both compounds reveals differences similar to those found for related structurally characterised pairs such as, for example,  $\text{fc}(\text{PPh}_2)_2/\text{fc}[\text{P(S)Ph}_2]_2$  and  $\text{fcBr}(\text{PPh}_2)/\text{fcBr}[\text{P(S)Ph}_2]$  (Table 1), which are due to the different coordination numbers (3 vs. 4, the latter causing larger bond angles) and valencies (3 vs. 5, the latter giving rise to shorter bond lengths) of phosphorus [59–61]. The P–C<sub>phenyl</sub> distances tend to be slightly longer than the corresponding P–C<sub>ferrocenyl</sub> distance, which can be traced back to the higher group electronegativity of phenyl vs. ferrocenyl [62, 63].

## Experimental Section

NMR spectra were recorded with the Varian spectrometers NMRS-500 (500 MHz) and MR-400 (400 MHz). <sup>31</sup>P NMR data were collected by proton-decoupled methods.

Chemical shifts ( $\delta$ ) are given in ppm and are referenced to the signal due to the residual protio impurities of the solvent used relative to tetramethylsilane for  $^1\text{H}$ .  $^{31}\text{P}$  chemical shifts were referenced to external  $\text{Ph}_3\text{PO}$  ( $\delta = 23.7$  ppm) [64]. Coupling constants are given as absolute values in Hz. All preparations involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques or in a conventional argon-filled glove box. Solvents and reagents were appropriately dried and purified by conventional methods and stored under inert gas atmosphere. 1-Bromo-1'-diphenylphosphinoferrocene [65] and trisyl azide [66] were synthesised according to published procedures. Raney nickel was prepared from aluminium-nickel alloy [67].



Sulphur (107 mg, 3.34 mmol) was added to a solution of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{-Br})]$  (1.50 g, 3.34 mmol) in toluene (25 mL). The mixture was refluxed for 2 h and subsequently allowed to cool to room temperature. Volatile com-

ponents were removed *in vacuo*. The remaining solid was dissolved in THF (25 mL) and the solution cooled to  $0^\circ\text{C}$ . A solution of *n*BuLi in hexane (2.10 mL of a 1.60 M solution, 3.36 mmol) was added dropwise with stirring. After 10 min a solution of trisyl azide (1.04 g, 3.36 mmol) in THF (5 mL) was added dropwise with stirring and exclusion of light. After 30 min the solution was allowed to warm to room temperature.  $\text{LiAlH}_4$  powder (256 mg, 6.75 mmol) was added after a further 3 h. Stirring was continued in the dark for 16 h and the reaction quenched by addition of water (0.50 g, 27.8 mmol). Volatile components were removed *in vacuo*. The residue was extracted with toluene ( $3 \times 10$  mL) and the combined extracts filtered through a celite pad, affording a clear solution. Pivalaldehyde (860 mg, 10.0 mmol) was added. The mixture was stirred in the presence of 4 Å molecular sieves (1.0 g), which were removed by filtration (celite pad) after 72 h. A sample of the filtrate (*ca.* 1 mL) was reduced to dryness *in vacuo* and subjected to NMR analysis (*vide infra*), which revealed the clean formation of the imine derivative  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-N=CH}t\text{Bu})]$ .

Table 2. Crystal structure data for  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$  and  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$ .

	$[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-P(S)Ph}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$	$[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{-PPh}_2\}(\eta^5\text{-C}_5\text{H}_4\text{-NHCH}_2t\text{Bu})]$
Crystal colour and shape	orange block	yellow block
Crystal size, mm <sup>3</sup>	0.12 × 0.19 × 0.21	0.15 × 0.13 × 0.22
<i>T</i> (K)	173(2)	100(2)
Empirical formula	$\text{C}_{27}\text{H}_{30}\text{FeNPS}$	$\text{C}_{27}\text{H}_{30}\text{FeNP}$
<i>M<sub>r</sub></i>	487.40	455.34
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
<i>a</i> , Å	11.6971(11)	9.649(3)
<i>b</i> , Å	18.0040(16)	11.143(3)
<i>c</i> , Å	11.9634(11)	11.892(5)
$\alpha$ , deg	90	80.43(3)
$\beta$ , deg	103.655(7)	89.16(3)
$\gamma$ , deg	90	69.69(2)
<i>V</i> , Å <sup>3</sup>	2448.2(4)	1181.2(7)
<i>Z</i>	4	2
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.32	1.28
$\mu$ , mm <sup>-1</sup>	0.8	0.7
<i>F</i> (000), e	1024	480
No. of frames measured	270	174
$\theta$ range, deg	2.09–25.35	1.74–24.75
<i>hkl</i> range	$-14 \leq h \leq 13$ $-21 \leq k \leq 20$ $-13 \leq l \leq 14$	$-10 \leq h \leq 11$ $-12 \leq k \leq 13$ $-13 \leq l \leq 13$
Refl. measd./unique/ <i>R</i> <sub>int</sub>	11 823/4436/0.0282	8755/3969/0.0690
Refl. observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3807	2716
Data/restraints/parameters	4436/0/286	3969/0/278
Final <i>R</i> (obs. refl.)	0.0454	0.0442
Final <i>R<sub>w</sub></i> (all refl.)	0.1231	0.0968
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>-3</sup>	0.52/−0.49	0.38/−0.44

