The C_α-Deprotonated Iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ as an *N*,*N*-Chelating Ligand for Iron and Zinc

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The iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ (Py = NC_5H_4) is deprotonated at the C_α-position in a reaction with $[M\{N(SiMe_3)_2\}_2]$ (M = Fe^{2+}, Zn^{2+}) to give metallaspirocycles in which the metal cations are *N*,*N*-chelated by the ring- and imino-nitrogen atoms of both monoanionic ligands. The molecular structures of $[M\{Ph_2P(CHPy)(NSiMe_3)\}_2]$ [M = Fe (**1**), Zn (**2**)] are discussed and general trends in the bonding of the $[Ph_2P(CHPy)(NSiMe_3)]^-$ anion on metal coordination are deduced.

Introduction

Iminophosphoranes of the general type R_3PNR' are valuable building blocks in organometallic and organic syntheses.[1] Their reactivity is mainly due to the inherent polarity of the phosphorus−nitrogen bond, which makes them reactive towards both electrophilic and nucleophilic reagents.[2] In silylated iminophosphoranes, $R_3PNSiMe_3$, the Si−N bond is cleaved in reactions with main-group[3] or transition-metal halides,[4] resulting in the $[R_3PN]^-$ building block, which has similar steric and electronic characteristics to the ubiquitous cyclopentadienyl ligand.[5] In addition, the incorporation of heteroaromatic substituents at the phosphorus centre instead of commonly used alkyl or phenyl groups alters and augments the reactivity and coordination modes of iminophosphoranes. In reactions of pyridyl-substituted iminophosphoranes and amino(imino)phosphoranes with organolithium compounds and lithium amides reduction of the phosphorus(V) centre by P−C or P−N bond cleavage is observed to give phosphanylamides or phosphanides.[6] Likewise, transiminations are observed when treating iminophosphoranes with imines.[7]

Additionally, *P*-alkyl-substituted iminophosphoranes can easily be deprotonated to give attractive building blocks for metallacycles.[8] The introduction of alkyl bridges between the phosphorus atom and the donating heterocycle in the ligand periphery of iminophosphoranes provides not only the opportunity of a higher geometrical adaptability by a wider bite but can also allow the formation of anionic species. Delocalisation of the carbanionic charge to the donating atoms would enable the ligand to respond to the various requirements of metal atoms with their different radii and polarisability. Recently, Leung et al. reported some main-group metal complexes of $iPr_2P(CH_2Py)(NSiMe_3)$ and $[2,6\text{-}(Me_3SiNP\mathit{i}Pr_2CH_2)_2(\mathit{cy}\text{-}C_5H_3N)]$, obtained by deprotonation with organolithium compounds, alkylmagnesium compounds or group-14 amides. Metathesis with group-14 halides gave 1,3-dimetallacyclobutanes (Scheme 1).[9,10]

In the literature the imino nitrogen atom is commonly described as a two-electron σ-donor with only minor π-acceptor properties.[1] However, we recently reported the syntheses and coordination modes of the iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ (Py = NC_5H_4) and its anion in alkali metal complexes and provided experimental evidence that the P=N bond in iminophosphoranes has to be regarded as a P^+-N^- single bond with high electrostatic contributions,[11] as already predicted from theoretical investigations.[12,13] Thus, we found both lone pairs at the sp^3-hybridized imino nitrogen atom in $[(Et_2O)Li\{Ph_2P(CHPy)(NSiMe_3)\}]$ to be directed towards the cation. Hence, the metal−imino nitrogen interactions cannot be regarded as simple 2e-donor bonds (Figure 1).

This bifurcated 4e-coordination pattern and the sidearm donation capability of the pyridyl nitrogen atom in the $[Ph_2P(CHPy)(NSiMe_3)]^-$ anion prompted us to investigate reactions of the iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ with transition metal amides $[M\{N(SiMe_3)_2\}_2]$. In this contribution we report the complexes of divalent iron and zinc (M = Fe, Zn).

Results and Discussion

Syntheses

The reaction of the iron(II) amide $[Fe\{N(SiMe_3)_2\}_2]_2$[14] with the iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$[11] in a 1:2 ratio in polar solvents such as THF or Et_2O results, even at −78 °C, in dark-red to black solutions containing

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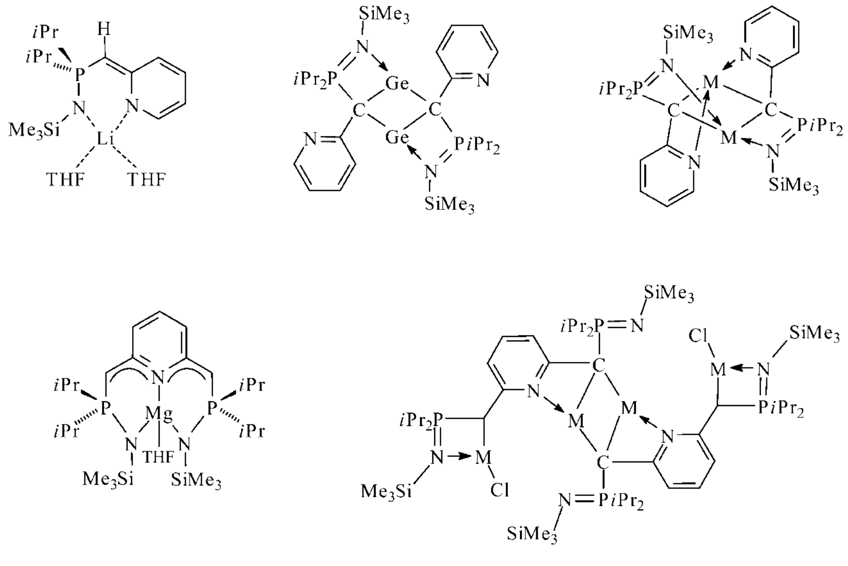


