Formation of Ferriophosphanyl- and Ferrioarsanyl-Functionalized Carbocation Salts by Alkylation, Protonation, and Silylation of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}Pn{=}C(NMe_2)_2$ (Pn = P, As)[1,2]

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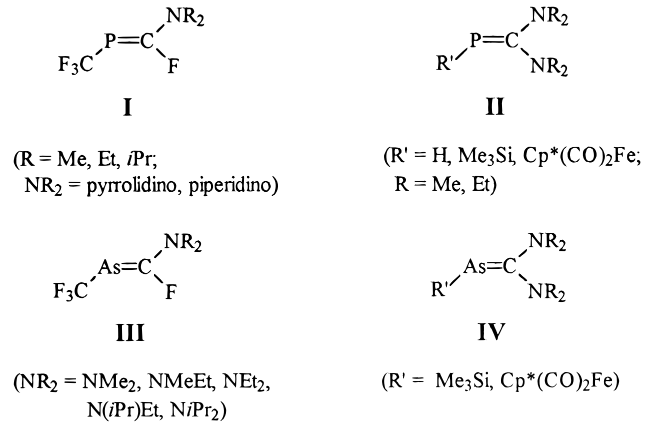
Reaction of equimolar amounts of the metallophosphaalkene η^5-Cp*$(CO)_2FeP{=}C(NMe_2)_2$ (**1a**) and the metalloarsaalkene η^5-Cp*$(CO)_2FeAs{=}C(NMe_2)_2$ (**1b**) with ethereal HBF_4 or the trifluoromethanesulfonates $ROSO_2CF_3$ (R = CH_3, Me_3SiCH_2, Me_3Si), respectively, afforded the phosphanyl-substituted carbenium salts [η^5-Cp*$(CO)_2FeP(R)C(NMe_2)_2$]X (**2a**, R = H, X = BF_4; **3a**, R = CH_3, X = SO_3CF_3; **4a**, R = Me_3SiCH_2, X = SO_3CF_3; **5a**, R = Me_3Si, X = SO_3CF_3) as well as their arsenic analogues [η^5-Cp*$(CO)_2FeAs(R)C(NMe_2)_2$]X (**2b**, R = H, X = BF_4; **3b**, R = CH_3, X = SO_3CF_3; **4b**, R = Me_3SiCH_2, X = SO_3CF_3; **5b**, Me_3Si, X = SO_3CF_3). The cations feature a trigonal-planar bis(amino)carbenium center, which is connected to a phosphorus or arsenic atom with pyramidal configuration. The molecular structure of **3b** has been determined by X-ray diffraction analysis.

Introduction

In the vast majority of phosphaalkenes and arsaalkenes the phosphorus−carbon and arsenic−carbon double bonds are polarized in the sense $Pn^{\delta+}{=}C^{\delta-}$ (Pn = P, As), which agrees with the difference in electronegativities of the elements forming the multiple bonds.[3,4] However, an inverse polarity $Pn^{\delta-}{=}C^{\delta+}$ is encountered in a series of phosphaalkenes **I**[5] and **II**[4,6−8] and arsaalkenes **III**[9] and **IV**[10] featuring one or two amino substituents at the tricoordinate carbon atom of the double bond (Scheme 1). This is mainly achieved by electron delocalization from the amino group into the pnictogen−carbon double bond (Scheme 2).[11]

Scheme 1. Inverse Phospha- and Arsaalkenes



During the course of our investigations on the ligand behavior of the metallophosphaalkene η^5-Cp*$(CO)_2Fe$-$P{=}C(NMe_2)_2$[12] and the metalloarsaalkene η^5-Cp*$(CO)_2$-$FeAs{=}C(NMe_2)_2$,[2] it became evident that the zwitterionic structures are stabilized by ligation of the molecules to 16 VE fragments such as [$Ni(CO)_3$], [$Fe(CO)_4$], or [$Cr(CO)_5$]. In keeping with this, the tricoordinate phosphorus and arsenic atoms in the complexes have pyramidal configuration and are linked to the carbon atom of a

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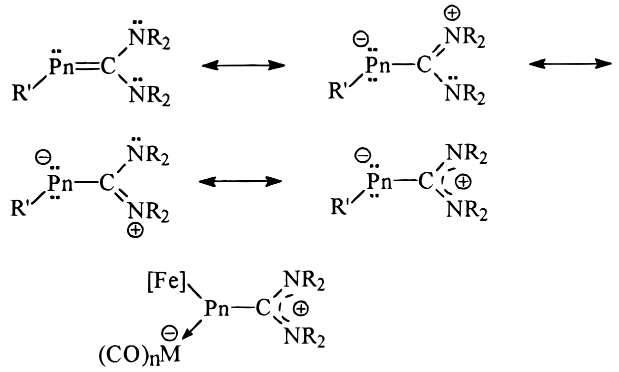
Scheme 2. Resonance Structures of Inverse Arsa- and Phosphaalkenes and Their Complexes (Pn = As, P; [Fe] = [Cp*(CO)$_2$Fe])