LiAlH<sub>4</sub> powder (637 mg, 16.8 mmol) was added to the solution. The mixture was stirred for 14 h, quenched with water (1.22 g, 67.7 mmol) and filtered through a celite pad, which was subsequently washed with toluene (2 × 5 mL). The filtrate was taken to dryness *in vacuo*. The crude product was purified by column chromatography on neutral alumina. Unpolar impurities (mainly diphenylphosphinoferrrocene) were eluted with *n*-hexane. The product was eluted with *n*-hexane-diethyl ether (1 : 1) as a yellow band. Yield 191 mg (12% over all steps).

Data for [Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-P(S)Ph<sub>2</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-N=CH*t*Bu)]: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.11 (s, 9 H, Me), 4.05, 4.33, 4.45, 4.48 (4 m, 4 × 2 H, cyclopentadienyl CH), 7.41–7.48 (m, 6 H, Ph), 7.69–7.75 (m, 4 H, Ph), 8.01 (s, 1 H, CH*t*Bu). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 26.9, 36.8, 64.4, 68.6, 70.0, 71.8 (d, *J* = 10.1 Hz), 73.6 (d, *J* = 10.1 Hz), 74.1 (d, *J* = 12.5 Hz), 107.2, 129.0, 128.7 (d, *J* = 12.5 Hz), 131.6 (d, *J* = 10.9 Hz), 145.4 (d, *J* = 14.8 Hz), 172.8. – <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 41.5.

Data for [Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-P(S)Ph<sub>2</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)]: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 0.94 (s, 9 H, Me), 2.59 (d, *J* = 7.0 Hz, 2 H, CH<sub>2</sub>), 3.05 (t, *J* = 7.0 Hz, 1 H, NH), 3.68, 4.01, 4.25, 4.45 (4 m, 4 × 2 H, cyclopentadienyl CH), 6.98 (m, 6 H, Ph), 7.84–7.91 (m, 4 H, Ph). – <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ = 27.7, 31.6, 56.7, 59.2, 64.5, 71.2 (d, *J* = 4.7 Hz), 73.1 (d, *J* = 14.8 Hz), 75.7 (d, *J* = 7.0 Hz), 113.0, 128.3, 128.5 (d, *J* = 14.0 Hz), 134.0 (d, *J* = 19.5 Hz), 140.6 (d, *J* = 11.7 Hz). – <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 41.7. – HRMS ((+)-ESI): *m/z* = 487.116860 (calcd. 487.118084 for C<sub>27</sub>H<sub>30</sub>FeNPS, [M]<sup>+</sup>)

[Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)]

Raney nickel was prepared from 5.0 g of aluminium-nickel alloy and suspended in ethanol (20 mL). A solution of [Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-P(S)Ph<sub>2</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)] (191 mg, 0.39 mmol) in ethanol (10 mL) was added. The

mixture was stirred vigorously for 72 h and filtered through a celite pad, which was subsequently washed with ethanol (2 × 5 mL). The filtrate was taken to dryness *in vacuo*, affording the product as yellow crystals. Yield 173 mg (97%). – <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 0.82 (s, 9 H, Me), 1.93 (t, *J* = 7.0 Hz, 1 H, NH), 2.45 (d, *J* = 7.0 Hz, 2 H, CH<sub>2</sub>), 3.71, 3.80, 4.17, 4.27 (4 m, 4 × 2 H, cyclopentadienyl CH), 7.03 (m, 6 H, Ph), 7.51–7.58 (m, 4 H, Ph). – <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ = 27.7, 31.6, 56.7, 59.2, 64.5, 71.2 (d, *J* = 4.7 Hz), 73.1 (d, *J* = 14.0 Hz), 75.7 (d, *J* = 7.0 Hz), 113.0, 128.3, 128.5 (d, *J* = 14.0 Hz), 134.0 (d, *J* = 19.5 Hz), 140.6 (d, *J* = 11.7 Hz). – <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = –16.3. – HRMS ((+)-ESI): *m/z* = 455.147394 (calcd. 455.146011 for C<sub>27</sub>H<sub>30</sub>FeNP, [M]<sup>+</sup>).

#### 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. Diffraction experiments were carried out using MoK<sub>α</sub> radiation (λ = 0.71073 Å) on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption corrections were done by integration using X-RED [68]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by Direct Methods (SHELXS-97) and refined using alternating cycles of least-squares refinements against *F*<sup>2</sup> (SHELXL-97) [69, 70]. All H atoms were placed in constrained positions (except H1 in [Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-P(S)Ph<sub>2</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)] and H28 in [Fe{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-NHCH<sub>2</sub>*t*Bu)]) and included according to the riding model with the 1.2 fold isotropic displacement parameters. Pertinent crystallographic data are collected in Table 2. Graphical representations were made using ORTEP-3 WIN [71, 72].

CCDC 1007976–1007977 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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