Transition-Metal Substituted Phosphaalkenes, 41[‡]

Syntheses and Structures of *C*-Monoamino-*P*-ferriophosphaalkenes $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CR^1(NR^2_2)]$ (R^1 = Ph, *t*Bu, 3,4,5-$(MeO)_3C_6H_2$; NR^2_2 = NMe_2, Piperidino)

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Dedicated to Professor Gerd Becker on the occasion of his 60th birthday

Keywords: Phosphaalkenes / Iron / Condensation reactions

Reaction of equimolar amounts of the carbenium iodides $[Me_2N(R)CSMe]I$ [**1a**: R = Ph; **1b**: *t*Bu; **1c**: 3,4,5-$(MeO)_3C_6H_2$], [pip(Ph)CSMe]I (**1d**) (pip = piperidino), and $LiP(SiMe_3)_2 \cdot$ DME afforded phosphaalkenes $Me_2N(R)C{=}PSiMe_3$ (**2a–c**) and pip(Ph)C=$PSiMe_3$ (**2d**). Combination of **2a–d** with $[(\eta^5\text{-}C_5Me_5)(CO)_2FeCl]$ led to the formation of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(R)NMe_2]$ [**3a**: R = Ph; **3b**: *t*Bu; **3c**: 3,4,5-$(MeO)_3C_6H_2$] and $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(Ph)pip]$ (**3d**). Compounds **2a–d** and **3a–d** were characterized by means of spectroscopy (IR, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR). The molecular structures of **3a** and **3b** were determined by X-ray diffraction analysis. The results of an X-ray study on $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}C(Ph)SiMe_3]$ (**3g**) for comparison are also included. All experimental observations are rationalized by the assumption that complexes **3a**, **3c**, and **3d** are phosphaalkenes with an inverse π-electron distribution ($P^{\delta-}$ $C^{\delta+}$) and are comparable to $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2]$ (**3e**), whereas **3b** is better regarded as phosphaalkene with a normal polarization ($P^{\delta+}$ $C^{\delta-}$) of the P=C bond, similar to that given in **3g**.

Introduction

Within the last 15 years metallophosphaalkenes have emerged from being laboratory curiosities to become versatile synthons in organoelement and coordination chemistry.[1] P-metallophosphaalkenes are now accessible by a variety of different synthetic pathways (Scheme 1).

In methods (a)[2] and (b),[3] the P=C double bond was built up during a sequence of condensation and rearrangement steps, whereas in routes (c),[4] (d),[5] and (e),[6] reactants with preformed P=C bonds were involved. The organophosphorus precursor of route (f) is a phosphaalkyne, the bond order of which was reduced from 3 to 2 by hydroruthenation.[7] To date it is obvious that all the synthetic principles depicted in Scheme 1 suffer from limited generality. Thus, route (e) was limited to Fe and Ru derivatives. The ferriophosphaalkene **3e** is interesting because its P=C bond displays an inverse π-electron distribution. This leads to a highly nucleophilic phosphorus center, and consistently, to a rich and versatile chemistry with inorganic, organometallic, and organic electrophiles.[1,8]

We were now interested in experimentally determining the borderline between "classically polarized" metallophosphaalkenes such as $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)R$, (R = $SiMe_3$, Ph)[4] and $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(OSiMe_3)(R)$ (R = Ph, *t*Bu, Mes)[2] on the one hand, and "inversely polarized" phosphaalkenes on the other hand.

One possible experimental approach to this target was based on the replacement of one amino substituent in **3e** by an organic group that cannot participate in π-conjugation with the P=C bond.

Results and Discussion

For the preparation of ferriophosphaalkenes with only one amino group at the methylene carbon atom, a synthetic route according to reaction (e) (Scheme 1) seemed promising. The required P-silylated phosphaalkenes were formed by the reaction of equimolar amounts of the (methylthiomethylene)immonium iodides **1a–d** and $LiP(SiMe_3)_2 \cdot$ DME[9] in a mixture of *n*-pentane and 1,2-dimethoxyethane (DME, −75 °C → room temperature). Within 24 h the reaction mixtures slowly turned orange.

Orange $Me_3SiP{=}CR^1(NR^2_2)$ (**2a–d**) were isolated as oils in moderate yields (38–62%) after filtration and removal of solvents. Phosphaalkenes **2a** and **2b** were purified by vacuum distillation to afford light yellow oils. The distillates were still contaminated with some $P(SiMe_3)_3$, which was invariably formed as a by-product. Due to its inherent thermolability, the attempted distillation of **2c** and **2d** was thwarted by decomposition. This approach parallels our

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[‡] Part 40: L. Weber, M. H. Scheffer, H.-G. Stammler, A. Stammler, *Eur. J. Inorg. Chem.* **1999**, 1607–1611.