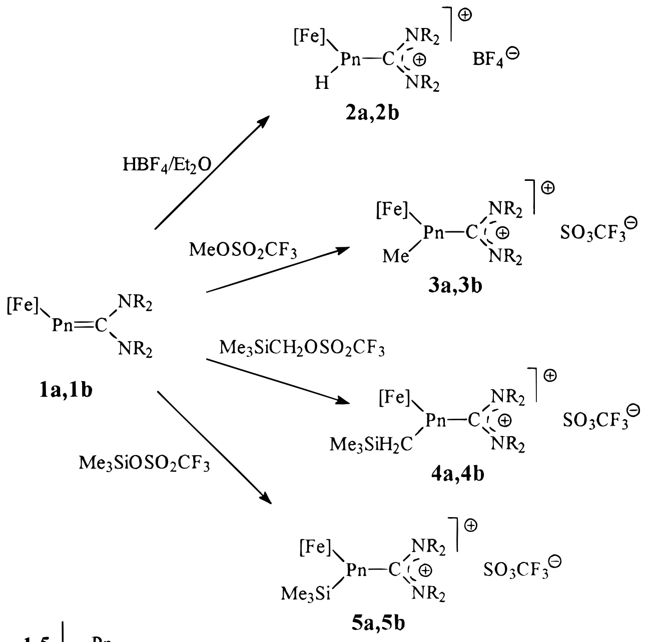
planar carbenium unit via P−C or As−C single bonds. With regard to the considerable nucleophility at the pnictogen atom in phospha- and arsaalkenes with inverse electron density, it was obvious to study their reactivity toward protic acids and alkylating and silylating reagents. Prior to this account, the protonation and methylation of the P atom in [Cp(CO)$_3$WP=C(SiMe$_3$)$_2$] was briefly mentioned in a communication, but no X-ray structural data on the products were given.[13]

More recently, the rutheniophosphaalkene RuCl(P=CH*t*Bu)(CO)(PPh$_3$)$_2$ was subjected to protonation at the P atom by HCl[14] and to methylation by methyl iodide.[15] Similarly, complex RuCl(P=CH*t*Bu)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$ was converted to the salt [RuCl{P(H)=CH(*t*Bu)}(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]BF$_4$ by treatment with ethereal HBF$_4$.[16]

Results and Discussion

Treatment of the ferriophosphaalkene **1a** and the ferrioarsaalkene **1b** with an equimolar amount of ethereal HBF$_4$ (54%) in diethyl ether in the temperature range −50 to 20 °C afforded the yellow salts **2a** and **2b** in high yield (Scheme 3).

Scheme 3. Reactivity of 1a and 1b toward Various Electrophiles ([Fe] = [Cp*(CO)$_2$Fe])



1-5	Pn
a	P
b	As

Protonation at the phosphorus or arsenic atom, respectively, was evident from the spectra. The IR spectra of **2a** and **2b** showed medium intense bands at ν = 2309 and 2088 cm^{-1}, which are readily assigned to a PH- or AsH-stretching vibration. Consistently in the ^{1}H NMR spectrum of **2a** a doublet at δ = 2.82 ($^1J_{PH}$ = 205.0 Hz) was attributed to the proton at the P atom. Upon protonation the ^{31}P NMR signal of **1a** (δ = 141.0 in *n*-hexane) was shifted upfield and appeared in **2a** as a broad singlet at δ = −78.4 ($w_{1/2}$ = 810 Hz).

From a formal point of view **2a** may be regarded as an η^1-complex of HP=C(NMe$_2$)$_2$[6] and the cationic 16 VE fragment [η^5-Cp*(CO)$_2$Fe]$^+$. The unligated phosphaalkene showed a doublet at δ = −62.0 ($^1J_{PH}$ = 159.8 Hz) in its ^{31}P NMR spectrum.[6] Interestingly, the protonation of Cp(CO)$_3$WP=C(SiMe$_3$)$_2$ (δ^{31}P = 505.2) to give [Cp(CO)$_3$WP(H)C(SiMe$_3$)$_2$]$^+$ (δ^{31}P = 187.0) caused an even greater shielding and a much larger PH coupling ($^1J_{PH}$ = 367 Hz),[13] which agreed with a trigonal-planar phosphorus atom in the cation. Similarly, protonation of RuCl(P=CH*t*Bu)(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$ to afford the cation [RuCl{P(H)=CH(*t*Bu)}(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$]$^+$ was accompanied by a strong shielding of the ^{31}P NMR signal from δ = 391.0 to δ = 164.3 ($^1J_{PH}$ = 376.4 Hz).[16]

Protonation of **1a** to give **2a** caused a slight high-field shift of the doublet for the tricoordinate carbon atom from δ = 202.4 to 200.88 and a marked decrease of the coupling constant $^1J_{PC}$ from 97.0 Hz in **1a** to 60.2 Hz in **2a**. A comparison of this with the resonance of the tricoordinate C atom in HP=C(NMe$_2$)$_2$ (δ^{13}C = 207.6; d, $^1J_{PC}$ = 67.8 Hz)[6] is also useful. The ^{13}C NMR resonance of the carbonyls in **1a** (δ = 220.3) were shielded on going to **2a** (δ = 214.94), which points to a decreased σ-donor/π-acceptor capacity of the organophosphorus ligand in the cation. In keeping with this, the ν(CO) bands in the IR spectrum of **2a** (1994, 1945 cm^{-1}) were hypsochromically shifted with respect to **1a** (1973, 1925 cm^{-1}). Similar spectroscopic observations account for the arsenic analogues **1b** and **2b**. Here the ^{13}C NMR resonances of the tricoordinate carbon atom (δ = 214.77) were more shielded upon protonation (δ = 199.99) than in the P analogues.

