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Fumarodinitrile: A Versatile Reagent in Phosphaalkene and Arsaalkene Chemistry

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Reaction of equimolar amounts of the ferriophosphaalkene Cp*(CO)$_2$FeP═C(Ph)NMe$_2$ (**1a**) and fumarodinitrile in diethyl ether afforded the ferriophosphetane Cp*(CO)$_2$FeP−CH(CN)−CH(CN)−C(Ph)NMe$_2$ (**2a**). Analogously, Cp*(CO)$_2$FeP═C(*t*Bu)NMe$_2$ (**1b**) was converted into Cp*(CO)$_2$FeP−CH(CN)−CH(CN)−C(*t*Bu)NMe$_2$ (**2b**). Evidence for the cyclic structure of **2a**,**b** in the crystal was provided by the X-ray structural analysis of **2a**. Whereas the phosphetane ring of **2b** is retained in solution, product **2a** in CH$_2$Cl$_2$ solution underwent an isomerization to give the acyclic secondary ferriophosphane Cp*(CO)$_2$Fe−P(H)−CH(CN)−C(CN)═C(Ph)-NMe$_2$ (**3a**) as a mixture of isomers. The ferriophosphane Cp*(CO)$_2$FeP[CH(CN)−CH$_2$CN]-[CH(CN)−C(CN)═C(*t*Bu)NMe$_2$] (**5**) was isolated in less than 1% yield from the reaction of **1b** and the alkene. The reaction of ferrioarsaalkene Cp*(CO)$_2$FeAs═C(Ph)NMe$_2$ (**6**) and fumaronitrile gave rise to the formation of the ferrioarsetane Cp*(CO)$_2$FeAsCH(CN)−CH-(CN)−C(Ph)NMe$_2$ (**7**), which unlike **2a** resists ring opening in solution.

Introduction

The substitution pattern at a functional group often influences its electron distribution, imposing changes to its structure and chemical reactivity. By this, the synthetic potential of a functionality may be increased considerably. This is particularly obvious in the chemistry of phosphaalkenes, which with alkyl and aryl substituents exhibit a [σ+π] bond polarity P$^{\delta+}$═C$^{\delta-}$ about the P═C double bond.[1] The π-bond itself is essentially nonpolar in these species and thus responsible for their alkene-like reactivity in a variety of cycloadditions. The introduction of one or two amino substituents at the carbon atom of the P═C double bond causes an inversion of the distribution of the [σ+π] electron density as well as of the π-electron density.[2]

We are interested in the chemical consequences of this kind of “umpolung”. In the course of our studies on ferriophosphaalkenes[3] and ferrioarsaalkenes[4] of the type Cp*(CO)$_2$Fe−E═CR^{1}R^2 (E = P, As) we tested their chemical behavior toward electron-deficient alkenes. In a first study we reacted Cp*(CO)$_2$FeP═C(NMe$_2$)$_2$ (**I**), a metallophosphaalkene with an inverse π-electron distribution (P$^{\delta-}$═C$^{\delta+}$), with fumarodinitrile (**II**) and dimethyl fumarate (**III**), which led to the formation of the P-metalated 1,2-dihydrophosphetes **VI** and **VII** with vivid evolution of dimethylamine.[5] In the ^{31}P NMR spectra of the reaction mixture there was no evidence for the hypothetical intermediates **IV** and **V** (Scheme 1). Compound Cp*(CO)$_2$FeP═C(SiMe$_3$)$_2$ (**VIII**),[6] as a typical representative of a phosphaalkene with a classical distribution of electron density, underwent reaction with **II** to afford the dark violet ferriophosphane Cp*-(CO)$_2$Fe−P[CH(SiMe$_3$)$_2$][(*Z*)-C(CN)═CH(CN)] (**IX**) as the result of the formal insertion of the P═C bond into a C−H bond of the alkene and an (*E*)/(*Z*)-isomerization of the latter.[3]

In this paper we give an account on the reactivity of fumarodinitrile toward the ferriophosphaalkenes (*E*)-Cp*(CO)$_2$FeP═C(Ph)NMe$_2$ (**1a**)[7] and (*Z*)-Cp*(CO)$_2$FeP═C(*t*Bu)NMe$_2$ (**1b**)[7] and toward the related arsaalkene (*E*)-Cp*(CO)$_2$FeAs═C(Ph)NMe$_2$ (**6**).[8]

Results and Discussion

Ferriophosphaalkene **1a** was combined with an equimolar amount of fumarodinitrile in diethyl ether at room temperature. Product **2a** separated from the filtered reaction mixture at 4 °C as orange needles in 77% yield (Scheme 2).

Compound **2a** is analogous to the elusive intermediate **IV** in the reaction of **I** with fumarodinitrile. No dimethylamine elimination to yield **4** was observed from **2a**.

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[1] Reviews: (a) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Thieme: Stuttgart, 1990; pp 157−219. (b) Dillon, K. B., Mathey, F.; Nixon, J. F. In *Phosphorus: The Carbon Copy*; Wiley: New York, 1998; pp 88−127.

[2] Review: Weber, L. *Eur. J. Inorg. Chem.* **2000**, 2425−2441.

[3] Review: Weber, L. *Angew. Chem.* **1996**, *108*, 292−310; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 271−288.

[4] Review: Weber, L. *Chem. Ber.* **1996**, *129*, 367−379.

[5] Weber, L.; Kaminski, O.; Stammler, H.-G.; Neumann, B.; Romanenko, V. D. *Z. Naturforsch.* **1993**, *48b*, 1784−1794.

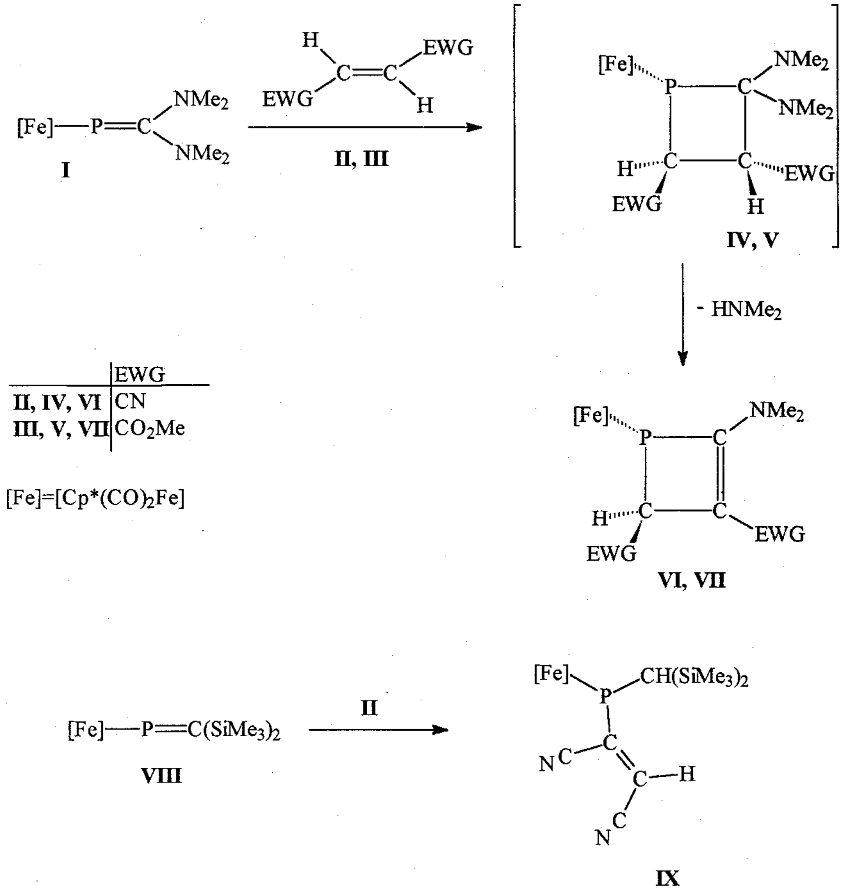
[6] Gudat, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* **1986**, *5*, 593−595.