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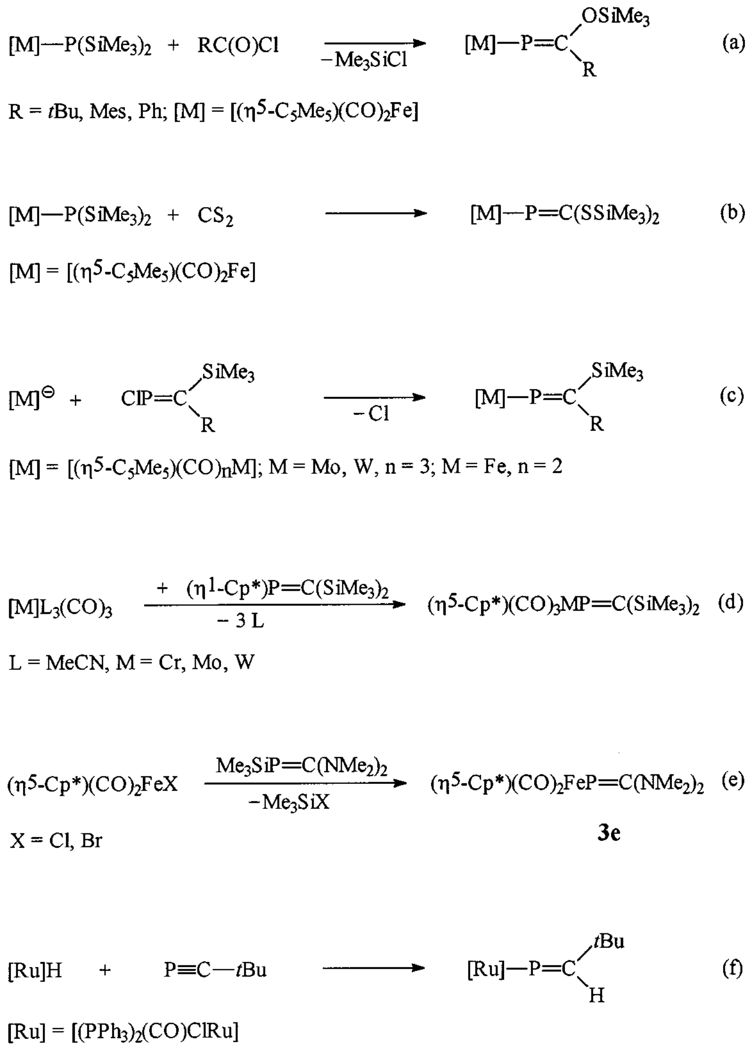
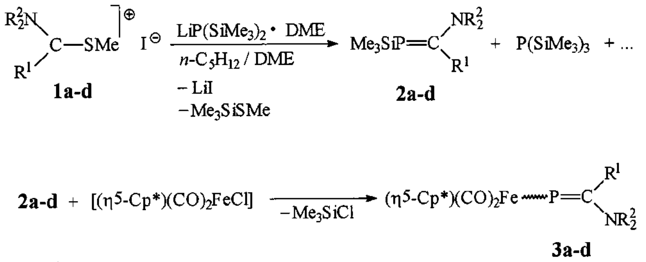


Scheme 1. Synthetic routes to P-metallophosphaalkenes



1-3	R^1	NR^2_2
a	Ph	NMe_2
b	tBu	NMe_2
c	$(3,4,5\text{-}MeO)_3C_6H_2$	NMe_2
d	Ph	pip

Scheme 2. Synthesis of phosphaalkenes **2a−d** and **3a−d**; pip = NC_5H_{10}

previous synthesis of $Me_3SiP{=}C(NMe_2)_2$ (**2e**) from $LiP(SiMe_3)_2 \cdot DME$ and $[(Me_2N)_2CSMe]I$,[10] and constitutes a generalization of the reaction principle. The novel phosphaalkenes **2a−d** are sensitive to oxygen and moisture. Upon combination of **2a−d** with one equivalent of $(\eta^5\text{-}C_5Me_5)(CO)_2FeCl$[11] in a mixture of *n*-pentane and DME, a reaction occurred in the temperature range −75 to 20 °C to give the red microcrystalline ferriophosphaalkenes **3a−d** in 34 to 67% yield.

The replacement of one dimethylamino group in $Me_3SiP{=}C(NMe_2)_2$ (**2e**) ($\delta^{31}P = 46.5$)[10] by an aryl ring resulted in slight downfield shifts to $\delta = 50.3$ (**2c**), 54.3 (**2a**), and 59.5 (**2d**). The introduction of one *tert*-butyl group, however, was accompanied by a more pronounced deshielding in **2b** ($\delta = 68.7$).

In the $^{13}C\{^1H\}$ NMR spectra of **2a**, **2c**, and **2d**, the doublets of the methylene carbon atoms of the P=C bond are insignificantly shifted $\delta\ ^{13}C = 204.7{-}205.1$ when compared with **2e** ($\delta = 204.0$). Also, the coupling constants $^1J_{P,C}$ decrease from 85.0 Hz in **2e** to 64.4−65.4 Hz. Interestingly, in the *tert*-butyl derivative **2b** the carbon atom of the P=C bonds was observed at much lower field ($\delta = 219.7$) with an increased coupling constant ($^1J_{P,C} = 94.1$ Hz). Two discrete singlet resonances for the methyl groups of the dimethylamino function in **2a** and **2c** are paralleled by two broad singlets, each accounting for 3-H atoms in the ^1H-NMR spectra, and point to a hindered rotation of the amino group about the N-C_{sp^2} bond at room temperature. In **2b** only one resonance for the NMe_2 group in the $^{13}C\{^1H\}$ as well as the ^1H-NMR spectra was measured. The replacement of the trimethylsilyl group in **2a−d** by the [(η^5-C_5Me_5)$(CO)_2Fe$] fragment caused strong downfield shifts in the $^{31}P\{^1H\}$-NMR spectra. Ferriophosphaalkenes **3a** (δ = 232.0), **3c** (δ = 225.4), and **3d** (δ = 225.4) also display more deshielded $^{31}P\{^1H\}$-NMR resonances in comparison to (η^5-C_5Me_5)$(CO)_2FeP=C(NMe_2)_2$ (**3e**) (δ = 135.5).[6] This observation indicates that the inverse polarity in the novel products is considerably reduced with respect to **3e**. This effect is much more evident with the *tert*-butyl-substituted ferriophosphaalkene **3b**, where a singlet at $\delta^{31}P$ = 409.0 was registered. At this point it is helpful to compare our data with the ^{31}P-NMR-resonances of the "classically" polarized ferriophosphaalkenes (η^5-C_5Me_5)$(CO)_2FeP=C(SiMe_3)_2$ (δ = 641.5)[4] and (η^5-C_5Me_5)$(CO)_2FeP=C(Ph)(SiMe_3)$ (δ = 520.7).[4] On the ground of ^{31}P-NMR spectroscopy, compound **3b** should not be considered as an inversely polarized phosphaalkene. The ^{13}C nuclei of the P=C bond in **3a−d** experience small high fields ($\Delta\delta^{13}C$ = 2.4−5.0 ppm) relative to precursors **2a−d**. The $^1J_{P,C}$ coupling constants of **2a**, **2c**, and **2d** were increased by ca. 20 Hz. An opposite trend, however, was observed with **2b** and **3b**, where the metallation was accompanied by a decrease of the coupling constant $^1J_{P,C}$ by 18.8 Hz. Again, a bonding situation in **3b** different from that in **3a**, **c**, and **d** might be anticipated. In the ^{13}C-NMR spectra of **3a−d** the carbonyl ligands give rise to singlets in the narrow range of δ = 218.0 to 218.5. The high-field shift in comparison to (η^5-C_5Me_5)$(CO)_2$-$FeP=C(NMe_2)_2$ (**3e**) agrees with a smaller degree of charge transfer from the organophosphorus ligand via the iron atom onto the carbonyls in **3a−d**. This is also reflected in the IR spectra of **3a−d**, where two intense ν(CO) bands at 1987−1989 cm^{-1} and 1940−1941 cm^{-1} are hypsochromically shifted when compared with **3e** (1973 and 1925 cm^{-1}). In the classically polarized phosphaalkenes (η^5-C_5Me_5)-$(CO)_2FeP=C(SiMe_3)_2$ (**3f**) and (η^5-C_5Me_5)$(CO)_2FeP=C(Ph)(SiMe_3)$ (**3g**) the $^{13}C(CO)$ NMR signals were observed at δ = 217.6 and 216.1, respectively, and the ν(CO) bands in the IR spectra occurred at $\tilde{\nu}$ = 1988 and 1942 or 1993 and 1940 cm^{-1}, respectively.[4]