Alkylation of **1a** at the P atom and of **1b** at the As atom was effected by treatment with equimolar amounts of methyl trifluoromethanesulfonate (triflate) and trimethylsilylmethyl triflate in diethyl ether at −60 °C. Products **3a**, **4a** and **3b**, **4b** were precipitated spontaneously as orange or yellow powdery solids in good yields

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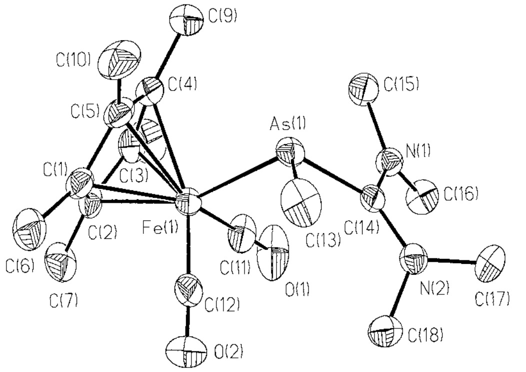

Figure 1. Structure of the cation of **3b** in the crystal (ellipsoids at 50% probability). selected bond lengths [Å] and angle [deg]: Fe1−As1 2.4122(8), As1−C13 1.981(5), As1−C14 1.999(4), N1−C14 1.338(6), C14−N2 1.334(5), N1−C15 1.466(6), N1−C16 1.461(6), N2−C17 1.471(6), N2−C18 1.454(6), Fe1−C11 1.754(5), Fe1−C12 1.753(5); C11−Fe1−C12 95.1(2), Fe−C11−O1 177.9(5), Fe1−C12−O2 177.3(4), Fe1−As1−C13 110.71(16), Fe1−As1−C14 105.67(12), C13−As1−C14 101.7(2), As1−C14−N1 116.3(3), As1−C14−N2 125.0(3), C14−N2−C17 123.2(4), C14−N2−C18 122.8(4), C17−N2−C18 113.9(4), C14−N1−C15 122.7(4), C14−N1−C16 123.0(4), C15−N1−C16 113.3(4).

(Scheme 3). Ferriophosphaalkene **1a** was also efficiently alkylated by the oxonium salt [Me_3O][BF_4]. Here, however, longer reaction times were required. A comparable alkylation of **1b** with Meerwein's salt failed. Observation of a doublet in the ^1H NMR spectrum of **3a** at $\delta = 1.38$ ($^2J_{PH} = 4.9$ Hz) underlined the alkylation at the pnictogen atom. This assumption was also confirmed by an X-ray structural analysis of **3b**. Doublets in the ^{13}C NMR spectrum at $\delta = 205.25$ ($^1J_{PC} = 62.5$ Hz) (**3a**) and 204.99 ($^1J_{PC} = 67.4$ Hz) (**4a**) were attributed to the carbon atom adjacent to the phosphorus. The corresponding resonances in **3b** and **4b** appeared as singlets at $\delta = 203.20$ and 204.43, respectively. Alkylation of **1a** and **1b** caused upfield shifts of the carbonyl resonances to $\delta = 215.82$ to 216.95. Reaction of **1a** and **1b** with trimethylsilyl triflate in diethyl ether at −70 °C gave rise to the precipitation of **5a** and **5b** as yellow solids in 92% and 88% yield, respectively. In the ^{31}P NMR spectrum of **5a** a singlet was observed at $\delta = -78.4$. The carbenium carbon atom in this compound resonated as a doublet at $\delta^{13}C = 202.43$ ($^1J_{PC} = 59.0$ Hz), whereas in the ^{13}C NMR spectrum of **5b** a singlet at $\delta = 200.08$ was attributed to this carbon atom. Here again it seems appropriate to compare the data of the cationic η^1-phospha- and arsaalkene complexes with the free ligands. In Me_3Si-$P{=}C(NMe_2)_2$ the NMR resonances of the P=C unit appeared at $\delta^{31}P = -47.1$ s and $\delta^{13}C = 204.0$ (d, $^1J_{PC} = 85.0$ Hz).[6] A singlet at $\delta = 213.5$ in the ^{13}C NMR spectrum of $Me_3SiAs{=}C(NMe_2)_2$ was assigned to the tricoordinate carbon atom.[10] The mass spectra (CI) of the salts **2a**,**b**, **3a**,**b**, and **4a**,**b** were characterized by intense peaks for the cations.

X-ray Structural Analysis of 3b. An ORTEP drawing of **3b** is shown in Figure 1; selected bond lengths and angles are given in the caption.

The analysis shows that methylation at the arsenic atom of the ferrioarsaalkene **1b** results in a serve distortion of the organoarsenic ligand. In contrast to free **1b**, which exhibits a slightly elongated As−C double bond of 1.876(8) Å[10] (theoretical value in $HAs{=}CH_2$: 1.79 Å[17]), the bond length between the arsenic atom of pyramidal configuration (sum of angles = 318.1°) and the trigonal-planar atom C(14) (sum of angles = 359.7°) amounts to 1.999(4) Å and is thus comparable to the As−C(13) single bond of 1.981(5) Å between the heteroatom and the methyl group. This situation is comparable to the molecular structure of complex η^5-$Cp^*(CO)_2FeAs[Fe(CO)_4]C(NMe_2)_2$, where a similar distortion of the organoarsenic unit upon coordination was encountered.[2] It, however, sharply contrasts with the molecular structure of $RuCl[P(Me){=}CH(\mathit{t}Bu)]I(CO)(PPh_3)_2$, in which the phosphaalkene ligand has trigonal-planar geometry at phosphorus and carbon and a P=C bond length of 1.657(8) Å.[15] Here, obviously, the addition of MeI to the Ru−P unit of the rutheniophosphaalkene precursor is of no consequence to the structural integrity of the P=C unit. The iron−arsenic bond length [2.4122(8) Å] is shortened when compared with **1b** [2.443(2) Å][10] and is similar to the Fe−As single bond in 1,2-dihydroarsete η^5-$Cp^*(CO)_2Fe{-}AsC^a(NMe_2){=}C^b(CO_2Me){-}C^cH(CO_2Me)$ (As−C^c) [2.4018(9) Å].[10] The presence of the single bond As−C(14) in **3b** is consistent with a zwitterionic structure As^-C^+, which is stabilized by coordination to the [$Cp^*(CO)_2Fe^+$] unit and by π-conjugation of the lone pairs of electrons on the nitrogen atoms. Accordingly, relatively short carbon−nitrogen bonds C(14)−N(1) [1.338(6) Å] and C(14)−N(2) [1.334(5) Å] were found in this structure. Both nitrogen atoms are planar [sum of angles at N(1), 359.1°; N(2), 360.1°].