[7] Weber, L.; Kleinebekel, S.; Rühlicke, A.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **200**, 1185−1191.

[8] Weber, L.; Kleinebekel, S.; Lönnecke, P. *Z. Anorg. Allg. Chem.* **2001**, *627*, 863−868.

10.1021/om010990c CCC: $22.00

Scheme 1



Solutions of compound **2a** in methylene chloride were not stable at ambient temperature, and after 24 h of stirring the metallophosphetane was converted into the secondary metallophosphane **3a** by a ring-opening process. In keeping with this, the $^{31}P\{^{1}H\}$ NMR spectrum of a freshly prepared solution of **2a** displayed singlets at $\delta = 188.3$ and 154.8 in the ratio of 6:3, which we attribute to two isomers of the four-membered heterocycle. In the high-field region of the spectrum four singlets at $\delta = -5.2$, -4.8, -2.5, and 0.8 in the ratio of 4.5:5:1:1 were observed, which indicate the presence of four additional components. In the proton-coupled spectrum the resonances at $\delta = -5.2$ and 0.8 appear as doublets with $J_{PH} = 164.2$ and 162.1 Hz, respectively. The signals at $\delta = -4.8$ and -2.5 were observed as doublets of doublets with $J_{PH} = 158.7$; 8.8 Hz and 151.7; 7.4 Hz. In contrast to this, the resonance at $\delta = 188.3$ was split into a doublet with $J_{PH} = 15$ Hz, whereas the singlet at $\delta = 154.8$ remained unaffected. The size of the J_{PH} couplings is consistent with a PH bond at a tricovalent phosphorus atom, as observed in $[Cp^*(CO)_2FeP(H)C(Ph)NMe_2)]^+$ ($^{1}J_{PH} = 214.4$ Hz).[9] A spectrum of the same sample of **2a** recorded after 24 h showed the complete disappearance of the two low-field signals. The rearrangement of the initial product **2a** to the acyclic phosphane **3a** was also performed on a preparative scale.

As already mentioned in a previous paper, the absence of a π-conjugation between the Me_2N group and the P=C function places (Z)-$Cp^*(CO)_2Fe{-}P{=}C(tBu)NMe_2$ (**1b**) ($\delta^{31}P = 409.0$) in the borderline between inversely polarized phosphaalkenes such as **I** ($\delta^{31}P = 135$)[5] and classically polarized phosphaalkenes such as $Cp^*(CO)_2FeP{=}C(SiMe_3)_2$ (**VIII**) ($\delta^{31}P = 641.5$).[6] The reaction of **1b** and fumarodinitrile furnished the ferriophosphetane **2b** as a single isomer. The product was isolated from diethyl ether at −4 °C as a yellow microcrystalline solid in 53% yield. From the concentrated mother liquor a few crystals of compound **5** separated at 4 °C (yield < 1%) (Scheme 3). Solutions of product **2b** appear to be inert toward ring cleavage at room temperature.

In the $^{31}P\{^{1}H\}$ NMR spectrum of **2b** a singlet was observed at $\delta = 165.6$, which was not further split in the ^{1}H-coupled spectrum. Thus, the cycloaddition of phosphaalkene **1b** is accompanied by a strong high-field shift of $\Delta\delta = 243.4$. The ^{31}P NMR shift of **2a** and **2b** may be compared with the resonances of the metalated P atoms in the P-ferriophosphete **VI**[5] ($\delta = 112.8$) and in the P-ferriodiphosphetane **8** ($\delta = 128.2$).[10] To obtain information on the reactivity of ferrioarsaalkenes toward electron-deficient alkenes, particularly with respect to their phosphorus analogues, ferrioarsaalkene (E)-$Cp^*(CO)_2FeAs{=}C(Ph)NMe_2$ (**6**)[8] was subjected to reaction with fumarodinitrile under comparable conditions. The only tractable product from this process was ferrioarsetane **7**, which was isolated as orange crystals in 50% yield. Inspection of the ^{1}H NMR spectrum of **7** revealed two singlets for the protons of the pentameth-

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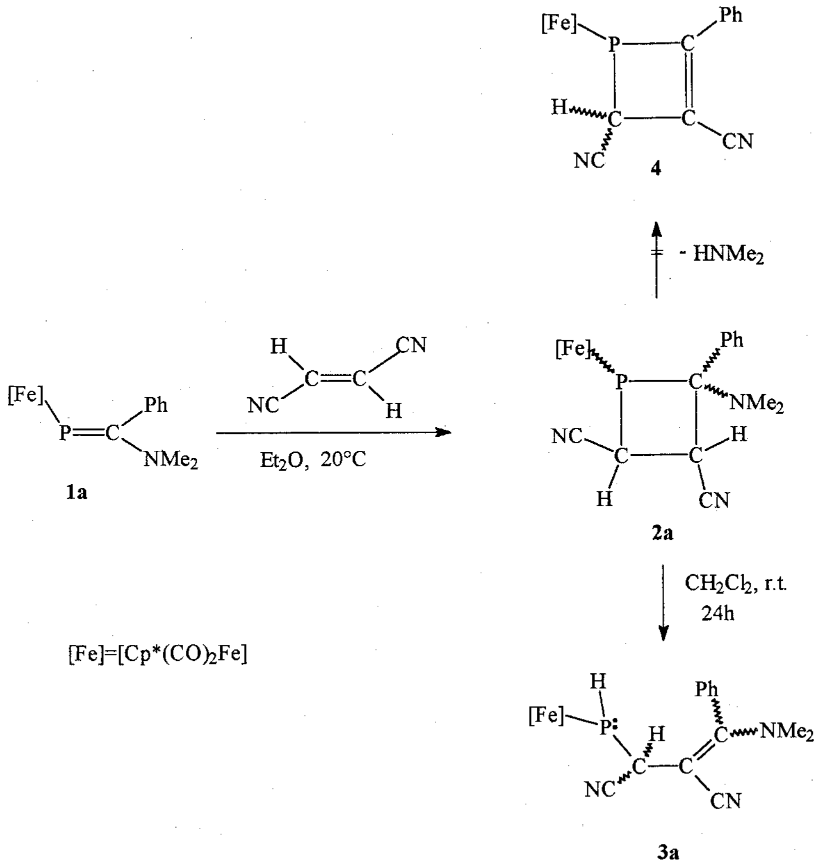
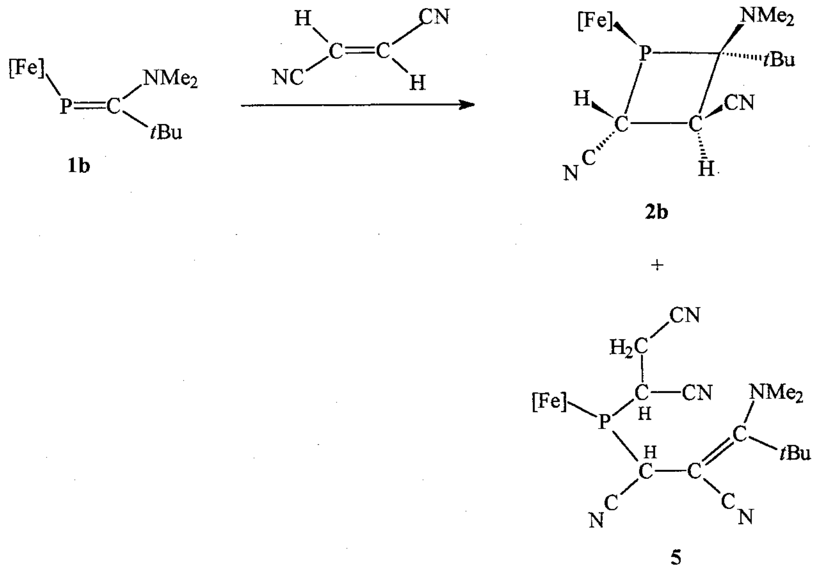
[9] Weber, L.; Scheffer, M. H.; Stammler, H.-G.; Neumann, B.; Schoeller, W. W.; Sundermann, A.; Laali, K. *Organometallics* **1999**, *18*, 4216−4221.