M = Sn, Pb

Scheme 1. Main-group metal complexes of $iPr_2P(CH_2Py)(NSiMe_3)$ (top) and $[2,6\text{-}(Me_3SiNPiPr_2CH_2)_2(cy\text{-}C_5H_3N)]$ (bottom)

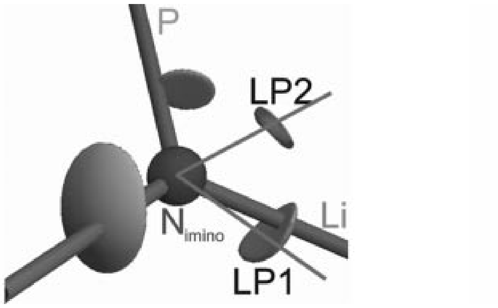


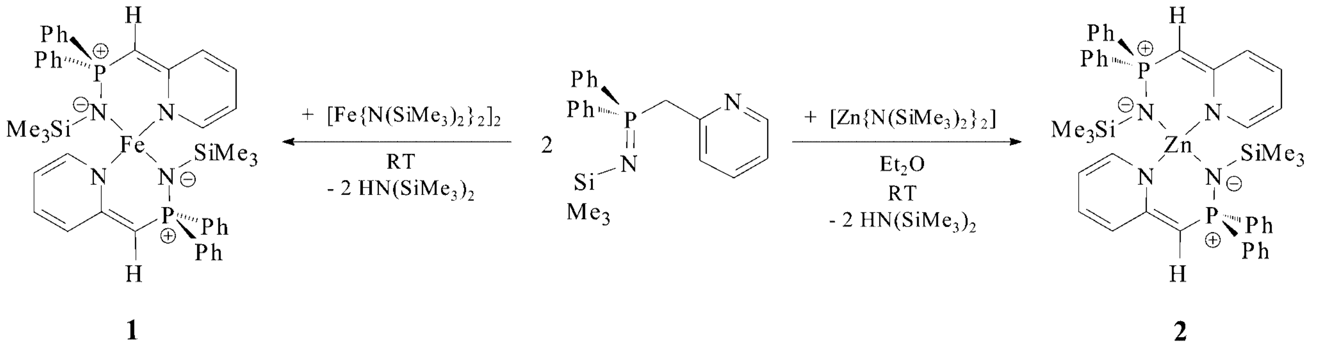
Figure 1. Bifurcated donation of the valence shell charge concentrations derived from experimental charge density studies of the imino nitrogen atom in $[(Et_2O)Li\{Ph_2P(CHPy)(NSiMe_3)\}]$

several products. In contrast, the addition of pure $[Fe\{N(SiMe_3)_2\}_2]_2$ to the solid iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ at room temperature gives immediately a red oily suspension of solid $[Fe\{Ph_2P(CHPy)(NSiMe_3)\}_2]$ (**1**) in liquid $HN(SiMe_3)_2$, formed by the C_α-deprotonation of the iminophosphorane (Scheme 2, left). A similar reaction of the iminophosphorane with $[Zn\{N(SiMe_3)_2\}_2]$[15] gives the isomorphous zinc derivative $[Zn\{Ph_2P(CHPy)(NSiMe_3)\}_2]$ (**2**; Scheme 2, right).

After workup, both complexes were isolated in high yields and their molecular structures determined by X-ray diffraction experiments. Both compounds **1** and **2** are insoluble in nonpolar solvents. The complexes were analysed by IR spectroscopy and elemental analysis. For the iron complex **1** no NMR spectroscopic data were available due to its paramagnetic nature. The NMR resonances for the zinc derivative **2** are given in the Exp. Sect.

Structure Discussion

The solid-state structure of **1** is depicted in Figure 2. The central iron(II) cation is chelated by the nitrogen atoms N1−N4 of the two ligands. The coordination sphere is best described as a distorted tetrahedron with the angles at the iron cation varying from 100.92(8) to 124.40(8)°. In the metallaspirocycle, the two six-membered FeN_2C_2P rings adopt a distorted boat conformation, each with the deprotonated carbon atoms C1 and C22 displaced by, on average, 45 pm



Scheme 2. Syntheses of $[Fe\{Ph_2P(CHPy)(NSiMe_3)\}_2]$ (**1**) and $[Zn\{Ph_2P(CHPy)(NSiMe_3)\}_2]$ (**2**) in the reaction of $Ph_2P(CH_2Py)(NSiMe_3)$ with the corresponding metal amide $[M\{N(SiMe_3)_2\}_2]_2$ (M = Fe, Zn)