There are no significant cation−anion contacts. The shortest distance [3.962 Å] is found between C(14) and one oxygen atom [O(8)] of the triflate anion.

On the basis of these structural features with regard to the structure of the aforementioned ruthenium phosphaalkene complex, compounds **2**−**5a,b** are best viewed as phosphanyl- and arsanyl-functionalized carbenium salts rather than as η^1-phosphaalkene or η^1-arsaalkene complexes.

Theoretical Results and Discussion

We have calculated the equilibrium structures of a series of homologous pnictogenodiaminocarbenium ions $[(H_2N)_2CXH_2]^+$ (**X-1**, X = N, P, As). The resulting structural parameters (Figure 2) are in good agreement with the experimental findings.

This confirms our assumption that weakening of the X−C bond in favor of pyramidalization at the pnictogen atom (in case of X = P, As) is caused by the amino groups attached to the carbon atom and is not an effect due to coordination to a transition metal center. For the case X = N (the guanidinium ion) a detailed study of the electronic structure can be found in the recent literature.[17] Accordingly, the elongation of the $C{-}NH_2$ bond and the decrease of the activation barrier for the rotation of one amino group in **N-1** in comparison with the unsubstituted aminocarbenium ion can be explained easily by the partial saturation of the acceptor orbital (the empty p orbital at the carbon atom). Because all three π donors in **N-1** naturally are of equal strength a

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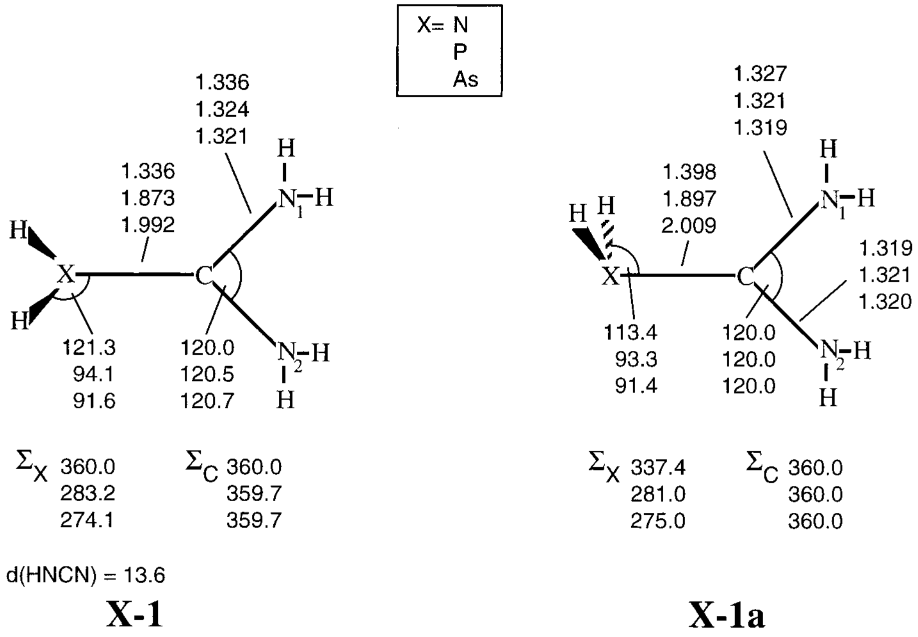

Figure 2. Selected bond lengths [Å] and angles [deg] determined for the equilibrium structure **X-1** (C_s symmetry) and a structure **X-1a** in which the XH_2 group is twisted by 90° (C_s symmetry).

Table 1. Charges and Bond Orders Determined from the NBO Analysis[a]

	q(X)	q(C)	q(N_1)	q(N_2)	q(XH_2)	b(XC)	b(N_1C)	b(N_2C)
N-1	−0.816	+0.690	−0.816	−0.816	+0.103	1.298	1.298	
N-1a	−0.938	+0.711	−0.780	−0.755	−0.038	1.087	1.381	1.417
$[CH_2NH_2]^+$ [17]	−0.691	+0.231			+0.259			
P	+0.400	+0.265	−0.775	−0.775	+0.449	0.956	1.401	
P-a	+0.361	+0.278	−0.770	−0.762	+0.410	0.897	1.421	1.433
$[CH_2PH_2]^+$ [20]	+0.845	−0.667			+1.057			
As	+0.473	+0.263	−0.777	−0.777	+0.462	0.894	1.412	
As-a	+0.450	+0.271	−0.774	−0.769	+0.438	0.857	1.427	1.431
$[CH_2AsH_2]^+$ [20]	+0.917	−0.640			+1.057			

[a] Data for the corresponding $[CH_2XH_2]^+$ ions taken from the literature are given for comparison. (For the theoretical methods used to determine these see the references cited.)