[10] Weber, L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733−738.

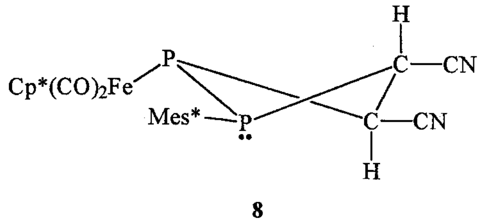
Scheme 2



Scheme 3



ylcyclopentadienyl ring at $\delta = 1.72$ and 1.85, which is due to two isomers **7a** and **7b** in a molar ratio of 2:1 (Scheme 4). In contrast to ferriophosphetane **2a** solutions of **7** did not undergo ring-opening reactions. The molecular structure of the major isomer **7a** was determined by a single-crystal X-ray analysis. Although the poor quality of the crystals, grown from a diethyl ether solution at 4 °C, prevented a precise analysis, the topology of the molecule was revealed beyond any doubt. Its knowledge is useful for the assignment of the spectroscopic data.

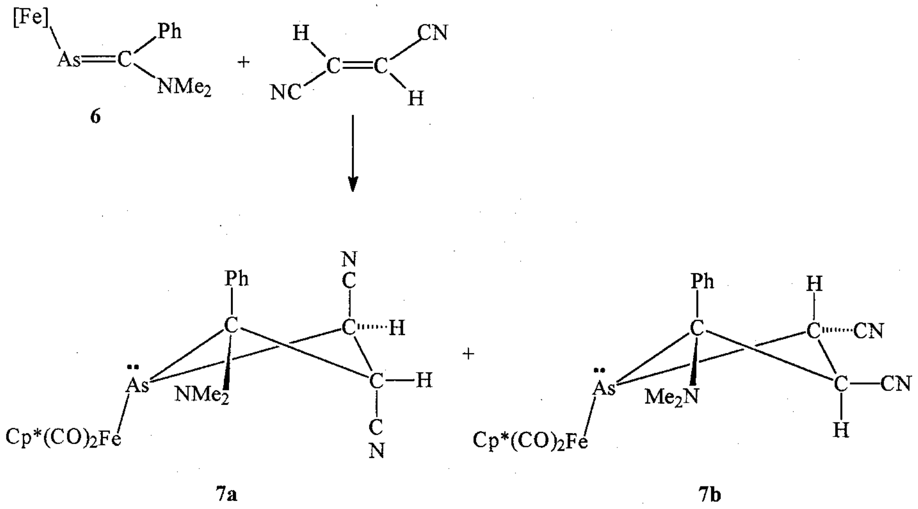


8

Figure 1. Formula of **8**.

The molecule may be described as a puckered As-ferrioarsetane in which the Cp*(CO)$_2$Fe fragment and

Scheme 4



the phenyl group occupy axial positions in a mutual *trans*-orientation. In precursor **6** a *cis*-disposition of these units was observed.[8]

Two axial positions at the ring are occupied by the two *trans*-oriented cyano substituents, leaving the hydrogen atoms in equatorial positions in a mutual *trans*-geometry, which well agrees with the coupling constant $^3J_{HH} = 5.6$ Hz between these protons at $\delta = 3.22$ and 4.96 in the major isomer.

Singlets at $\delta = 1.85$ and 2.06 are attributed to the protons of the Cp* and Me_2N units of the major isomer. In the minor isomer **7b** the protons at the four-membered heterocycle are registered as doublets at $\delta = 3.43$ and 4.43 ($^3J_{HH} = 12.6$ Hz). This coupling constant points to a torsion angle HCCH of nearly 180°, as it is given in a molecule where both hydrogen atom are placed axially.

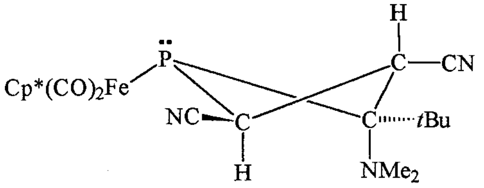
On the grounds of the available data a structural alternative where the iron complex fragment is equatorially linked to the arsenic atom in the minor isomer, however, cannot be excluded.

The IR spectrum of **7** displays intense ν(CO) bands at $\tilde{\nu} = 1992$ and 1943 cm^{-1} and a sharp band of medium intensity at $\tilde{\nu} = 2219$ cm^{-1}, which is assigned to the stretching vibration of the cyano group.

For a more detailed discussion of the spectroscopic and structural features of the (2+2) cycloadducts between compounds **1a**, **1b** and fumarodinitrile it seems appropriate to first consider phosphetane **2b**, which was obtained as a single isomer.

Here a comparison to the structure of ferriophosphetane **8** seems helpful. In the crystal this molecule displays a puckered four-membered cycle in an all-*trans* configuration with the non-hydrogen ligands in equatorial dispositions. This situation led to a $^3J_{HH}$ coupling for the *trans*-oriented ring hydrogen atoms of 10.8 Hz.[10]

Thus, it is reasonable to postulate a similar puckered four-membered ring structure for **2b** with the most bulky substituents in equatorial sites. In keeping with this, the ring hydrogen atom in the α-position of the phosphorus atom is observed as a doublet of doublets at $\delta = 3.36$ with $^3J_{HH} = 11.7$ Hz and $^2J_{PH} = 4.1$ Hz. The ring proton in the β-position of the heteroatom resonates as a doublet of doublets at $\delta = 4.10$ ($^3J_{PH} = 5.7$ Hz; $^3J_{HH} = 11.7$ Hz). Singlets at δ^1H = 0.99, 1.36, and 2.74 are readily assigned to the protons of the *tert*-butyl, Cp*, and NMe_2 groups.



2b

Figure 2. Proposed structure of **2b**.