This spectroscopic evidence may be interpreted as with **3b**, as if the borderline between the inversely polarized ferriophosphaalkene **3e** and the more classically polarized compounds **3f** and **3g** has been trespassed.

To further substantiate this idea, X-ray structural analyses of **3a** and **3b** were necessary.

X-ray Structural Analysis of 3a

Single crystals of **3a** were grown from toluene at −30 °C. The molecular structure of **3a** is related to that of the metallophosphaalkene **3e**.[6] The molecule displays a distorted "piano stool" geometry [P(1)−Fe(1)−C(11) 91.8(1)°, P(1)−Fe(1)−C(12) 93.3(1)°, C(11)−Fe(1)−C(12) 96.5(2)°] (Figure 1).

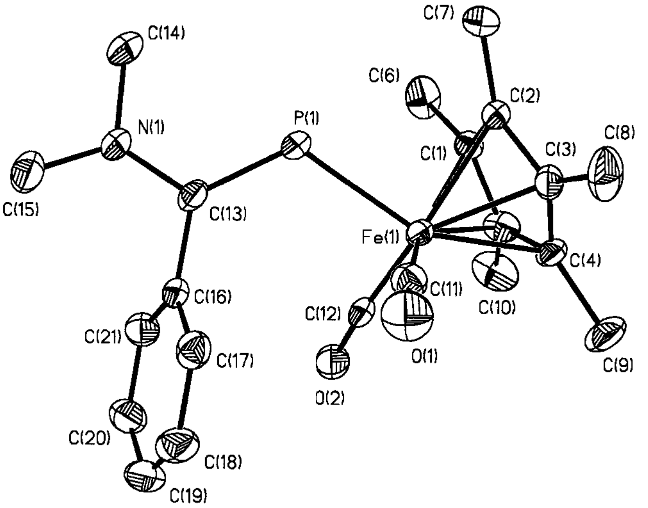


Figure 1. Molecular structure of **3a** in the crystal; selected bond lengths [Å] and angles [°]: Fe(1)−P(1) 2.316(1), Fe(1)−C(11) 1.764(4), Fe(1)−C(12) 1.766(4), P(1)−C(13) 1.717(4), N(1)−C(13) 1.399(4), N(1)−C(14) 1.452(5), N(1)−C(15) 1.449(5), C(13)−C(16) 1.495(5), O(1)−C(11) 1.138(5), O(2)−C(12) 1.137(4); P(1)−Fe(1)−C(11) 91.8(1), P(1)−Fe(1)−C(12) 93.3(1), C(11)−Fe(1)−C(12) 96.5(2), Fe(1)−C(11)−O(1) 176.2(4), Fe(1)−C(12)−O(2) 174.1(3), Fe(1)−P(1)−C(13) 118.9(1), P(1)−C(13)−N(1) 120.0(3), P(1)−C(13)−C(16) 126.1(2), N(1)−C(13)−C(16) 113.7(3), C(13)−N(1)−C(14) 118.5(3), C(13)−N(1)−C(15) 120.8(3), C(14)−N(1)−C(15) 113.3(3)