D_3 symmetrical structure results. Things are different if X is one of the heavier pnictogen atoms P or As. They are weaker π donors, so they lose the competition for the acceptor orbital, although for the unsubstituted pnictogenocarbenium ions $[H_2CXH_2]^+$ strong π-donation to the carbon atom was demonstrated by quantum chemical calculations.[19-21] Short X−C bonds, high barriers for rotation, and a positive group charge of +1 for the XH_2 groups indicate a C−X double bond in $[H_2CXH_2]^+$ (Table 2).

On the other hand in the case of **P-1** and **As-1** the X−C bonds are significantly longer and the X atom becomes pyramidalized. The activation barrier is reduced to a magnitude known for single bonds. Because of the minor contribution of X−C π bonding in **P-1** and **As-1** the structural changes caused by twisting the XH_2 group are also insignificant in comparison with **N-1**. A smaller group charge (≈+0.5) of the XH_2 group is another hint that charge donation from the pnictogen atom to the carbon atom is reduced (Table 1). This is also demonstrated nicely by a plot of ELF in the plane of the π system, which clearly shows the lone pair character of the elctron pair in **P-1** while it is forming the double bond in $[H_2CPH_2]^+$ (Figure 3).

Table 2. Total and Relative Energies for the Equilibrium Structures X-1 and the Twisted Structures X-1a Corresponding to Transition States for the Rotation[a]

	X		
	N	P	As
E(**X-1**) [au]	−205.7803156	−492.3439599	−2384.7541247
E(**X-1a**) [au]	−205.7602149	−492.3427863	−2384.7535959
N_{imag}(**X-1a**)	1	1	0
ΔE_{rot} [kJ/mol]	52.8	3.1	1.4
ΔE_{rot} + ZPVE [kJ/mol]	52.8	3.4	1.9

[a] For **As-1a** this structure is found to be a stable rotational conformer.

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 argon prior to use. Infrared spectra were recorded with a Bruker FT-IR IFS66 spectrometer. ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectra were recorded at 22 °C using a Bruker AC 100 (^1H, 100.13 MHz, ^{31}P, 40.53 MHz), a Bruker Avance DRX 500, and a Varian

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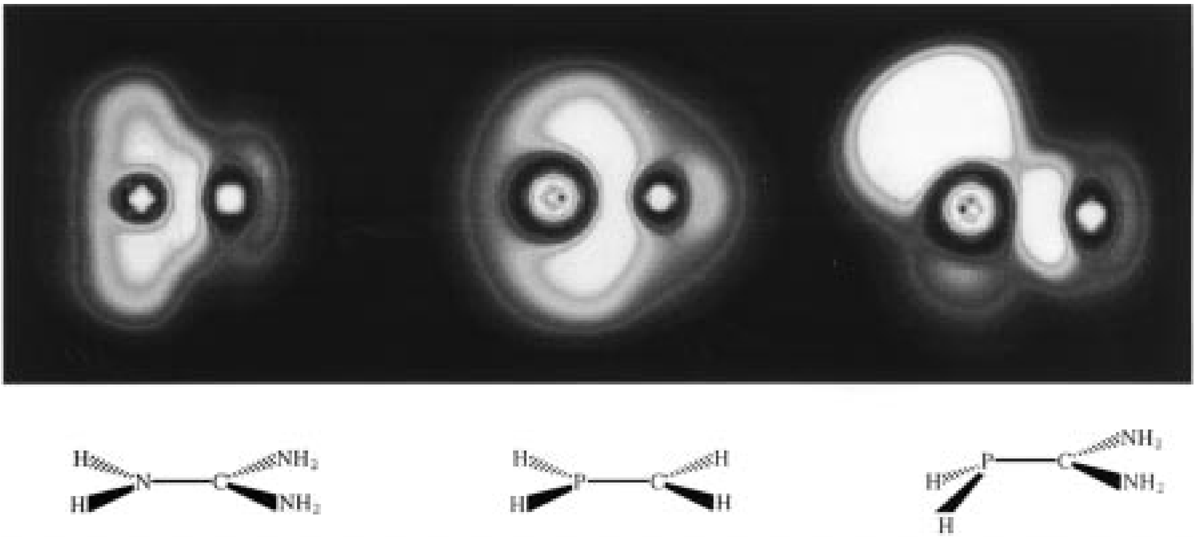

Figure 3. Plot of the electron localization (ELF) in a plane containing the X−C bond perpendicular to the R−C−R plane. The electron density was calculated at the 6-31G(p,d)/B3LYP//6-31G(p,d)/B3LYP level. White: large values of ELF, high localization of the exchange hole-areas dominated by electron pairs.

Nova 500 (^{1}H, 500.13 MHz; ^{11}B, 160.46 MHz; ^{13}C, 125.75 MHz; ^{31}P, 202.46 MHz); references: $SiMe_4$ (^{1}H, ^{13}C), $BF_3\cdot EtO_2$ (^{11}B), 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 η^5-Cp*$(CO)_2(CO)_2$Fe−P=C$(NMe_2)_2$ (**1a**)[8] and η^5-Cp*$(CO)_2$Fe−As=C$(NMe_2)_2$ (**1b**)[10] were synthesized according to literature procedures. An ethereal solution of HBF_4 (54%), $[Me_3O][BF_4]$, methyl triflate, trimethylsilylmethyl triflate, and trimethylsilyl triflate were purchased commercially (Aldrich).