In the $^{13}C\{^1H\}$ NMR spectrum of **2b** the tertiary ^{13}C nuclei of the heterocycle are observed as doublets at $\delta = 21.2$ ($J_{PC} = 22.6$ Hz) and 34.3 ($J_{PC} = 21.5$ Hz). A doublet at $\delta = 83.1$ ($^2J_{PC} = 25.3$ Hz) is assigned to the quaternary carbon atom in α-position to the phosphorus atom. The cyano groups give rise to doublets at $\delta = 118.6$ ($^2J_{PC} = 18.4$ Hz) and 121.4 ($^3J_{PC} = 13.8$ Hz). Singlets at $\delta = 217.1$ and 217.7 are caused by the terminal carbonyl ligands. The IR spectrum of **2b** is dominated by two intense bands at $\tilde{\nu} = 1993$ and 1939 cm^{-1} for the stretching vibrations of the CO ligands. In precursor **1b** these bands were observed at $\tilde{\nu} = 1987$ and 1940 cm^{-1}. A sharp band of medium intensity at $\tilde{\nu} = 2223$ cm^{-1} is due to the ν(CN) mode.

In the ^{1}H NMR spectrum of a freshly prepared solution of **2a** the resonances of both isomers of the four-membered ring are revealed in addition to those of the rearranged species **3a**. Singlets at $\delta = 2.22$ and 2.54 in a ratio of 1:2 are readily assigned to the hydrogen atoms of the dimethylamino group in both isomers. A doublet of doublets at $\delta = 3.91$ ($^2J_{PH} = 15.1$ Hz, $^3J_{HH} = 8.8$ Hz) and a doublet at $\delta = 4.64$ ($^3J_{HH} = 8.8$ Hz) are due to the *trans*-oriented ring hydrogen atoms of the major isomer, whereas the corresponding resonances in the minor isomer are observed as a pseudo-triplet at $\delta = 3.42$ ($J = 6.1$ Hz) and as a doublet at $\delta = 4.65$ ($J = 6.1$ Hz). The molecular structure of the major isomer confirms these assignments. The IR spectrum of **2a** shows two intense ν(CO) bands at $\tilde{\nu} = 1998$ and 1948 cm^{-1} and a sharp ν(CN) band of medium intensity at $\tilde{\nu} = 2225$ cm^{-1}.

Orange needles, obtained from the ethereal reaction mixture at 4 °C, were subjected to an X-ray structure

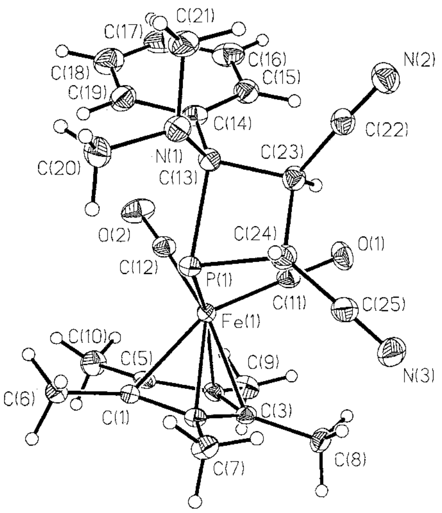


Figure 3. Molecular structure of **2a** in the crystal (hydrogens omitted, 50% probability thermal ellipsoids).

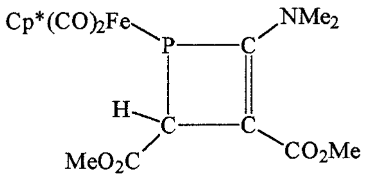
determination. The analysis reveals two independent molecules in the asymmetric unit. As the bonding parameters of both molecules do not differ significantly, the discussion is confined to only one molecule. The analysis displays the picture of a puckered phosphetane (torsion angles: C(24)−P(1)−C(13)−C(23) = 21.4°; P(1)−C(13)−C(23)−C(24) = −26.5°; C(13)−P(1)−C(24)−C(23) = −22.0°; C(13)−C(23)−C(24)−P(1) = 26.7°) which is attached to the $Cp^{*}(CO)_2Fe$ fragment via an Fe−P single bond of 2.297(1) Å.

The latter adopts a distorted piano stool configuration with two nearly linear terminal carbonyl ligands [O(1)−C(11)−Fe = 176.4(3)°; O(2)−C(12)−Fe = 171.0(3)°]. The most interesting feature of the structure is the geometry of the organophosphorus ligand. The complex iron group and the dimethyl amino substituent at the ring are placed axially in a mutual *trans*-disposition. Consistently, the phenyl group is *cis*-oriented to the metal in an equatorial ring position. A similar stereochemistry is present in precursor **1a**, and these results agree with the NMR data of the major isomer.

The 1,2-dicyanoethylene fragment of the heterocycle maintained the *trans*-configuration of the free fumarodinitrile. Interestingly, both cyano groups are located equatorially with a torsion angle C(22)−C(23)−C(24)−C(25) = −81.6°. The iron atom and the cyano group C(25)−N(3) as well as the amino group and the cyano unit C(22)−N(2) are in mutual *cis*-dispositions. The hydrogen atoms at C(23) and C(24) are axially located, featuring a torsion angle H(23A)−C(23)−C(24)−H(24A) of 164.5°. The endocyclic distances C(13)−C(23) [1.569(4) Å] and C(23)−C(24) [1.526(4) Å] are consistent with the standard value of a C−C-single bond [1.55 Å].

In contrast to this, the endocyclic PC distances P(1)−C(24) [1.926(3) Å] and P(1)−C(13) [1.943(4) Å] clearly exceed the standard value of PC single bonds [1.85 Å]. Such elongated PC bonds are not unusual in four-membered phosphorus−carbon heterocycles.

In **9** the corresponding PC bond length is 1.920(3) Å,[5] whereas in **10** and **11** PC distances of 1.918(3), 1.930(3), or 1.931(12)−1.967(12) Å were determined.[11] The P atom is trigonal pyramidal with bond angles ranging from 73.8(1)° [C(24)−P(1)−C(13)] to 116.4(1)° [Fe(1)−P(1)−C(13)] (sum of angles = 302.5°). The endocyclic angle C(24)−P(1)−C(13) is significantly compressed in comparison to the endocyclic angles at C(13) [88.3(2)°], C(23) [97.3(2)°], and C(24) [90.2(2)°]. This situation is comparable to endocyclic angles in **10** [at the P atoms 77.2(2)° and 76.9(2)° and at the C atoms 94.2(3)° and 93.9(3)°]. As indicated by the ^{31}P NMR data, compound **3a** was formed as a mixture of four stereoisomers. In line with the parameters taken from the ^{1}H-coupled ^{31}P NMR spectrum it is possible to also analyze the ^{1}H NMR spectrum of the acyclic phosphanes. The protons at the phosphorus atom of the major isomers of **3a** are assigned to doublets of doublets at $\delta = 2.62$ ($^{1}J_{PH} = 164.0$, $^{2}J_{PH} = 5.7$ Hz) and $\delta = 3.18$ ($^{1}J_{PH} = 162.8$, $^{2}J_{PH} = 8.8$ Hz). A doublet of doublets at $\delta = 3.23$ ($^{3}J_{HH} = 5.7$, $^{2}J_{PH} = 3.6$ Hz) and a triplet at $\delta = 2.68$ ($|J| = 8.8$ Hz) are due to the protons at the carbon atoms in the α-position of the P atoms.