Two of the legs are represented by nearly linear terminal carbonyl ligands. The organophosphorus ligand is connected with the $(C_5Me_5)(CO)_2Fe$ fragment by a Fe−P single bond of 2.316(1) Å, which compares well with that in **3e** [2.325(2) Å]. The same holds true for the P=C bond lengths in both molecules [**3a**: 1.717(4) Å; **3e**: 1.709(5) Å], which fall in the typical region of 1.70−1.76 Å usually determined for amino-substituted phosphaalkenes.[12] The P=C bond is in an (*E*) configuration, with the iron atom and the phenyl group on the same side of the molecule. Presumably due to steric congestion, the angles Fe(1)−P(1)−C(13) [118.9(1)°] and P(1)−C(13)−C(16) [126.1(2)°] are markedly different. The phenyl ring is twisted out of the plane defined by the atoms Fe(1), P(1), and C(13) by 70.7°. The angle at the P atom in **3e** was found to be 117.9(2)°. The carbon atom C(13) in **3a** is in a trigonal-planar configuration (sum of angles = 359.8°), featuring a bond length of 1.399(4) Å to the slightly pyramidal nitrogen atom (sum of angles = 352.6°). The plane defined by the atom C(13), C(14), and C(15) encloses an angle of 16.6° with the plane through the atoms Fe(1), P(1), and C(13). This allows for effective π-conjugation of the lone-pair at the nitrogen atom with the P=C bond. In line with this, bond N(1)−C(13) is markedly shorter than the calculated value for a $C_{(sp^2)}-N_{(sp^2)}$ single bond (1.45 Å).[12] In **3e**, the pyramidal geometry was only observed for the N atom of the *trans*-oriented dimethylamino group [sum of angles = 350.5°, *d*(CN) = 1.410(7) Å]. The NMe_2 unit in a *cis*-disposition to the iron atom of **3e** was planar [sum of angles = 360.0°, *d*(CN) = 1.372(8) Å].

X-ray Structural Analysis of 3b

Single crystals of **3b** were grown from toluene at −30 °C. Again the molecule possesses a distorted piano stool configuration at the (η^5-C_5Me_5)$(CO)_2Fe$ unit (Figure 2).

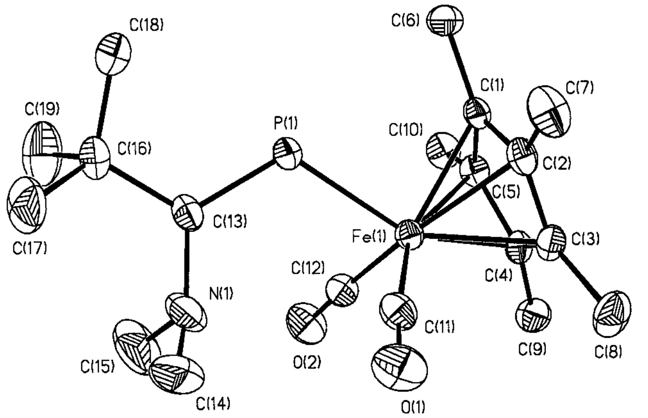


Figure 2. Molecular structure of **3b** in the crystal; selected bond lengths [Å] and angles [°]: Fe(1)−P(1) 2.276(1), Fe(1)−C(11) 1.756(3), Fe(1)−C(12) 1.756(3), P(1)−C(13) 1.697(3), N(1)−C(13) 1.448(4), N(1)−C(14) 1.447(5), N(1)−C(15) 1.449(5), C(13)−C(16) 1.551(4); P(1)−Fe(1)−C(11) 89.7(1), P(1)−Fe(1)−C(12) 90.0(1), C(11)−Fe(1)−C(12) 97.1(1), Fe(1)−C(11)−O(1) 173.8(3), Fe(1)−C(12)−O(2) 174.6(3), Fe(1)−P(1)−C(13) 117.0(1), P(1)−C(13)−N(1) 120.8(2), P(1)−C(13)−C(16) 118.8(2), N(1)−C(13)−C(16) 120.4(2), C(13)−N(1)−C(14) 118.1(3), C(13)−N(1)−C(15) 118.0(3), C(14)−N(1)−C(15) 112.1(3)

The Fe−P bond of 2.276(1) Å, however, is much shorter than in **3a**. Interestingly, the dimethylamino group at the P=C double bond [P(1)−C(13) = 1.697(3) Å] is oriented nearly perpendicular to the plane defined by the atoms Fe(1), P(1), and C(13) (= 86.7°) thus preventing any notable π-conjugation. In keeping with this, the atomic distance N(1)−C(13) of 1.448(4) Å is much longer than in **3a** and compares well with the remaining bond lengths N(1)−C(14) [1.447(5) Å], and N(1)−C(15) [1.449(5) Å]. The nitrogen atom is slightly pyramidal [sum of angles = 348.2°] with its lone pair directed towards the carbonyl ligands. The atom C(13) is trigonal-planarly ligated with a *tert*-butyl group in *trans*-disposition to the bulky (η^5-C_5Me_5)$(CO)_2Fe$ unit. The valence angle at the P atom [117.0(1)°] compares well with those in **2a** and **2e** (vide supra). The peculiarities in the spectroscopic data of **2b** in relation to those of **2a** and **2e** can be rationalized by a non-existent N(lone pair)−P=C π conjugation, which is the prerequisite for excess electron density to the P atom. The lack of electronic repulsion between an electron abundant phosphorus atom and the (also) electron-rich iron-complex fragment in **3b** allows for a much shorter Fe−P distance. To further support these arguments, the X-ray structural analysis of the "classically" polarized ferriophosphaalkene [(η^5-C_5Me_5)$(CO)_2FeP=C(Ph)(SiMe_3)$] (**3g**)[4,13] is included in this paper.

X-ray Structural Analysis of 3g

Single crystals of **3g** were grown from *n*-pentane at −4 °C. The analysis shows that the molecule is bisected by a mirror plane defined by the atoms Si(1), C(10), P(1), and Fe(1) (Figure 3).