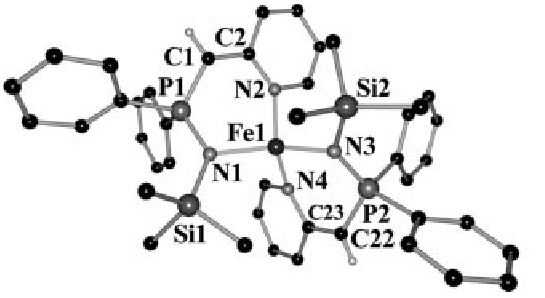


Figure 2. Solid-state structure of [Fe{$Ph_2P(CHPy)(NSiMe_3)$}$_2$] (**1**); selected bond lengths [pm] and angles [°]: Fe−N1 204.6(2), Fe−N3 204.2(2), Fe−N2 207.5(2), Fe−N4 207.9(2), P1−N1 161.2(2), P2−N3 161.3(2), N1−Si1 173.7(2), N3−Si2 173.7(2), P1−C1 172.5(2), P2−C22 172.7(2), P−C_{Ph} av. 182.2, C1−C2 139.4(3), C22−C23 140.3(3), C2−N2 137.9(3), C23−N4 137.5(3); P1−C1−C2 124.08(19), P2−C22−C23 123.42(19), P1−N1−Si1 132.07(12), P2−N3−Si2 129.83(12)

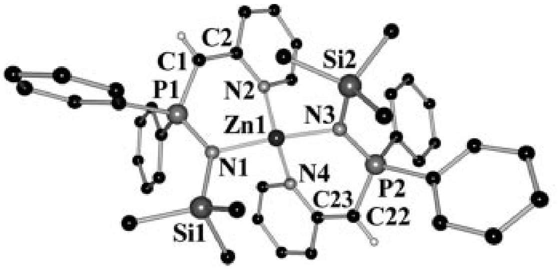


Figure 3. Solid-state structure of [Zn{$Ph_2P(CHPy)(NSiMe_3)$}$_2$] (**2**); selected bond lengths [pm] and angles [°]: Zn−N1 201.70(15), Zn−N3 201.15(16), Zn−N2 203.96(16), Zn−N4 203.88(16), P1−N1 160.92(16), P2−N3 161.43(16), N1−Si1 173.41(16), N3−Si2 173.43(16), P1−C1 172.1(2), P2−C22 172.28(19), P−C_{Ph} av. 181.6, C1−C2 138.9(3), C22−C23 139.6(3), C2−N2 137.5(2), C23−N4 137.5(2); P1−C1−C2 123.75(15), P2−C22−C23 123.35(15), P1−N1−Si1 131.10(10), P2−N3−Si2 128.80(10)

from the respective best N−P−C−N plane (29 pm for the Fe^{2+} cation).

The Fe−N_{imino} distances (av. 204.4 pm) are equal within their estimated standard deviations (esds). They are in the range typically found for iron(II) complexes in which the cation is coordinated to imino functions, for example in [Fe{(*o*-C_6H_4)$Ph_2PNSiMe_3$}$_2$] (211.1 pm),[16] [Fe{2-($RNPPh_2$)-6-R′(*c*-C_5H_3N)}Cl_2] (R = 2,6-Me_2-C_6H_3, 2,6-*i*Pr_2-C_6H_3; R′ = Ph, H_2CPh, $SiMe_3$; 204.8−206.7 pm)[17] or in the 12 VE iron(II) complex [Fe(H_2CPh)-{HC(CMeNAr)$_2$}] (198.2 pm).[18] The Fe−N_{imino} distances in **1** are about 24.4 pm shorter than in the dibromoiron(II) compound [{2,6-($Ph_2PNSiMe_3$)Py}$FeBr_2$], where the Fe−N contacts are on average 228.8 pm,[19] reflecting the pronounced amidic character of the Fe−N_{imino} bonds.

It seems remarkable that the Fe−N_{py} distances in **1** (av. 207.7 pm) are only 3.3 pm longer than the Fe−N_{imino} contacts. They are much shorter than in the donor base coordinated complexes [(H_2NCH_2Py)Fe][Br]$_2$ (Fe−N_{py}: av. 222.3 pm),[20] [(Hpy)$_2$(H_2O)$_4$Fe][$MeCO_2$]$_2$ (221.3 pm)[21] or [Fe{2-($RNPPh_2$)-6-R′(*cy*-C_5H_3N)}Cl_2] (R = 2,6-Me_2-C_6H_3, 2,6-*i*Pr_2-C_6H_3; R′ = Ph, H_2CPh, $SiMe_3$; 218.4−222.9 pm),[17] but similar to those in [Fe{C(H)(Si*t*$BuMe_2$)Py}$_2$]$_2$ (209.7 and 218.9 pm),[22] where the pyridyl nitrogen atom acts as a side-arm donor, like in **1**.

The solid-state structure of the isomorphous zinc derivative [Zn{$Ph_2P(CHPy)(NSiMe_3)$}$_2$] (**2**) is shown in Figure 3.