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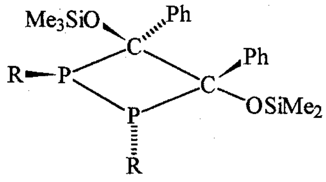

10 R= iPr

11 R=CH2Ph

We attribute singlets at $\delta = 2.88$, 2.89, 2.97, and 2.98 to the methyl protons of the amino groups. The protons at the Cp* rings of the major isomers give rise to singlets at $\delta = 1.66$ and 1.75, whereas singlets at $\delta = 1.78$ and 1.85 are caused by the methyl groups at the ring ligand of the minor isomers.

The $^{13}C\{^{1}H\}$ NMR spectrum of **3a** shows doublets at $\delta = 9.3$ ($^{3}J_{PC} = 5.7$ Hz) and $\delta = 9.4$ ($^{3}J_{PC} = 8.0$ Hz) for the methyl groups of the Cp* ligands of the major isomers. The quaternary carbon atoms of the ring ligand resonate as singlets at $\delta = 96.5$ and 96.8.

Doublets at $\delta = 23.8$ ($^{1}J_{PC} = 37.9$ Hz), 24.8 ($^{1}J_{PC} = 33.3$ Hz), 25.5 ($^{1}J_{PC} = 39.7$ Hz), and 26.8 ($^{1}J_{PC} = 32.3$ Hz) were due to the carbon atoms in α-position to the P atom in the two minor and the two major isomers, respectively. The methyl groups of the amino functions give rise to singlets at $\delta = 42.9$ and 43.5 for the major and the minor isomers, respectively. The cyano-substituted olefinic carbon atoms of **3a** were observed as doublets at $\delta = 78.1$ ($^{2}J_{PC} = 11.4$ Hz) and $\delta = 78.6$ ($^{2}J_{PC} = 8.0$ Hz), whereas the amino-substituted olefinic carbon atoms gave rise to singlets at $\delta = 161.7$ and 162.1 for the major and at $\delta = 162.5$ and 163.1 for the minor isomers of **3a**. The ^{13}C nuclei of the cyano substituents were observed in the range $\delta = 120.6-122.4$.

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[11] Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur* **1983**, *14*, 267−283.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 2a in the Crystal

Fe(1)−C(11)	1.750(3)
Fe(1)−C(12)	1.769(3)
Fe(1)−P(1)	2.297(1)
P(1)−C(24)	1.926(3)
P(1)−C(13)	1.943(4)
O(1)−C(11)	1.158(4)
O(2)−C(12)	1.152(4)
N(1)−C(20)	1.463(4)
N(1)−C(21)	1.466(4)
N(1)−C(13)	1.477(4)
N(2)−C(22)	1.142(4)
N(3)−C(25)	1.152(4)
C(13)−C(14)	1.508(4)
C(22)−C(23)	1.488(4)
C(23)−C(24)	1.526(4)
C(24)−C(25)	1.445(4)
C(11)−Fe(1)−C(12)	94.4(1)
C(11)−Fe(1)−P(1)	95.4(1)
C(12)−Fe(1)−P(1)	96.0(1)
C(24)−P(1)−C(13)	73.8(1)
C(24)−P(1)−Fe(1)	112.2(1)
C(13)−P(1)−Fe(1)	116.4(1)
C(20)−N(1)−C(21)	108.5(2)
C(20)−N(1)−C(13)	119.4(2)
C(21)−N(1)−C(13)	113.9(2)
O(1)−C(11)−Fe(1)	176.4(3)
O(2)−C(12)−Fe(1)	171.0(3)
N(1)−C(13)−C(14)	115.4(3)
N(1)−C(13)−C(23)	107.8(2)
C(14)−C(13)−C(23)	114.8(2)
N(1)−C(13)−P(1)	108.4(2)
C(14)−C(13)−P(1)	118.7(2)
C(23)−C(13)−P(1)	88.3(2)
N(2)−C(22)−C(23)	176.1(3)
C(22)−C(23)−C(24)	116.4(2)
C(22)−C(23)−C(13)	117.8(2)
C(24)−C(23)−C(13)	97.3(2)
C(25)−C(24)−C(23)	116.7(3)
C(25)−C(24)−P(1)	121.2(2)
C(23)−C(24)−P(1)	90.2(2)
N(3)−C(25)−C(24)	178.3(3)
C(24)−P(1)−C(13)−C(23)	21.4
P(1)−C(13)−C(23)−C(24)	−26.5
C(31)−P(1)−C(24)−C(23)	−22.0
C(13)−C(23)−C(24)−P(1)	26.7
Fe(1)−P(1)−C(13)−N(1)	166.0
Fe(1)−P(1)−C(13)−C(14)	31.7
Fe(1)−P(1)−C(24)−C(25)	−31.4
C(14)−C(13)−C(23)−C(22)	87.4
N(1)−C(13)-C(23)−C(22)	−42.8
C(22)−C(23)−C(24)−C(25)	−81.6
H(23A)−C(23)−C(24)−H(24A)	164.5

The IR spectrum of solid **3a** displays two very strong ν(CO) bands at 1938 and 1991 cm^{-1} and a strong band at $\nu = 1553$ cm^{-1} for the stretching vibration of the polar olefinic double bond. Sharp bands of low intensity at $\nu = 2184$ and 2222 cm^{-1} are assigned to the ν(C≡N) stretching vibrations, whereas a weak absorption at $\nu = 2364$ cm^{-1} may be due to a ν(PH) mode. Additional evidence for the acyclic structure of **3a** in solution comes from the X-ray structural analysis of **5**, which formally would result from the insertion of fumarodinitrile into the PH bond of an acyclic isomer of **2b**, although this molecule could not be detected spectroscopically in the reaction mixture.

Single crystals of **5** were obtained from diethyl ether at 4 °C. The analysis (Figure 4, Table 2) displays a molecule with a distorted piano stool geometry [C(11)−Fe(1)−P(1) = 93.8(1)°; C(12)−Fe(1)−P(1) = 97.4(1)°; C(11)−Fe(1)−C(12) = 93.1(1)°] with two nearly linear carbonyl ligands [Fe(1)−C(11)−O(1) = 178.0(2)°; Fe(1)−C(12)−O(2) = 174.4(2)°]. The most interesting part of