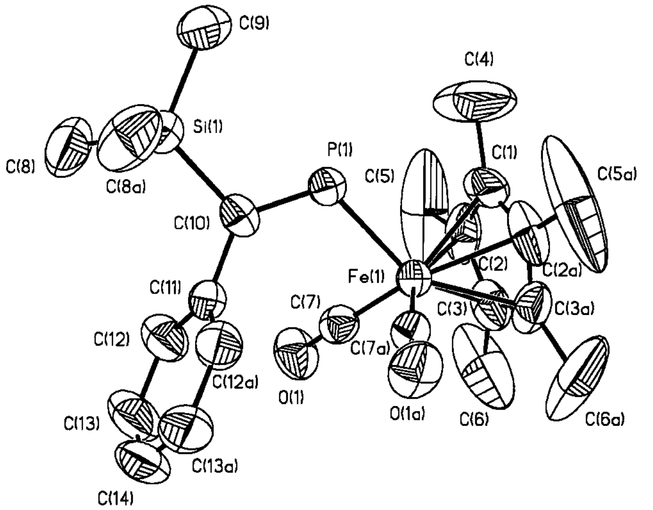


Figure 3. Molecular structure of **3g** in the crystal; selected bond lengths [Å] and angles [°]: Fe(1)−P(1) 2.269(2), Fe(1)−C(7) 1.749(5), P(1)−C(10) 1.665(6), C(10)−Si(1) 1.887(7), C(10)−C(11) 1.484(8), O(1)−C(7) 1.148(5); P(1)−Fe(1)−C(7) 90.2(2), C(7)−Fe(1)−C(7a) 99.0(3), Fe(1)−P(1)−C(10) 119.3(2), P(1)−C(10)−Si(1) 117.6(5), P(1)−C(10)−C(11) 129.4(5), Si(1)−C(10)−C(11) 112.9(4), Fe(1)−C(7)−O(1) 174.5(4)

The pentamethylcyclopentadienyl ring is disordered. The organophosphorus ligand in the "piano stool"-configured complex fragment is of primary interest for our discussion. As is observed for **3a**, an (*E*) configuration at the P=C double bond with an orthogonally directed phenyl ring in the vicinity of the $Fe(CO)_2$ unit is observed. However, in marked contrast to **3a** the bond Fe(1)−P(1) [2.269(2) Å] is shorter and compares more favorably with the bond encountered in **3b**. The P=C double bond of **3g** [1.665(6) Å] is shorter than in the inversely polarized phosphaalkenes **3a** and **3e**, and more typical for "classically polarized" phosphaalkenes without π-donating atoms at the methylene carbon atom. The valence angle Fe(1)−P(1)−C(10) of 119.3(2)° compares well with the corresponding data in **3a**, **3b**, and **3e**. The angle P(1)−C(10)−C(11) [129.5(4)°] at the trigonal planar carbon atom C(10) [sum of angles = 360.0°] is markedly more obtuse than the angle P(1)−C(10)−Si(1) [117.6(5) Å] at the side opposite to the bulky iron-complex fragment.

Conclusions

In a series of ferriophosphaalkenes of the type [(η^5-C_5Me_5)$(CO)_2FeP=CR^1(NR^2_2)$] (R^1 = Ph, *t*Bu, 3,4,5-$(MeO)_3C_6H_2$; NR^2_2 = NMe_2, pip) it was demonstrated that the phenomenon of an inverse electron density distribution $P^{\delta-}$ $C^{\delta+}$ is only realized whenever an allylic-like π-conjugation of the lone pair at the N atom with the P=C π-bond is possible. In such molecules, where the lone pair at the nitrogen atom is oriented perpendicular to the PC-π-system, a classical behavior concerning the polarity of the P=C bond ($P^{\delta+}$ $C^{\delta-}$) is observed. In an earlier paper Appel already pointed to a correlation between ^{31}P-NMR shifts of amino-substituted phosphaalkenes and the dihedral angle between the plane that includes the atoms P, C, N, and the NR_2 plane.[14]

Experimental Section

All manipulations were performed under dry nitrogen. Solvents were rigorously dried with an appropriate drying agent and freshly distilled before use. − The following compounds were prepared according to literature procedures: Thioamides PhC(S)NMe_2, *t*BuC(S)NMe_2, and {3,4,5-$(MeO)_3C_6H_2$}C(S)NMe_2 were obtained from the corresponding amides and P_4S_{10}.[15] PhC(S)pip was synthesized from benzaldehyde, piperidine, and sulfur.[16] The carbenium salts [PhC(SMe)NMe_2]I (**1a**)[17] and [PhC(SMe)pip]I (**1d**)[18] resulted from the corresponding thioamides and methyl iodide. [η^5-Cp*$(CO)_2$FeCl],[11] $LiP(SiMe_3)_2 \cdot$ DME[9] − IR spectra: Bruker FT-IR VECTOR 22. − ^{1}H-, ^{13}C-, ^{29}Si-, and ^{31}P-NMR spectra at room temp.; Bruker AC 100 (^{1}H, 100.13 MHz; ^{31}P, 40.53 MHz), Bruker Avance DRX 500 (^{1}H, 500.13 MHz; ^{13}C, 125.75 MHz; ^{29}Si, 99.53 MHz; ^{31}P, 202.46 MHz) references: $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si), 85% D_3PO_4 (^{31}P).

[Me_2N(*t*Bu)CSMe]I (1b): A solution of iodomethane (9.38 g, 66.1 mmol) in diethyl ether (60 mL) was added dropwise at ambient temp. to an ethereal solution (250 mL) of *t*BuC(S)NMe_2 (9.38 g, 66.1 mmol). Stirring was continued for 24 h. The precipitate was filtered, washed with diethyl ether (2 × 30 mL) and dried in vacuo to give 10.52 g (56%) of **1b** as a white powder. − ^{1}H NMR ($CDCl_3$): $\delta = 1.44$ (s, 9 H, *t*Bu), 2.94 (s, 3 H, SCH_3), 3.76 (s, 6 H, NCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 23.3$ (s, SCH_3), 28.7 [s, $C(CH_3)_3$], 44.3 [s, $C(CH_3)_3$], 49.4 (s, NCH_3), 53.5 (s, NCH_3), 203.7 (s, CH_3SC). − $C_8H_{18}INS$ (287.2): calcd. C 33.46, H 6.32, N 4.88; found C 33.41, H 6.05, N 4.90.