Preparation of Compounds. [η^5-Cp*$(CO)_2$FeP(H)C$(NMe_2)_2$]BF_4 (2a). To a chilled (−50 °C) solution of **1a** (0.72 g, 1.90 mmol) in diethyl ether (50 mL) was slowly added 0.3 mL of a 54% HBF_4 in diethyl ether, whereby spontaneously a yellow precipitate was formed. It was warmed to −25 °C, and the mixture was stirred for 30 min. It was filtered, and the filtered precipitate was washed (3 × 10 mL of diethyl ether and 2 × 5 mL of *n*-pentane). The resulting yellow solid was dried at 10^{-3} Torr to give 0.82 g (92%) of **2a**. IR (Nujol, cm^{-1}) ν: 2309 (m, PH), 1994 (s, FeCO), 1945 (s, FeCO), 1061 (m, BF), 1047 (m, BF), 1033 (m, BF). ^{1}H NMR ($CDCl_3$) δ: 1.83 (s, 15H, C_5Me_5), 2.82 (d, $^1J_{PH}$ = 205.0 Hz, PH), 3.18 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 9.55 [s, $C_5(CH_3)_5$], 44.27 (s, NCH_3), 97.80 [s, $C_5(CH_3)_5$], 200.88 (d, $^1J_{PC}$ = 60.2 Hz. PC), 213.85 (s, FeCO), 214.94 (s, FeCO). ^{31}P NMR ($CDCl_3$) δ: −78.4 (s, br). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −1.48 s. MS/CI *m/z*: 379 {(100), [Cp*$(CO)_2$Fe−P(H)C$(NMe_2)_2$]$^+$}. Anal. Calcd for $C_{17}H_{28}BF_4FeN_2O_2P$ (466.05): C, 43.81; H, 6.06; N, 6.01. Found: C, 43.68; H, 6.15; N, 5.88. ^{1}H and ^{31}P NMR and IR spectra for **2a** are included in the Supporting Information.

[η^5-Cp*$(CO)_2$FeAs(H)C$(NMe_2)_2$]BF_4 (2b). Analogously **1b** (0.71 g, 1.68 mmol) was treated with ethereal 54% HBF_4 (0.23 mL) to yield a yellow powder **2b** (0.75 g, 88%). IR (Nujol, cm^{-1}) ν: 2088 (m, AsH), 1995 (s, FeCO), 1926 (s, FeCO), 1074 (m, BF), 1062 (m, BF), 1047 (m, BF), 1032 (m, BF). ^{1}H NMR ($CDCl_3$) δ: 1.81 (s, 15H, C_5Me_5), 2.84 (s, 1H, AsH), 3.19 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 9.51 [s, $C_5(CH_3)_5$], 44.91 (s, NCH_3), 96.81 [s, $C_5(CH_3)_5$], 199.99 (s, AsC), 215.20 (s, FeCO), 216.00 (s, FeCO). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −1.47 s. MS/CI *m/z*: 423 {(100), [Cp*$(CO)_2$Fe−As(H)C$(NMe_2)_2$]$^+$}. Anal. Calcd for $C_{17}H_{28}AsBF_4FeN_2O_2$ (509.99): C, 40.04; H, 5.53; N, 5.49. Found: C, 39.74; H, 5.47; N, 5.35.

[η^5-Cp*$(CO)_2$FeP(Me)C$(NMe_2)_2$]SO_3CF_3 (3a). An etheral solution (15 mL) of 1.01 mmol of $CH_3SO_3CF_3$ was added dropwise to a cold (−60 °C) solution of **1a** (0.38 g, 1.01 mmol) in 25 mL of diethyl ether, whereupon an orange precipitate separated. Stirring was continued for 1.5 h at −25 °C. It was filtered, and the filtered residue was washed (3 × 5 mL Et_2O, 2 × 5 mL *n*-C_5H_{12}) and dried at 10^{-3} Torr to afford 0.60 g (81%) of **3a** as an orange powder. According to ^{1}H NMR, the compound was solvated with one molecule of diethyl ether. IR (KBr, cm^{-1}) ν: 1993 (s, FeCO), 1949 (s, FeCO). ^{1}H NMR ($CDCl_3$) δ: 1.35 (d, $^2J_{PH}$ = 5.2 Hz, 3H, PCH_3), 1.85 (s, 15H, C_5Me_5), 3.13 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR ([D$_6$]acetone) δ: 9.88 [s, $C_5(CH_3)_5$], 11.00 (d, $^1J_{PC}$ = 25.8 Hz, PCH_3), 44.04 (s, NCH_3), 44.10 (s, NCH_3), 98.82 [s, $C_5(CH_3)_5$], 130.16 (q, $^1J_{CF}$ = 274.4 Hz, CF_3), 205.25 (d, $^1J_{PC}$ = 62.5 Hz, PCN_2), 215.82 (s, FeCO). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: −26.4 s. − MS/CI *m/z*: 149 [(100), $SO_3CF_3^+$], 393 {(34), [Cp*$(CO)_2$FeP(Me)C$(NMe_2)_2$]$^+$}. Anal. Calcd for $C_{23}H_{40}F_3FeN_2O_6PS$ (616.45): C, 44.81; H, 6.54; N, 4.54. Found: C, 44.70; H, 6.13; N, 4.43.