The central zinc cation is fourfold coordinated by the nitrogen atoms N1−N4 of the two anionic ligands. The coordination polyhedron around the Zn^{2+} ion is a nearly ideal tetrahedron [the angles vary from 103.70(6) to 111.31(6)°]. Like in **1**, both monoanionic [$Ph_2P(CHPy)(NSiMe_3)$]$^-$ units act as bidentate *N,N*-chelates and the two six-membered rings of the metallaspirocycle each show a distorted boat conformation. The displacement of the deprotonated carbon atoms and the metal centre from the best plane of the ligand (av. 45 pm for C1/C22 and 21 pm for Fe) is similar to **1**.

In **2**, the distances between the zinc atom and the imino nitrogen atoms N1 and N3 (av. 201.43 pm) are equal within the esds. In general, Zn−N contacts span a wide range from 182 pm for covalently bonded zinc amides to 231 pm for donor-base complexed dimethylzinc;[23] in **2** they are similar to Zn−N_{imino} interactions in the related zinc bis(iminophosphorane)methanides [Zn{HC(Ph_2PNR}$_2$X] [R = Mes, $SiMe_3$; X = Me, N($SiMe_3$)$_2$, $OCPh_3$], where the contacts vary from 198.6 to 208.3 pm.[24] In the *ortho*-deprotonated [Zn(*o*-$C_6H_4PPh_2NSiMe_3$)$_2$] the Zn−N contacts are 14.4 pm longer (215.8 pm).[25] Thus, the Zn1−N1/3 contacts in **2** are in the range for covalently bonded zinc amides. The Zn−N_{py} distances are identical (Zn1−N3/4: av. 203.92 pm) and only 2.5 pm longer than the Zn−N_{imino} interactions. The average value quoted for Zn−N_{py} contacts is 208.3 pm.[26] To judge the covalent or dative character of the Zn−N_{py} bonds, complex **2** is best compared with the bis(1,4-dihydropyridin-1-yl)bis(pyridine)zinc system:[27] the Zn−N_{py} distances in **2** are 4.4 pm longer than the covalent bonds in bis(1,4-dihydropyridin-1-yl)bis(pyridine)zinc (197 pm), but 11.6 pm shorter than the dative ones (213 pm), clearly emphasising the amidic character of the Zn−N_{py} interactions in **2**.

The geometrical parameters of the anionic ligands of both complexes **1** and **2** are almost equal. Thus, in the following discussion the averages are given; the exact parameters are listed in the captions of Figures 1 and 2, respectively.

The P1−C1 and P2−C22 bonds in **1** and **2** (av. 172.5 pm) are about 12 pm shorter than formal P−C single bonds (185 pm);[28] they are in the range found for ylidic P^+−C^- interactions (163−173 pm).[12,29] In addition, the C1/22−C2/23 contacts (av. 139.6 pm) are 10 pm shorter than the corresponding bond length in the neutral starting material $Ph_2P(CH_2Py)(NSiMe_3)$ (182.57 pm).[11] As a consequence, the C2−N2 and C23−N4 bonds in the pyridyl substituents (average 137.6 pm) are 4.4 pm longer than in the starting material (133.17 pm).[11] The sum of the angles at the imino nitrogen atoms in both complexes is about 360°, illustrating a planar coordination sphere at these atoms. For the pyridyl nitrogen atoms N2 and N4, a marginal pyramidal environment is observed, with a mean sum of the angles of 355.5° in **1** and 356.3° in **2**. All these parameters are very similar to those found in the alkali metal derivatives

$[(Et_2O)Li\{Ph_2P(CHPy)(NSiMe_3)\}]$ and $[\{Ph_2P(CH_2Py)(NSiMe_3)\}M\{Ph_2P(CHPy)(NSiMe_3)\}]$ (M = Li, Na), containing the same anion,[11] and to the related $[(THF)Mg\{2,6\text{-}(Me_3SiNP\mathit{i}Pr_2CH)_2(\mathit{c}\text{-}C_5H_3N)\}]$.[10] In the metallacyclobutanes $[\{2\text{-}[M\{C(\mathit{i}Pr_2PNSiMe_3)\}]\text{-}6\text{-}[M\{HC(\mathit{i}Pr_2PNSiMe_3)\}X]\}(\mathit{c}\text{-}C_5H_3N)]_2$ (M = Sn, X = Cl; M = Pb, X = $N(SiMe_3)_2$], which contain the mono- and dianionic derivative of $[2,6\text{-}(Me_3SiNP\mathit{i}Pr_2CH_2)_2(\mathit{c}\text{-}C_5H_3N)]$, longer $P-C_\alpha(H)$ (av. 178.6 pm) and $C_\alpha(H)-C_{Py}$ distances (av. 147.3 pm) are found than in **1** and **2** due to the observed $[M]-C_\alpha$ bonds in addition to the [M]−N contacts.[10] Whereas in the metallacyclobutanes the negative charge is accumulated at the deprotonated carbon centres, in **1** and **2** it is delocalised over the [HC−Py] backbone of the ligand, leading to a perturbation of the aromatic ring systems and charge accumulation at the pyridyl nitrogen atom. The increased electron density in the pyridyl substituents leads to a displacement of the metal cations from the ring plane towards the π-density of the pyridyl substituent, which explains the short $M-N_{py}$ distances in **1** and **2**.