[{3,4,5-$(MeO)_3C_6H_2$}C(NMe_2)SMe]I (1c): A solution of {3,4,5-$(MeO)_3C_6H_2$}C(S)NMe_2 (9.1 g, 35.6 mmol) in diethyl ether (500 mL) was slowly combined with iodomethane (5.06 g, 35.6 mmol). After 24 h of stirring at room temp. it was filtered to afford 6.28 g (44%) of **1c** as a colorless powder. − ^{1}H NMR ($CDCl_3$): $\delta = 2.29$ (s, 3 H, SCH_3), 3.53 (s, 3 H, NCH_3), 3.81 (s, 3 H, *p*-OCH_3), 3.86 (s, 6 H, *m*-OCH_3), 6.99 (s, 2 H, H-phenyl). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 18.7$ (s, SCH_3), 45.8 (s, NCH_3), 49.0 (s, NCH_3), 57.2 (s, *m*-OCH_3), 60.8 (s, *p*-OCH_3), 104.1 (s, C-*o*-phenyl), 124.2 (s, C-*i*-phenyl), 140.1 (s, C-*p*-phenyl), 154.3 (s, C-*m*-phenyl), 190.7 (s, $CSCH_3$). − $C_{13}H_{20}INO_3S$ (397.4): calcd. C 39.30, H 5.07, N 3.53; found C 39.02, H 5.10, N 3.53.

$Me_3SiP=C(Ph)NMe_2$ (2a): To a slurry of [Me_2N(Ph)CSMe]I (**1a**) (27.60 g, 89.8 mmol) in a mixture of *n*-pentane (100 mL) and 1,2-dimethoxyethane (DME) (100 mL) at 0 °C was slowly added a solution of $LiP(SiMe_3)_2 \cdot$ DME (24.70 g, 89.8 mmol) in a mixture of *n*-pentane (70 mL) and DME (70 mL). The dark yellow slurry was warmed to room temp. and stirred for another 16 h. It was filtered, and the filter cake was washed with 30 mL of DME and then with two portions of 30 mL of *n*-pentane. Solvents and volatile components were removed in vacuo to afford a deep orange residue. The crude product was purified by vacuum distillation (bp = 55−75 °C, 5Pa) to give 11.50 g (54%) of **2a** as a light yellow oil, which contained small amounts of $P(SiMe_3)_3$ as an impurity. − ^{1}H NMR (C_6D_6): $\delta = 0.10$ (d, $^3J_{P,H} = 4.7$ Hz, 9 H, $SiCH_3$), 2.20 (s, br, 3 H, NCH_3), 3.07 (s, br, 3 H, NCH_3), 6.96−7.03 (m, 5 H, Ph). − $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 2.5$ (d, $^2J_{P,C} = 16.6$ Hz, $SiCH_3$), 42.1 (s, NCH_3), 42.3 (s, NCH_3), 127.1−128.3 (C-*o*-, *m*-, *p*-phenyl), 143.5 (d, $^2J_{P,C} = 9.0$ Hz, C-*i*-phenyl), 204.7 (d, $^1J_{P,C} = 65.2$ Hz, P=C). − $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -4.1$ (d, $^1J_{P,Si} = 56.1$ Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 54.3$ s. Analytically samples of **2a** could not be obtained due to partial decomposition to $P(SiMe_3)_3$.

$Me_3SiP=C(tBu)NMe_2$ (2b): A slurry of **1b** (7.97 g, 28.0 mmol) in a mixture of 60 mL of *n*-pentane and 30 mL of DME was treated at −30 °C with a solution of $LiP(SiMe_3)_2 \cdot$ DME in 60 mL of a 1:1 mixture of *n*-pentane and DME. Stirring at room temp. was stopped after 3 h, and the slurry was filtered. From the dark yellow filtrate 2.31 g (38%) of yellow **2b** was isolated by distillation (bp: 55−60 °C, 10 Pa). − ^{1}H NMR (C_6D_6): $\delta = 0.31$ (d, $^3J_{P,H} = 13.9$ Hz, 9 H, $SiCH_3$), 1.35 (d, $^3J_{P,H} = 1.2$ Hz, 9 H, *t*Bu), 2.76 (s, 6 H, NCH_3). − $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 2.7$ (d, $^2J_{P,C} = 13.0$ Hz, $SiCH_3$), 31.6 [s, $C(CH_3)_3$], 43.7 [d, $^2J_{P,C} = 25.0$ Hz, $C(CH_3)_3$], 47.80 (s, NCH_3), 219.7 (d, $^1J_{P,C} = 94.1$ Hz, P=C). − $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -3.1$ (d, $^1J_{P,Si} = 74.5$ Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6: $\delta = 68.7$ s. − Analytically pure samples of **2b** could not be obtained. Major impurity is $P(SiMe_3)_3$.

$Me_3SiP=C[3,4,5-(MeO)_3C_6H_2]NMe_2$ (2c): A slurry of **1c** (17.80 g, 45.0 mmol) in a mixture of 50 mL of *n*-pentane and 50 mL of DME was cooled to −70 °C, and a solution of $LiP(SiMe_3)_2 \cdot$ DME (12.40 g, 45.0 mmol) was added dropwise. It was warmed to room temp. and stirred for 4 h. Filtration and removal of volatile components in vacuo led to 8.20 g of crude orange **2c** (56%). The thermolabile oil was contaminated with $P(SiMe_3)_3$ and decomposed completely upon distillation. − ^{1}H NMR (C_6D_6): $\delta = 0.17$ (d, $^3J_{P,H} = 4.5$ Hz, 9 H, $SiCH_3$), 2.34 (s, br, 3 H, NCH_3), 3.15 (s, br, 3H. NCH_3), 3.38 (s, 6 H, *m*-OCH_3), 3.81 (s, 3 H, *p*-OCH_3), 6.27 (s, 2 H, Ph). − $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 2.6$ (d, $^2J_{P,C} = 12.6$ Hz, $SiCH_3$), 42.0 (s, NCH_3), 42.2 (s, NCH_3), 55.7 (s, *m*-OCH_3), 60.7 (s, *p*-OCH_3), 105.5 (d, $^3J_{P,C} = 14.6$ Hz, C-*o*-phenyl), 138.6 (d, $^2J_{P,C} = 9.3$ Hz, C-*i*-phenyl), 138.8 (s, C-*p*-phenyl), 153.7 (s, C-*m*-phenyl), 204.8 (d, $^1J_{P,C} = 65.4$ Hz, P=C). −$^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -4.1$ (d, $^1J_{P,Si} = 56.1$ Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 50.3$ s. Analytically pure samples of **2c** could not be obtained. Major impurity is $P(SiMe_3)_3$.