[η^5-Cp*$(CO)_2$FeP(Me)C$(NMe_2)_2$]BF_4 (3a′). The corresponding tetrafluoroborate was obtained by reaction of **1a** (0.58 g, 1.53 mmol) and 0.24 g (1.53 mmol) $(Me_3O)(BF_4)$ in CH_2Cl_2 (50 mL) at room temperature for 12 h, whereupon the color of the solution turned from red to orange. It was filtered. The filtrate was concentrated to ca. 20 mL and layered with 10 mL of diethyl ether. Compound **3a′** was isolated as an orange powder after 24 h (0.65 g, 89% yield). IR (KBr, cm^{-1}) ν: 1991 (s, FeCO), 1939 (s, FeCO), 1933 (s, FeCO), 1095 (m, BF), 1061 (m, BF), 1048 (m, BF), 1034 (m, BF). ^{1}H NMR ($CDCl_3$) δ: 1.33 (d, $^2J_{PH}$ = 5.5 Hz, 3H, PCH_3), 1.83 (s, 15H, C_5Me_5), 3.10 (s, 12H, NCH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: −26.6 s. ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −1.62 s.

[η^5-Cp*$(CO)_2$FeAs(Me)C$(NMe_2)_2$]SO_3CF_3 (3b). Analogous to the preparation of **3a**, combination of **1b** (0.13 g, 0.31 mmol) with an equimolar amount of $CH_3SO_3CF_3$ in diethyl ether at −60 °C led to the formation of a yellow precipitate, which was crystallized from CH_2Cl_2 (5 mL) at −28 °C for 3 days to yield brown crystalline **3b** (0.15 g, 85%). IR (KBr, cm^{-1}) ν: 1986 (s, FeCO), 1935 (s, FeCO). ^{1}H NMR (CD_2Cl_2) δ: 1.39 (s, 3H, $AsCH_3$), 1.83 (s, 15H, C_5Me_5), 3.20 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 7.01 (s, $AsCH_3$), 9.71 [s, C_5 $(CH_3)_5$], 44.56 (s, NCH_3), 97.2 [s, $C_5(CH_3)_5$], 203.20 (s, $AsCN_2$), 216.60 (s, FeCO). Anal. Calcd for $C_{19}H_{30}AsF_3FeN_2O_5S$ (586.28): C, 38.93; H, 5.16; N, 4.78. Found: C, 38.67; H, 5.29; N, 4.68.

[η^5-Cp*$(CO)_2$FeP(CH_2SiMe_3)C$(NMe_2)_2$]SO_3CF_3 (4a). A sample of trimethylsilylmethyl triflate (0.98 g, 4.12 mmol) was slowly added to a chilled ethereal solution (−78 °C, 70 mL) of **1a** (1.56 g, 4.12 mmol). The slurry was allowed to warm to room temperature within a period of 2 h. The orange-red precipitate was filtered off, washed (2 × 10 mL of Et_2O, 1 ×

10 mL of n-C_5H_{12}), and dried at 10^{-3} Torr to afford 2.25 g (89%) of **4a**. IR (Nujol, cm^{-1}) ν: 1997 (s, FeCO), 1945 (s, FeCO), 1271 [s, $\delta(SiMe_3)$], 855 [m, $\rho(SiMe_3)$]. ^1H NMR (CD_2Cl_2) δ: 0.07 (s, 9H, $SiMe_3$), 0.92 (s, br, 2H, PCH_2Si), 1.85 (s, 15H, C_5Me_5), 3.14 (s, 12H, NCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 0.40 (s, $SiCH_3$), 10.12 [s, $C_5(CH_3)_5$], 14.08 (d, $^1J_{PC}$ = 17.9 Hz, PCSi), 44.69 (s, NCH_3), 98.90 [s, $C_5(CH_3)_5$], 204.99 (d, $^1J_{PC}$ = 67.4 Hz, PCN_2), 216.35 (s, FeCO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: −27.1 s. Anal. Calcd for $C_{22}H_{38}F_3FeN_2O_5PSSi$ (614.52): C, 43.00; H, 6.23; N, 4.56. Found: C, 43.11; H, 6.30; N, 4.62.

[η^5-Cp*(CO)$_2$FeAs(CH$_2$SiMe$_3$)C(NMe$_2$)$_2$]SO$_3$CF$_3$ (4b). As described before, reaction of **1b** (0.50 g, 1.18 mmol) with 0.28 g (1.18 mmol) of $Me_3SiCH_2OSO_2CF_3$ afforded 0.66 g (85%) of **4b** as a yellow powder. IR (Nujol, cm^{-1}) ν: 1990 (s, FeCO), 1938 (s, FeCO), 1272 [s, $\delta(SiMe_3)$], 857 [m, $\rho(SiMe_3)$]. ^1H NMR (CD_2Cl_2) δ: 0.08 (s, 9H, $SiMe_3$), 0.37 and 1.56 (AB-spin system, J_{AB} = 15.0 Hz, $AsCH_2Si$), 1.84 (s, 15H, C_5Me_5), 3.20 (s, br, 12H, NCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: −0.42 (s, $SiCH_3$), 9.88 [s, $C_5(CH_3)_5$], 11.35 (s, AsCSi), 45.12 (s, NCH_3), 97.67 [s, $C_5(CH_3)_5$], 204.43(s, $AsCN_2$), 216.86 (s, FeCO), 216.95 (s, FeCO). Anal. Calcd for $C_{22}H_{38}AsF_3FeN_2O_5SSi$ (658.46): C, 40.13; H, 5.82; N, 4.25. Found: C, 40.04; H, 5.91; N, 4.22.