The P−N bonds in **1** and **2** are, on average, 161.2 pm long. They are at the upper end of the range found for P−N bonds in iminophosphoranes (147−162 pm)[30] and reflect the trend of P−N bond elongation on weakening the electrostatic P^+-N^- interaction because of the presence of the adjacent deprotonated C_α position and the additional *N*-metal coordination.[9,11,31] The Si−N distances in **1** and **2** are, on average, 173.6 pm long and are therefore about 5.5 pm longer than in the neutral iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ (168.08 pm).[11] Similar changes in Si−N bond lengths have been found in the alkali-metal derivatives of $Ph_2P(CH_2Py)(NSiMe_3)$[11] and in bis(iminophosphorane)methanides[32] with regard to the parent starting materials.[33] The long Si−N bonds found in **1** and **2** are a result of the strong interactions of the negatively charged imino nitrogen atoms with the doubly charged cations, reducing the electrostatic contributions in the Si−N interactions.

Spectroscopic Investigations

The IR spectra of **1** and **2** show signals at 1360 cm^{-1} for both complexes. These signals are in the range found for P−N stretching modes (1140−1370 cm^{-1}),[1,34] and are shifted 11 cm^{-1} to higher wavenumbers relative to the starting iminophosphorane (ν_{PN} = 1349 cm^{-1}). A similar shift to higher wavenumbers was detected unambiguously by DFT assignment earlier from the starting material $Ph_3PNSiMe_3$ (ν_{PN} = 1319 cm^{-1}) to the *ortho*-metallated $[(Et_2O)Li(\mathit{o}\text{-}C_6H_4PPh_2NSiMe_3)\}_2]$ (ν_{PN} = 1328 cm^{-1}).[35]

Due to the presence of a d^6 Fe^{II} centre in a tetrahedral coordination, no NMR spectroscopic data could be obtained for the paramagnetic iron complex **1**. In the ^{31}P NMR spectrum of **2**, the phosphorus nuclei resonate at δ = 26.4 ppm. Like for the alkali-metal derivatives of $Ph_2P(CH_2Py)(NSiMe_3)$,[11] deprotonation at the C_α atom results in a downfield shift from the resonance of the starting iminophosphorane (δ = −0.32 ppm). The negative charge and metal coordination at the *P*-bound nitrogen atom decrease the electron density at the phosphorus centre. The almost invariant ^{15}N NMR spectroscopic shift of the imino nitrogen atoms in **2** (δ = −348 ppm) and the iminophosphorane (δ = −343 ppm) indicate that the charge density at this nitrogen atom is less affected by the deprotonation. However, the ^{15}N NMR resonance for the pyridyl ring nitrogen atoms in the anionic ligands of **2** (δ = −182 ppm) differs remarkably from that of the parent iminophosphorane (δ = −61 ppm); it is considerably shifted to higher fields. This resonance is in the range observed earlier for the $[Ph_2P(CHPy)(NSiMe_3)]^-$ anion and is in accordance with charge accumulation at the pyridyl ring nitrogen atoms.[11]

Conclusion

Metal bis(trimethylsilyl)amides easily deprotonate the iminophosphorane $Ph_2P(CH_2Py)(NSiMe_3)$ at the methylene bridge to furnish *N,N*-chelating monoanionic ligands coordinating to the metal atom through the pyridyl and the imino nitrogen atoms. The negative charge is delocalised over the [HC−Py] backbone of the ligand, increasing the electron density in the pyridyl rings. Thus, the metal cations are shifted towards the π-density of the pyridyl rings. On metal coordination, the P−N and Si−N bonds in the ligands get simultaneously elongated, due to the decay of the electrostatic contributions in the P^+-N^- and Si^+-N^- bonds. Additionally, we found shorter $M-N_{imino}$ contacts than expected for M←N donor bonds. These geometrical parameters show that the imino nitrogen atom cannot be regarded as a simple two-electron donor. The $M-N_{imino}$ distances in complexes **1** and **2** reflect a high ionic contribution to the bonding. This leads to a description of the imino nitrogen atom between a monoanionic two- and four-electron donating centre.

Experimental Section

General Remarks: All manipulations were performed under dry N_2 with Schlenk techniques or in an argon-filled glovebox. All solvents were dried with Na/K alloy and distilled prior to use. IR spectroscopy was performed with a Bruker IFS 25 spectrometer. NMR spectra were recorded at room temperature with a Bruker DRX 300 spectrometer at 300.1 (^1H), 75.5 (^{13}C), 121.5 (^{31}P), 59.6 (^{29}Si) and 30.4 MHz ($^1H,^{15}N$ HMBC). Chemical shifts are given as δ values relative to $[D_8]$toluene for ^1H, ^{13}C and to external formamide for $^1H,^{15}N$ HMBC NMR, H_3PO_4 (85%) for ^{31}P and to $SiMe_4$ for ^{29}Si NMR. Elemental analyses were performed by the Microanalytisches Labor der Universität Würzburg.