$Me_3SiP=C(Ph)pip$ (2d): Similarly, crude thermolabile **2d** (2.27 g, 62%) was obtained as an orange oil from **1d** (4.80 g, 13.2 mmol) and $LiP(SiMe_3)_2$ DME (3.79 g, 13.8 mmol) in a mixture of *n*-pentane and DME at −50 °C. Stirring of the resulting yellow slurry at room temp. was maintained for 16 h. − ^{1}H NMR (C_6D_6): $\delta = 0.11$ (d, $^3J_{P,H} = 4.6$ Hz, 9 H, $SiCH_3$), 1.17 (s, br, 6 H, CH_2), 2.70 (s, br, 2 H, NCH_2), 3.90 (s, br, 2 H, NCH_2), 6.98−7.09 (m, 5 H, Ph). − $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 2.5$ (d, $^2J_{P,C} = 14.3$ Hz, $SiCH_3$), 24.5 (s, br, CH_2), 26.8 (s, br, CH_2), 50.9 (s, NCH_2), 127.5−128.8 (C-*o*-, *m*-, *p*- phenyl), 146.6 (d, $^2J_{P,C} = 8.6$ Hz, C-*i*-phenyl), 205.1 (d, $^1J_{P,C} = 64.8$ Hz, P=C). − $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = 3.5$ (d, $^1J_{P,Si} = 57.5$ Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 59.5$ s. Analytically pure samples of **2d** could not be obtained. Major impurity is $P(SiMe_3)_3$.

[(η^5-C_5Me_5)$(CO)_2$FeP=C(Ph)NMe_2] (3a): A solution of **2a** (4.60 g, 19.5 mmol) in DME (30 mL) was added to a slurry of [(η^5-C_5Me_5)-$(CO)_2$FeCl] (5.50 g, 19.5 mmol) in cold *n*-pentane (40 mL, −30 °C).

Table 1. Crystal data and data collection parameters

Compound	**3a**	**3b**	**3g**
formula	$C_{21}H_{26}FeNO_2P$	$C_{19}H_{30}FeNO_2P$	$C_{22}H_{29}FeO_2PSi$
M_r	411.25	391.26	440.36
crystal dimensions [mm]	0.6 × 0.45 × 0.3	0.5 × 0.4 × 0.15	0.25 × 0.15 × 0.15
crystal system	orthorhombic	monoclinic	monoclinic
space group	$Pca2_1$	$P2_1/n$	$P2_1/m$
a [Å]	13.689(5)	10.613(4)	8.820(4)
b [Å]	8.536(2)	12.821(6)	12.567(9)
c [Å]	17.590(4)	15.351(6)	10.804(4)
β [°]	90	104.67(3)	102.93(3)
V [Å^3]	2055.4(10)	2020.7(14)	1167.2(11)
Z	4	4	2
$\rho_{calcd.}$ [Mg m^{-3}]	1.329	1.286	1.253
μ [mm^{-1}]	0.826	0.836	0.779
F(000)	864	832	464
T [K]	173	173	293
2 θ [°]	4.8−60.0	4.2−60.0	3.9−60.0
no refl. collected	6180	6168	7530
no. refl. unique	5691	5883	3562
no. refl. $I > 2\sigma(I)$	4406	4201	1252
R(int)	0.0463	0.0426	0.1527
refined parameters	242	240	142
GOF	1.025	1.033	0.990
R_F [$I > 2\sigma(I)$]	0.0510	0.0543	0.0737
$wR_F{}^2$ [$I > 2\sigma(I)$]	0.1064	0.1291	0.1060
$\Delta\rho$ max/min [e Å^{-3}]	0.384/−0.630	0.915/−0.696	0.4/−0.4

After warming up to ambient temp. the solution was stirred for 16 h. Solvents and volatile components were removed in vacuo to give a dark brown solid residue. This material was triturated with diethyl ether, filtered, and the filter-cake was washed with diethyl ether (2 × 20 mL). The filtrate was concentrated until the appearance of the first crystals and than stored at −28 °C. Product **3a** (5.41 g, 67 mmol) was isolated as dark-red needles. − IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1989 vs, (CO), 1941 vs (CO). − ^{1}H NMR (C_6D_6): δ = 1.46 [s, 15 H, $C_5(CH_3)_5$], 2.91 (s, 3 H, NCH_3), 2.92 (s, 3 H, NCH_3), 7.05−7.53 (m, 5 H, Ph). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.0 [s, $C_5(\mathit{C}H_3)_5$], 43.7 (s, NCH_3), 95.7 [s, $\mathit{C}_5(CH_3)_5$], 126.9−129.8 (s, C-*o*-, *m*-, *p*-phenyl), 146.1 (d, $^2J_{P,C}$ = 7.7 Hz, C-*i*-phenyl), 199.8 (d, $^1J_{P,C}$ = 84.3 Hz, P=C), 218.1 (s, CO). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 232.0 s. − $C_{21}H_{26}FeNO_2P$ (411.3) calcd. C 61.33, H 6.37, N 3.41; found C 61.18, H 6.28, N 3.40.