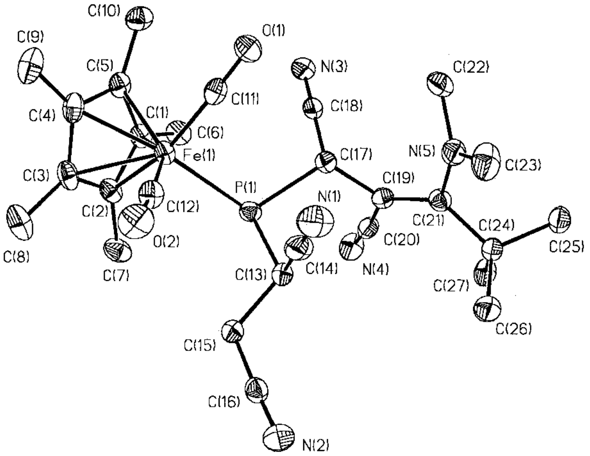
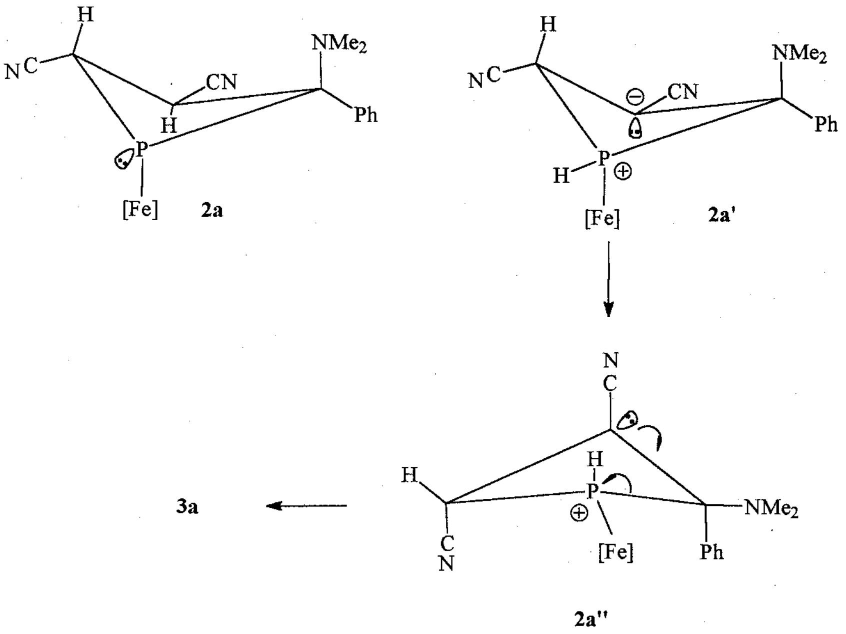


Figure 4. Molecular structure of **5** in the crystal (hydrogens omitted, 50% probability thermal ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 5 in the Crystal

Fe(1)−C(12)	1.759(2)
Fe(1)−C(11)	1.759(2)
Fe(1)−P(1)	2.296(1)
P(1)−C(13)	1.893(2)
P(1)−C(17)	1.921(2)
O(1)−C(11)	1.152(2)
O(2)−C(12)	1.150(2)
N(1)−C(14)	1.145(2)
N(2)−C(16)	1.152(3)
N(3)−C(18)	1.147(2)
N(4)−C(20)	1.149(2)
N(5)−C(21)	1.383(2)
N(5)−C(23)	1.456(3)
N(5)−C(22)	1.458(3)
C(13)−C(14)	1.475(3)
C(13)−C(15)	1.545(3)
C(15)−C(16)	1.464(3)
C(17)−C(18)	1.469(2)
C(17)−C(19)	1.531(2)
C(19)−C(21)	1.380(2)
C(19)−C(20)	1.436(2)
C(21)−C(24)	1.546(2)
C(12)−Fe(1)−C(11)	93.1(1)
C(12)−Fe(1)−P(1)	97.4(1)
C(11)−Fe(1)−P(1)	93.8(1)
C(13)−P(1)−C(17)	93.5(1)
C(13)−P(1)−Fe(1)	112.8(1)
C(17)−P(1)−Fe(1)	108.7(1)
C(21)−N(5)−C(23)	125.2(2)
C(21)−N(5)−C(22)	121.6(2)
C(23)−N(5)−C(22)	113.2(2)
O(1)−C(11)−Fe(1)	178.0(2)
O(2)−C(12)−Fe(1)	174.4(2)
C(14)−C(13)−C(15)	112.2(2)
C(14)−C(13)−P(1)	112.1(1)
C(15)−C(13)−P(1)	108.8(1)
N(1)−C(14)−C(13)	175.0(2)
C(16)−C(15)−C(13)	112.1(2)
N(2)−C(16)−C(15)	177.4(3)
C(18)−C(17)−C(19)	112.4(2)
C(18)−C(17)−P(1)	107.0(1)
C(19)−C(17)−P(1)	112.6(1)
N(3)−C(18)−C(17)	178.4(2)
C(21)−C(19)−C(20)	126.6(2)
C(21)−C(19)−C(17)	121.8(2)
C(20)−C(19)−C(17)	111.6(1)
N(4)−C(20)−C(19)	172.6(2)
C(19)−C(21)−N(5)	117.2(2)
C(19)−C(21)−C(24)	125.0(2)
N(5)−C(21)−C(24)	117.8(1)

Scheme 5



the molecule is the organophosphorus ligand which is connected to the metal by an Fe−P single bond of 2.296(1) Å. The trigonal pyramidal phosphorus atom (sum of angles = 314.9°) is further linked to the two different organosubstituents by long PC single bonds [P(1)−C(13) = 1.893(2) Å; P(1)−C(17) = 1.921(2) Å]. The dimethylamino group and the cyano substituent C(20)−N(4) are located in a *cis*-disposition at a long C−C double bond [C(19)−C(21) (1.380(2) Å; cf. *d*(C=C) in C_2H_4 = 1.353 Å].[12] This bond lengthening may be explained by π-conjugation of the bond pair at the planar nitrogen atom N(5) (sum of angles = 360°) into the cyano group. Accordingly, bond N(5)−C(21) [1.383(2) Å] is shorter than a single bond between sp^2-hybridized N and C atoms (1.45 Å),[13] and bond C(19)−C(20) [1.436(2) Å] is shorter when compared to the C−C bonds involving the remaining cyano units of the molecule [C(13)−C(14) = 1.475(3) Å; C(15)−C(16) 1.464(3) Å; C(17)−C(18) = 1.469(2) Å].

Conclusions

Reaction of fumarodinitrile with ferriophosphaalkenes and a ferrioarsaalkene featuring different substituents at the carbon atoms of the P=C bond provides a convenient access to a variety of novel metalated organophosphorus and organoarsenic compounds. The present study has served to get some insight into the complexity of this two-component reaction.

Ferriophospha- and ferrioarsaalkenes with amino substituents at the tricoordinate carbon atom and fumarodinitrile undergo a [2+2] cycloaddition to afford phosphetanes and arsetanes as the initial products. In the cases of geminal bis-amino substitution as given in **IV** and **V** (Scheme 1) it is conceivable that the elimination of dimethylamine is induced by traces of acid. The transient carbenium ion is efficiently stabilized by the remaining amino group before deprotonation in the α-position occurs. Phosphaalkenes and arsaalkenes with only one amino group at the E=C backbone can no longer form such amino-stabilized carbenium ions. Consequently, an R_2NH elimination pathway is nonattractive and heterocycles **2b** and **7** are the final products. Ring cleavage of **2a** resulting in the formation of **3a** may be initiated by a proton transfer to the phosphorus atom to give **2a′**. Ring bending leads to conformation **2a″**, where the lone pair at carbon and the P−C bond to be broken adopt an anti-periplanar orientation. Conformation **2a″** implies an axial ring position for the phenyl group. With **2b** an analogous conformation **2b″** with the bulky *tert*-butyl group in an axial position as a prerequisite for ring cleavage is energetically unfavorable and does not occur. One reason an analogous ring opening is not observed with heterocycle **7** may be explained by the smaller bond energy of an AsH bond (245 kJ/mol) versus a PH bond (322 kJ/mol).[14]

Experimental Section

All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under N_2 prior to use. Infrared spectra were recorded with a Bruker FT-IR VECTOR 22 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were registered at 22 °C using Bruker AC 100 (^1H, 100.13 MHz, ^{31}P, 40.53 MHz) and Bruker AM Avance DRX 500 (^1H, 500.13 MHz, ^{13}C, 125.76 MHz, ^{31}P, 200.46 MHz). References: $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P).