$[Fe\{Ph_2P(CHPy)NSiMe_3\}_2]$ (1): Pure, liquid $[Fe\{N(SiMe_3)_2\}_2]_2$ (0.26 g, 0.69 mmol) was added by syringe to solid $Ph_2P(CH_2Py)(NSiMe_3)$ (0.50 g, 1.37 mmol) in a drybox. The suspension turned red immediately. It was stirred at room temp. for 1 h, then 20 mL of hexane was added and the suspension was stirred for an additional 2 h. After evaporation of the solvent and formed $HN(SiMe_3)_2$ in vacuo, 0.99 g (1.27 mmol, 93%) of red solid **1** was isolated. To crystallise **1**, the red powder was dissolved in hexane/Et_2O (2:1). After 3 d, red blocks, suitable for an X-ray diffraction experiment, were obtained. IR: ν_{PN} = 1360 cm^{-1}. $C_{42}H_{48}FeN_4P_2Si_2$ (782.81): calcd.

C 64.44, H 6.18, N 7.16; found C 64.36, H 6.21, N 7.12. M.p. (DTA) 258 °C.

[Zn{Ph$_2$P(CHPy)NSiMe$_3$}$_2$] (2): [Zn{N(SiMe$_3$)$_2$}$_2$] (0.29 g, 0.75 mmol) was dissolved in 10 mL of Et$_2$O and added slowly to a solution of Ph$_2$P(CH$_2$Py)(NSiMe$_3$) (0.50 g, 1.37 mmol) in 25 mL of Et$_2$O at room temp. After stirring of the yellow solution for 2 h, the volume of the solvent was reduced. Storage of the solution at 4 °C overnight yielded 0.54 g (0.68 mmol, 91%) of **2** as yellow plates. IR: ν_{PN} = 1360 cm^{-1}. ^{1}H NMR: δ = 0.17 (s, 18 H, SiMe$_3$), 3.32 (d, $^2J_{P,H}$ = 20.9 Hz, 2 H, 1-H), 5.53 (dd, $^3J_{5,6}$ = 5.6, $^3J_{5,4}$ = 6.6 Hz, 2 H, 5-H), 6.28 (d, $^3J_{3,4}$ = 8.8 Hz, 2 H, 3-H), 6.56 (dd, $^3J_{4,3}$ = 8.8, $^3J_{4,5}$ = 6.6 Hz, 2 H, 4-H), 7.12 (d, $^3J_{6,5}$ = 5.6 Hz, 2 H, 6-H), 7.01−7.06 (m, 12 H, *m*-, *p*-PhH), 7.73−7.91 (m, 8 H, *o*-PhH) ppm. ^{13}C NMR: δ = 4.7 (d, $^3J_{Si,C}$ = 3.8 Hz, SiMe$_3$), 59.2 (d, C-1), 106.5 (s, C-5), 120.2 (d, C-3), 134.8 (s, C-4), 146.9 (s, C-6), 166.6 (d, C-2), 128.5 (*m*-PhC), 131.0 (*p*-PhC), 133.1 and 133.4 (*o*-PhC), 138.2 (*i*-PhC) ppm. ^{29}Si NMR: δ = 1.32 (d, $^2J_{Si,P}$ = 1.8 Hz) ppm. ^{1}H,^{15}N-HMBC NMR: δ = −348 (NSiMe$_3$), −182 (PyN) ppm. ^{31}P NMR: δ = 26.4 (s) ppm. $C_{42}H_{48}N_4P_2Si_2Zn$ (792.33): calcd. C 63.67, H 6.11, N 7.07; found C 63.72, H 6.14, N 6.96. M.p. (DTA) 176 °C (dec.).

X-ray Crystallographic Study: All data were collected at 100(2) K[36] using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm) with a Bruker D8 goniometer platform, equipped with a Smart Apex CCD detector. Cell parameters were determined and refined using the SMART software.[37] A series of ω-scans was performed at several φ settings. Raw frame data were integrated using the SAINT program.[38] Empirical absorption correction was carried out with SADABS 2.05.[39] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL.[40] *R* values defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$. The positions of the hydrogen atoms H1 at C1 and H22 at C22 in **1** and **2** were taken from the difference Fourier map and refined freely. All other hydrogen atoms were refined using a riding model. The U_{iso} values for the hydrogen atoms of a CH$_3$ group were set to be 1.5 times and those of all other hydrogen atoms 1.2 times the U_{eq} values of the corresponding C atoms. All non-hydrogen atoms were refined anisotropically. The anisotropic displacement parameters (ADP) in the supplementary crystallographic data were drawn at the 50% probability level. **1:** $C_{42}H_{48}FeN_4P_2Si_2$, M_r = 782.81 g/mol, triclinic, space group $P\bar{1}$, a = 1028.83(6), b = 1081.12(6), c = 1836.20(11) pm, α = 85.8120(10), β = 81.1290(10), γ = 79.9010(10)°, V = 1.9845(2) nm^{-3}, Z = 2, $\rho_{calcd.}$ = 1.310 Mg·m^{-3}, μ = 0.556 mm^{-1}, $F(000)$ = 824. Data were collected from θ = 2.03 to 25.35°. 30624 reflections measured, from which 7251 were unique, R(int) = 0.0295, $wR2$(all data) = 0.1181, $R1[I > 2\sigma(I)]$ = 0.0414, for 7243 data and 474 parameters. **2:** $C_{42}H_{48}N_4P_2Si_2Zn$, M_r = 792.33 g/mol, triclinic, space group $P\bar{1}$, a = 1026.46(5), b = 1077.28(5), c = 1830.69(9) pm, α = 85.8180(10), β = 80.9470(10), γ = 79.7270(10)°, V = 1.96499(16) nm^{-3}, Z = 2, $\rho_{calcd.}$ = 1.339 Mg·m^{-3}, μ = 0.803mm^{-1}, $F(000)$ = 832. Data were collected from θ = 2.04 to 26.44°. 42026 reflections measured, from which 8072 were unique, R(int) = 0.0310, $wR2$(all data) = 0.0920, $R1[I > 2\sigma(I)]$ = 0.0347, for 8067 data and 474 parameters. CCDC-232887 (**1**) and -232888 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, New York, **1993**.