[(η^5-C$_5$Me$_5$)(CO)$_2$FeP=C(*t*Bu)NMe$_2$] (3b): A slurry of [(η^5-C$_5$Me$_5$)(CO)$_2$FeCl] (1.11 g, 4.0 mmol) in *n*-pentane (20 mL) was combined with the solution of **2b** (0.85 g, 4.0 mmol) in 20 mL of DME. Analogous work-up furnished compound **3b** (0.80 g, 51%) as red needles. − IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1987 vs (CO), 1940 vs (CO). − ^{1}H NMR (C_6D_6): δ = 1.48 [s, 15 H, $C_5(CH_3)_5$], 1.56 [s, 9 H, $C(CH_3)_3$], 2.93 (s, 6 H, NCH_3). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.1 [s, $C_5(\mathit{C}H_3)_5$], 34.0 [d, $^3J_{P,C}$ = 14.6 Hz, $C(\mathit{C}H_3)_3$], 46.4 (s, NCH_3), 48.4 [d, $^2J_{P,C}$ = 28.4 Hz, $\mathit{C}(CH_3)_3$], 96.1 [s, $\mathit{C}(CH_3)_5$], 217.3 (d, $^1J_{P,C}$ = 75.3 Hz, P=C), 218.3 (s, CO). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 409.0 s. − $C_{19}H_{30}FeNO_2P$ (391.3): calcd. C 58.32, H 7.73, N 3.58; found C 58.28, H 7.73, N 3.26.

[(η^5-C$_5$Me$_5$)(CO)$_2$FeP=C[3,4,5-(MeO)$_3$C$_6$H$_2$]NMe$_2$] (3c): Analogously, dark-red crystals (0.55 g, 34%) of **3c** were synthesized from [(η^5-C$_5$Me$_5$)(CO)$_2$FeCl] (0.91 g, 3.2 mmol) and **2c** (1.06 g, 3.2 mmol) in a 1:1 mixture of DME and *n*-pentane at −50 °C. Stirring at room temp. was maintained for 16 h. − IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1971 vs (CO), 1935 vs (CO). − ^{1}H NMR (C_6D_6): δ = 1.45 [s, 15 H, $C_5(CH_3)_5$], 2.99 (s, 3 H, NCH_3), 3.00 (s, 3 H, NCH_3), 3.54 (s, 6 H, *m*-OCH_3), 3.89 (s, 3 H, *p*-OCH_3), 6.75 (s, 2 H, Ph). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.0 [s, $C_5(\mathit{C}H_3)_5$], 4.35 (NCH_3), 42.6 (s, NCH_3), 55.6 (s, *m*-OCH_3), 55.9 (s, *m*-OCH_3), 60.6 (s, *p*-OCH_3), 95.8 [s, $\mathit{C}_5(CH_3)_5$], 107.4 (s, C-*o*-phenyl), 138.6 (s, C-*p*-phenyl), 141.3 (d, $^2J_{P,C}$ = 7.7 Hz, C-*i*-phenyl), 153.5 (s, C-*m*-phenyl). 199.8 (d, $^1J_{P,C}$ = 84.8 Hz, P=C), 218.5 (s, CO). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 225.4 s. − $C_{24}H_{32}FeNO_5P$ (501.3): calcd. C 57.50, H 6.43, N 2.79; found C 57.23, H 6.56, N 2.71.

[(η^5-C$_5$Me$_5$)(CO)$_2$FeP=C(Ph)pip] (3d): Compound **3d** (0.79 g, 38%) resulted as red-brown needles from the reaction of [(η^5-C$_5$Me$_5$)(CO)$_2$FeCl] (1.31 g, 4.6 mmol) and 1.28 g (4.6 mmol) of **2d** in an *n*-pentane/DME mixture at −78 °C. − IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1990 vs (CO), 1941 vs (CO). − ^{1}H NMR (C_6D_6): δ = 1.30−1.51 (m, 6 H, CH_2), 1.45 [s, 15 H, $C_5(CH_3)_5$], 3.44 (t, $^3J_{HH}$ = 5.4 Hz, NCH_2), 7.08−7.62 (m, 5 H, Ph). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.0 [s, $C_5(\mathit{C}H_3)_5$], 24.9 (s, CH_2), 26.2 (s, CH_2), 52.7 (d, $^3J_{P,C}$ = 18.4 Hz, NCH_2), 95.8 [s, $\mathit{C}_5(CH_3)_5$], 127.0−130.0 (C-*o*-, *m*-, *p*-phenyl), 146.5 (d, $^2J_{P,C}$ = 7.2 Hz, C-*i*-phenyl), 201.3 (d, $^1J_{P,C}$ = 82.9 Hz, P=C), 218.0 (s, CO). − ^{31}P{^{1}H} NMR (C_6D_6): δ = 256.4 s. − $C_{24}H_{30}FeNO_2P$ (451.3): calcd. C 63.87, H 6.70, N 3.10; found C 63.77, H 6.50, N 3.07.

X-ray Crystallography: Crystallographic data were collected with a Siemens P2$_1$ four circle diffractometer with Mo-K_α (graphite monochromator, λ = 0.71073 Å). Crystallographic programs used for the structure solution and refinement were from SHELXTL PLUS and SHELXL-97. The structures were solved by Direct Methods and were refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with U(H) = 1.2 U_{eq} for groups, U(H) = 1.5 U_{eq} for CH_3 groups. Crystal data of the compounds are listed in Table 1.[19]

Acknowledgments

This work was generously supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) and the Fonds der Chemischen Industrie (Frankfurt, Main, Germany) which are gratefully acknowledged.

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Received December 14, 1999
[I99458]