[η^5-Cp*(CO)$_2$FeP(SiMe$_3$)C(NMe$_2$)$_2$]SO$_3$CF$_3$ (5a). Analogously equimolar amounts of **1a** (0.38 g, 1.01 mmol) and $Me_3SiOSO_2CF_3$ (0.23 g, 1.01 mmol) were reacted in 40 mL of diethyl ether at −50 °C to give 0.60 g (92%) of **5a** as a yellow solid. IR (Nujol, cm^{-1}) ν: 1990 (s, FeCO), 1942 (s, FeCO), 1262 [s, $\delta(SiMe_3)$], 833 [m, $\rho(SiMe_3)$]. ^1H NMR (CD_2Cl_2) δ: 0.06 (s, 9H, $SiMe_3$), 1.85 (s, 15H, C_5Me_5), 3.17 (s, 12H, NCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 1.91 (s, $SiCH_3$), 9.70 [s, $C_5(CH_3)_5$], 44.60 (s, NCH_3), 98.40 [s, $C_5(CH_3)_5$], 202.43 (d, $^1J_{PC}$ = 59.0 Hz, PCN_2), 215.54 (s, FeCO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: −79.6 s. Anal. Calcd for $C_{21}H_{36}F_3FeN_2O_5PSSi$ (600.49): C, 42.00; H, 6.04; N, 4.67. Found: C, 40.72; H, 6.12; N, 4.77. (The low C-value is presumably due to insufficient combustion of the anion in the presence of the P−Si function.)

[η^5-Cp*(CO)$_2$FeAs(SiMe$_3$)C(NMe$_2$)$_2$]SO$_3$CF$_3$ (5b). Compound **1b** (0.34 g, 0.81 mmol) and $Me_3SiOSO_2CF_3$ (0.18 g, 0.81 mmol) were combined analogously in 60 mL of diethyl ether at −78 °C. Warming up the mixture to −50 °C led to the formation of a yellow precipitate. Stirring was continued for 30 min, during which the slurry was warmed to −30 °C. The cold mixture was filtered, and the filter cake was washed (2 × 5 mL of Et_2O and 1 × 5 mL of n-C_5H_{12}) and dried at 10^{-3} Torr to give 0.42 g (88%) of **5b** as a yellow solid. IR (KBr, cm^{-1}) ν: 1986 (s, FeCO), 1947 (s, FeCO), 1265 [s, $\delta(SiMe_3)$]. ^1H NMR ($CDCl_3$) δ: 0.03 (s, 9H, $SiMe_3$), 1.81 (s, 15H, C_5Me_5), 3.15 (s, 12H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 1.83 (s, $SiCH_3$), 9.59 [s, C_5 $(CH_3)_5$], 45.29 (s, NCH_3), 98.78 [s, $C_5(CH_3)_5$], 200.08 (s, $AsCN_2$), 215.19 (s, FeCO), 215.90 (s, FeCO). Anal. Calcd. for $C_{21}H_{36}AsF_3FeN_2O_5SSi$ (644.44): C, 39.14; H, 5.63; N, 4.35. Found: C, 36.98; H, 5.29; N, 4.59. (The low C-value is presumably due to insufficient combustion of the anion in the presence of the As−Si function.)

X-ray Structural Analysis of 3b.[22] Single crystals of **3b** were grown from CH_2Cl_2 at −28 °C. A brown crystal with the approximate dimensions of 0.3 × 0.3 × 0.4 mm was measured on a Siemens SMART CCD area detector system with a three-axis goniometer and with Mo Kα radiation (λ = 0.71073 Å) at 173 K. Crystal data and refinement details: space group $P\bar{1}$, cell dimensions a = 12.5475(7) Å, b = 15.1076(9) Å, c = 15.8947(9) Å, α = 63.401(1)°, β = 74.204(1)°, γ = 69.545(1)°, V = 2500.1(2) Å^3 (refined from 6115 reflections), Z = 4, d_{calcd} = 1.558 g cm^{-3}, μ = 2.054 mm^{-1}, data collections in ω at 0.3° scan width, at a detector distance of 5 cm ($2\theta_{max}$ = 54°), data reduction with the SAINT programm (V 4.050 Bruker AXS), semiempirical absorption correction with redundant data (SADABS programm, Siemens) max/min transmission 1.000/ 0.737. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-97, 24002 intensities read, 10678 unique (R_{int} = 0.0457) and 10678 with $I > 2\sigma(I)$, 597 parameters, hydrogen atoms treated as riding groups, R-indices for reflections with $I > 2\sigma(I)$: R_F = 0.0571; wR_{F^2} = 0.1476, GooF (F^2) = 0.970, $\omega^{-1} = \sigma^2(F_o^2) + 0.1062(P)^2$, where $P = (F_o^2 + 2F_c^2)/3$, maximum/minimum residual electron densities 1.188 and −1.478 e Å^{-3}.

Theoretical Methods. For all calculations the 6-31G(p,d) basis set was used.[23] The molecular structures were optimized within symmetry constraints at the density functional theory level (B3LYP functional[24]) guided by analytically calculated gradients. All stationary points were verified by analysis of the corresponding Hessian matrixes. For the calculations the GAUSSIAN 94[25] set of programs was used. To examine the charge distribution, we employed the NBO[26] partitioning scheme and the electron localization function (ELF).[27]

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, complete bond distances and angles, and thermal ellipsoid plots for compound **3b** as well as ^1H and ^{31}P NMR and IR spectra of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133801. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk).

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