[2] [2a] Y. G. Gololobov, I. N. Zhmurova, L. F. Kasukhin, *Tetrahedron* **1981**, *37*, 437. [2b] Y. G. Gololobov, L. F. Kasukhin, *Tetrahedron* **1992**, *48*, 1353.

[3] Review: K. Dehnicke, F. Weller, *Coord. Chem. Rev.* **1997**, *158*, 103.

[4] Review: K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* **1999**, *182*, 19.

[5] [5a] T. V. Lubben, P. T. Wolczanski, G. D. van Duyne, *Organometallics* **1984**, *3*, 977. [5b] D. W. Stephan, J. C. Stewart, F. Guerin, R. E. v. Spence, W. Xu, D. G. Harrison, *Organometallics* **1999**, *17*, 1116. [5c] D. W. Stephan, F. Guerin, R. E. v. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak, D. G. Harrison, *Organometallics* **1999**, *17*, 2046. [5d] K. Dehnicke, F. Weller, J. Strähle, *Chem. Soc. Rev.* **2001**, *30*, 125.

[6] [6a] S. Wingerter, M. Pfeiffer, A. Murso, C. Lustig, T. Stey, V. Chandrasekhar, D. Stalke, *J. Am. Chem. Soc.* **2001**, *123*, 1381. [6b] F. Baier, Z. Fei, H. Gornitzka, A. Murso, S. Neufeld, M. Pfeiffer, I. Rüdenauer, A. Steiner, T. Stey, D. Stalke, *J. Organomet. Chem.* **2002**, *661*, 111.

[7] [7a] S. A. Bell, S. J. Geib, T. Y. Meyer, *Chem. Commun.* **2000**, 1375. [7b] S. A. Bell, T. Y. Meyer, S. J. Geib, *J. Am. Chem. Soc.* **2002**, *124*, 10698. [7c] M. C. Burland, T. Y. Meyer, *Inorg. Chem.* **2003**, *42*, 3438.

[8] [8a] Review: A. Steiner, S. Zacchini, P. I. Richards, *Coord. Chem. Rev.* **2002**, *227*, 193. [8b] J. F. Bickley, M. C. Copsey, J. C. Jeffery, A. P. Leedham, C. A. Russell, D. Stalke, A. Steiner, T. Stey, S. Zacchini, *Dalton Trans.* **2004**, 989.

[9] W.-P. Leung, Z.-X. Wang, H.-W. Li, Q.-C. Yang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 8123.

[10] W.-P. Leung, Q. W.-Y. Ip, S.-Y. Wong, T. C. W. Mak, *Organometallics* **2003**, *22*, 4604.

[11] N. Kocher, D. Leusser, A. Murso, D. Stalke, *Chem. Eur. J.*, in press.

[12] Review: D. G. Gilheany, *Chem. Rev.* **1994**, *94*, 1339.

[13] [13a] A. Dobado, H. Martinez-García, J. M. Molina, M. R. Sundberg, *J. Am. Chem. Soc.* **1998**, *120*, 8461. [13b] D. B. Chesnut, *J. Phys. Chem. A* **2003**, *107*, 4307.

[14] [14a] R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. -P. Leung, K. Rypdal, *Inorg. Chem.* **1988**, *27*, 1782. [14b] M. M. Olmstead, P. P. Power, S. C. Shoner, *Inorg. Chem.* **1991**, *30*, 2547.

[15] H. Bürger, W. Sawdony, U. Wannagat, *J. Organomet. Chem.* **1965**, *3*, 113.

[16] S. Wingerter, M. Pfeiffer, T. Stey, M. Bolboacá, W. Kiefer, V. Chandrasekhar, D. Stalke, *Organometallics* **2001**, *20*, 2730.

[17] L. P. Spencer, R. Altwer, P. Wei, L. Gelmini, J. Gauld, D. W. Stephan, *Organometallics* **2003**, *22*, 3841.

[18] T. J. J. Sciarone, A. Meesma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2002**, 1580.