Elemental analyses were performed at the microanalytical laboratory of the University of Bielefeld and at Mikroanalytisches Laboratorium H. Kolbe, Mülheim/Ruhr. Compounds $Cp^*(CO)_2FeP{=}C(Ph)NMe_2$ (**1a**),[7] $Cp^*(CO)_2FeP{=}C(tBu)NMe_2$ (**1b**),[7] and $Cp^*(CO)_2FeAs{=}C(Ph)NMe_2$ (**6**)[8] were synthesized according to literature procedures. Fumarodinitrile was purchased commercially.

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(12) Staab, H. A. *Einführung in die theoretische organische Chemie*, 4th ed.; Verlag Chemie: Weinheim, 1966; pp 68−69.

(13) Chernega, A. N.; Ruban, A. V.; Romanenko, V. D.; Markovskii, L. N.; Korkin, A. A.; Antipin, M. Y.; Struchkov, Y. T. *Heteroat. Chem.* **1991**, *2*, 229−241.

(14) Pauling, L. *Grundlagen der Chemie*, 8th ed.; Verlag Chemie: Weinheim, 1969; p 795.

Preparation of Compounds: [Cp*(CO)$_2$FePCH(CN)CH(CN)C(Ph)NMe$_2$] (2a). At 20 °C a solution of 0.08 g (1.0 mmol) of fumarodinitrile in 10 mL of diethyl ether was added dropwise to a solution of **1a** (0.41 g, 1.0 mmol) in 40 mL of diethyl ether. After 1 h of stirring the solution was filtered and the filtrate was stored for 3 days at 4 °C to afford orange needles of product **2a** (yield: 0.38 g, 77%). IR (KBr, cm^{-1}) ν: 2224 (m, CN), 1997 (vs, FeCO), 1947 (vs, FeCO). ^{1}H NMR (C_6D_6): δ 1.67 (s, 15H, $C_5(CH_3)_5$), 2.22s and 2.54 (s, 6H, $N(CH_3)_3$), 3.42 ("t", $J = 6.1$ Hz) and 3.91 (dd, $J = 15.1$, 8.8 Hz, 1H, PCH), 4.64 (d, $J = 8.8$ Hz) and 4.65 (d, $J = 6.1$ Hz, 1H, PCCH), 7.08−7.50 (m, 5H, Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 154.8 (s, minor isomer), 188.3 (s, major isomer). MS/ESI(+): *m/z* 490 (MH$^+$), 462 (MH$^+$ − CO), 434 (MH$^+$ − 2CO). Anal. Calcd for $C_{25}H_{28}FeN_3O_2P$(489.34): C, 61.36; H, 5.77; N, 8.58. Found: C, 61.34; H, 5.84; N, 8.39.

Cp*(CO)$_2$FePH−CH(CN)−C(CN)═C(Ph)NMe$_2$ (3a). A solution of freshly prepared **2a** (0.38 g, 0.8 mmol) in 20 mL of methylene chloride was stirred at ambient temperature for 24 h. At that time in the ^{31}P{^{1}H} NMR spectrum of the mixture the signals of **2a** had completely disappeared. Solvent and volatile components were removed in vacuo to give quantitatively **3a** as a light yellow solid. IR (KBr, cm^{-1}): ν 2364 (w, PH), 2222 (w-m, CN), 2184 (m, CN), 1991 (vs, FeCO), 1938 (vs, FeCO), 1553 (s, C═C). ^{1}H NMR (CD_2Cl_2): δ 1.66s, 1.75s, 1.78s, and 1.85 (s, 15H, $C_5(CH_3)_5$); 2.62 (dd, $^{1}J_{PH} = 164.0$, $^{2}J_{PH} = 5.7$ Hz) and 3.18 (dd, $^{1}J_{PH} = 8.8$ Hz, 1H, PH), 2.88s, 2.89s, 2.97s, and 2.89 (s, 6H, $N(CH_3)_2$), 2.68 ("d", $|J| = 8.8$ Hz and 3.23 (dd,$^{3}J_{HH} = 5.7$, $^{2}J_{PH} = 3.6$ Hz, 1H, PCH), 7.29−7.47 (m, 5H, Ph-H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.3 (d, $^{3}J_{PC} = 5.7$ Hz), 9.4 (d, $^{3}J_{PC} = 8.0$ Hz), 9.5s, 9.6(s, $C_5(CH_3)_5$), 23.8 (d, $^{1}J_{PC} = 37.9$ Hz, PCH), 24.8 (d, $^{1}J_{PC} = 33.3$ Hz, PCH), 25.5 (d, $^{1}J_{PC} = 40.2$ Hz, PCH), 26.8 (d, $^{1}J_{PC} = 32.3$ Hz, PCH), 42.9s and 43.5 (s, $N(CH_3)_2$), 78.1 (d, $^{2}J_{PC} = 11.4$ Hz, C═*C*−CN) 78.6 (d, $^{2}J_{PC} = 8.0$ Hz, C═*C*−CN); 120.7 (d, $^{2}J_{PC} = 20.7$ Hz, PCH*C*N), 121.2 (d, $^{2}J_{PC} = 19.9$ Hz, PCH*C*N), 121.8 (d, $^{2}J_{PC} = 20.7$ Hz, PCH*C*N) 122.0s and 122.4s (C═C−*C*N); 128.9, 129.3, 129.4, 130.3, 130.4, 130.8 (*C*-Ph), 135.2s, 135.4s, 136.2s, 136.3 (s, i-*C*-Ph), 161.7s, 162.1s, 162.5s, and 163.1 (s, *C*═C−CN), 215.8, 216.0, 216.3, 216.7, 216.8, 216.9 (FeCO). ^{31}P NMR (CD_2Cl_2): δ −5.2 (d, $^{1}J_{PH} = 164.2$ Hz, PH), −4.8(dd, $^{1}J_{PH} = 158.7$, $^{2}J_{PH} = 8.8$ Hz, PH), −2.5 (dd, $^{1}J_{PH} = 151.7$ Hz, $^{2}J_{PH} = 7.4$ Hz, PH), 0.8 (d, $^{1}J_{PH} = 162.1$ Hz, PH). MS/ESI (+): *m/z* 490 (MH$^+$), 462 (MH$^+$ − CO), 434 (MH$^+$ − 2CO). Anal. Calcd for $C_{25}H_{28}FeN_3O_2P$ (489.34): C, 61.36; H, 5.77; N, 8.58. Found: C, 61.44; H, 5.71; N, 8.46.

Cp*(CO)$_2$FeP−CH(CN)CH(CN)C(*t*Bu)NMe$_2$ (2b) and Cp*(CO)$_2$FeP[CH(CN)−CH$_2$CN][CH(CN)−C(CN)═C(*t*Bu)-NMe$_2$] (5). A solution of fumarodinitrile (0.05 g, 0.6 mmol) in 10 mL of diethyl ether was added dropwise to a chilled solution (−40 °C) of **1b** in 30 mL of diethyl ether. It was warmed to ambient temperature and stirred for 24 h. Solvent and volatile components were removed in a vacuum, and the residue was triturated with 20 mL of diethyl ether. It was filtered, and the filter cake was washed with diethyl ether (4 × 5 mL). The filtrate was concentrated to ca. 20 mL and stored at 4 °C, whereupon **2b** (0.15 g, 53%) separated as a yellow powder. After filtration the mother liquor was concentrated to 10 mL and stored at 4 °C to afford a small amount of a yellow precipitate, consisting of **2b** and **5.** Upon recrystallization from diethyl ether, a few yellow needles (yield < 1%) of **5** were obtained. **2b**: IR (KBr, cm^{-1}): ν 2223 (m, CN), 1993 (vs, FeCO), 1939 (vs, FeCO). ^{1}H NMR (C_6D_6): δ 0.99 (s, 9H, $C(CH_3)_3$), 1.36 (s, 15H, $C_5(CH_3)_5$), 2.74 (s, 6H, $N(CH_3)_2$), 3.36 (dd, $^{3}J_{HH} = 11.7$, $^{2}J_{PH} = 4.1$ Hz, 1H, PCH), 4.10 (dd, $^{3}J_{HH} = 11.7$, $^{3}J_{PH} = 5.7$ Hz, 1H, PCCH). ^{13}C{^{1}H} NMR (C_6D_6): δ 8.9s, $C_5(CH_3)_5$), 21.2 (d, $^{1}J_{PC} = 22.6$ Hz, PCH), 29.8 (d, $^{3}J_{PC} = 8.0$ Hz, $C(CH_3)_3$), 34.3 (d, $^{2}J_{PC} = 21.5$ Hz, PC*C*H), 42.4 (d, $^{2}J_{PC} = 18.1$ Hz, $C(CH_3)_3$), 45.0 (s, $N(CH_3)_2$), 83.1 (d, $|J_{PC}| = 25.3$ Hz, P*C*N), 118.6 (d, $^{2}J_{PC} = 18.4$ Hz, PC*C*N), 121.4 (d, $^{3}J_{PC} = 13.8$ Hz, PCC*C*N), 217.1 (s, FeCO), 217.7 (s, FeCO). ^{31}P{^{1}H}NMR (C_6D_6): δ 165.6s. Anal. Calcd for $C_{23}H_{32}FeN_3O_2P$ (469.34): C, 58.86; H, 6.87; N 8.95. Found: C, 58.26; H, 7.10; N 8.83.

5: δ ^{31}P NMR (C_6D_6): isomer a: δ 204.9 ($^{2}J_{PH} = 13.8$ Hz); isomer b: 206.3 ($^{2}J_{PH} = 13.8$ Hz); **5a**:**5b** = 10:1. Due to the small amount of material, no further spectra or elemental analyses could be provided.

Cp*(CO)$_2$FeAsCH(CN)CH(CN)C(Ph)NMe$_2$ (7). Analogously to the preparation of **2a** 0.21 g (50%) of orange crystalline **7** was obtained from the reaction of 0.37 g (0.8 mmol) of **6** and 0.06 g (0.8 mmol) of fumarodinitrile in 35 mL of diethyl ether. IR (KBr, cm^{-1}): ν 2219 (m, CN), 1992 (vs, FeCO), 1943 (vs, FeCO). ^{1}H NMR (C_6D_6): δ 1.72s and 1.85 (s, 15H, $C_5(CH_3)_5$), 2.06s and 2.46 (s, 6H, $N(CH_3)_2$), 3.22 (d, $^{3}J_{HH} = 5.6$ Hz) and 3.43 (d, $^{3}J_{HH} = 12.6$ Hz, 1H, AsCH), 4.43 (d, $^{3}J_{HH} = 12.6$ Hz) and 4.96 (d, $^{3}J_{HH} = 5.6$ Hz, 1H, AsCCH), 7.20−7.64 (m, 5H, H−Ph). ^{13}C{^{1}H}NMR (CD_2Cl_2): δ. 7.9 (s, AsCH), 9.3 (s, $C_5(CH_3)_5$), 39.4 (s,AsC−*C*), 43.0 (s, $N(CH_3)_2$), 65.6 (s, AsCN), 97.4 (s, $C_5(CH_3)_5$), 121.3 (s, CN), 122.9 (s, CN), 122.95s, 125.9s, and 128.5 (s, *C*-Ph), 141.5 (s, *i*-C−Ph), 214.9 (s, FeCO), 217.5 (s, FeCO). Anal. Calcd for $C_{25}H_{28}AsFeN_3O_2$ (533.28): C, 56.31; H, 5.29, N, 7.88. Found: C, 56.34, H, 5.36, N, 7.73.

X-ray Structural Analysis of 2a. Single crystals of **2a** were grown from diethyl ether at 4 °C. An orange crystal of the approximate dimensions of 0.28 × 0.12 × 0.06 mm was measured on a Nonius Kappa CCD system with Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Crystal data and refinement details: space group $Pca2_1$, cell dimensions $a = 16.4240(2)$ Å, $b = 14.0020(2)$ Å, $c = 20.2780(3)$ Å, $V = 4663.31(11)$ Å^3 (refined from 5773 reflections), $Z = 8$, $d_{calcd} = 1.394$ g cm^{-3}, $\mu = 0.743$ mm^{-1}, absorption correction: multiscan max/min transmission 0.9568/0.8190. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-97, 50 786 intensities collected, 10 126 unique ($R_{int} = 0.046$) and 9073 with $I > 2\sigma(I)$, 578 parameters, hydrogen atoms treated as riding groups, *R*-indices for reflections with $I > 2\sigma(I)$: $R_F = 0.0376$; w$R_{F^2} = 0.0917$, GooF(F^2) = 1.060, maximum/minimum residual densities 0.986 and −0.588 e Å^{-3}.

X-ray Structural Analysis of 5. Single crystals of **5** were grown from diethyl ether at 4 °C. A yellow crystal of the approximate dimensions of 1.20 × 0.80 × 0.06 mm was measured on a Nonius Kappa CCD system with Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Crystal data and refinement details: space group $P\bar{1}$, all dimensions $a = 9.8590(1)$ Å, $b = 9.8900(1)$ Å, $c = 14.3870(2)$ Å, $\alpha = 76.2420(5)°$, $\beta = 89.5180(5)°$, $\gamma = 86.3360(6)°$, $V = 1359.75(3)$ Å^3 (refined from 6204 reflections), $Z = 2$, $d_{calcd} = 1.337$ g cm^{-3}, $\mu = 0.646$ mm^{-1}, absorption correction: multiscan max/min transmission 0.9622/0.5109. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-97, 44 023 intensities collected, 6210 unique ($R_{(int)} = 0.045$) and 5014 with $I > 2\sigma(I)$, 348 parameters, hydrogen atoms treated as riding groups, *R*-indices for reflections with $I > 2\sigma(I)$: $R_F = 0.0338$; $wR_{F^2} = 0.0793$, GooF(F^2) = 1.021, maximum/minimum residual electron densities 0.413 and −0.581 e Å^{-3}.

Acknowledgment. Financial support was provided by DFG and the Fonds der Chemischen Industrie, which is gratefully acknowledged.

Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, complete bond lengths and angles, and thermal ellipsoid plots for compounds **3a** and **5**. This material is available free of change via the Internet at http://pubs.acs.org.

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