[19] S. Al-Benna, M. J. Sarsfield, M. Thomton-Pett, D. L. Omsby, P. J. Maddox, P. Bres, M. Bochmann, *J. Chem. Soc., Dalton Trans.* **2000**, 4247.

[20] L. Wiehl, G. Kiel, C. P. Köhler, H. Spiering, P. Gütlich, *Inorg. Chem.* **1986**, *25*, 1565.

[21] B. Singh, J. R. Long, F. F. de Biani, D. Gatteschi, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 7030.

[22] W.-P. Leung, H. K. Lee, L.-H. Weng, B.-S. Luo, Z. -Y. Zhou, T. C. W. Mak, *Organometallics* **1996**, *15*, 1785.

[23] [23a] A. Haaland, K. Hedberg, P. P. Power, *Inorg. Chem.* **1984**,

23, 1972. [23b] J. Dekker, J. Boersma, L. Fernholt, A. Haaland, A. L. Speck, *Organometallics* **1987**, *6*, 1202.

[24] [24a] A. Kasani, R. McDonald, R. G. Cavell, *Organometallics* **1999**, *18*, 3775. [24b] M. S. Hill, P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.* **2002**, 4694.

[25] S. Wingerter, H. Gornitzka, G. Bertrand, D. Stalke, *Eur. J. Inorg. Chem.* **1999**, 173.

[26] W. A. Herrmann, W. R. Thiel, J. G. Kuchler, J. Behm, E. Herdtweck, *Chem. Ber.* **1990**, *123*, 1963.

[27] [27a] A. J. de Koning, J. Boersma, G. J. M. van der Kerk, *J. Organomet. Chem.* **1980**, *186*, 159. [27b] A. L. Spek, *Cryst. Struct. Commun.* **1982**, *11*, 1621.

[28] P. Rademacher, in *Strukturen organischer Moleküle*, VCH, Weinheim, **1987**.

[29] [29a] J. C. J Bart, *J. Chem. Soc. B* **1969**, 350. [29b] H. Schmidbaur, A. Schlier, C. M. F. Frazao, G. Müller, *J. Am. Chem. Soc.* **1986**, *108*, 976. [29c] H. Schmidbaur, J. Jeong, A. Schier, W. Graf, D. L. Wilkinson, G. Müller, *New J. Chem.* **1989**, *13*, 341.

[30] [30a] A. F. Cameron, N. S. Hair, D. G. Norris, *Acta Crystallogr., Sect. B* **1974**, *30*, 221. [30b] E. Niecke, D. Gudat, *Angew. Chem.* **1991**, *103*, 251; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 217. [30c] A. Steiner, D. Stalke, *Inorg. Chem.* **1993**, *32*, 1977. [30d] R. Fleischer, D. Stalke, *Inorg. Chem.* **1997**, *36*, 2413.

[31] [31a] V. Chandrasekhar, K. R. J. Thomas, *Struct. Bonding (Berlin, Ger.)* **1993**, *81*, 41. [31b] V. Chandrasekhar, K. R. Thomas, *J. Appl. Organomet. Chem.* **1993**, *7*, 1. [31c] V. Chandrasekhar, K. Vivekanandan, S. Nagendran, A. G. T. Senthil, N. R. Weathers, J. C. Yarbrough, A. W. Cordes, *Inorg. Chem.* **1998**, *37*, 6192.

[32] [32a] R. P. K. Babu, K. Aparna, R. McDonald, R. G. Cavell, *Inorg. Chem.* **2000**, *39*, 4981. [32b] M. T. Gamer, P. W. Roesky, *Z. Anorg. Allg. Chem.* **2001**, *627*, 877.

[33] Müller, M. Möhlen, B. Neumüller, N. Faza, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1748.

[34] [34a] R. B. King, J. C. Cloyd Jr., *Inorg. Chem.* **1975**, *14*, 1550. [34b] I. MacLeod, L. Manojlovic-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, R. Walker, *J. Organomet. Chem.* **1975**, *97* C7. [34c] T. G. Appleton, M. A. Bennett, *Inorg. Chem.* **1978**, *17*, 738. [34d] S. Hietkamp, D. J. Stufkens, K. Vrieze, *J. Organomet. Chem.* **1979**, *169*, 107.

[35] [35a] M. Balboáca, M. Pfeiffer, D. Stalke, W. Kiefer, in *Eighteenth International Conference on Raman Spectroscopy (ICORS 2002)*, John Wiley & Sons New York, **2002**, p. 601. [35b] M. Pfeiffer, M. Balboáca, D. Stalke, W. Kiefer, in *Eighteenth International Conference on Raman Spectroscopy (ICORS 2002)*, John Wiley & Sons New York, **2002**, p. 657. [35c] M. Bolboaca, T. Stey, A. Murso, D. Stalke, W. Kiefer, *Appl. Spectrosc.* **2003**, *57*, 970.

[36] [36a] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615. [36b] T. Kottke, R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465. [36c] D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171.

[37] Bruker, *SMART-NT, Data Collection Software, Version 5.6*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **2000**.

[38] Bruker, *SAINT-NT, Data Reduction Software, Version 6*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1999**.

[39] G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Göttingen, Germany, **2001**.

[40] Bruker, *SHELX-TL, Version 6*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **2000**.

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