Transition-Metal-Substituted Acyl Phosphanes and Phosphaalkenes. 32.[1] Transformation of an FeP=C Unit of a Phosphaalkene into a FeP=*C*—*N*—*N*=C Moiety by Chain Extension through Insertion of the 1,3-Dipole ($^-$N—N(Ar)—CH$^+$) of Sydnones

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Received February 5, 1997[⊗]

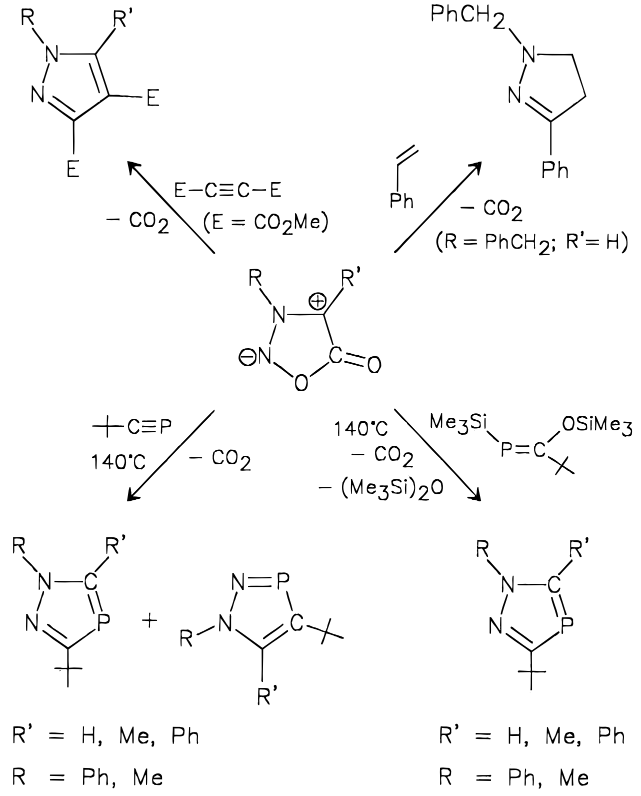
The metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2$ (**1**) underwent reaction with sydnones 3-aryl-NNOC(O)CH (aryl = C_6H_5 (**2a**), 4-FC_6H_4 (**2b**), 4-ClC_6H_4 (**2c**), 4-BrC_6H_4 (**2d**)) to afford the novel ferriophosphaalkenes $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(aryl)N{=}C(NMe_2)_2$ (**3a**−**d**). Compound **3a** forms the [2 + 2] phosphetanyl cycloadduct **4a** with dimethyl fumarate. The molecular structure of **3a** was determined by single-crystal X-ray diffraction.

Introduction

Mesoionic compounds[2] such as 1,2,3-oxadiazolium-5-olates (sydnones) are masked 1,3-dipoles, which smoothly convert alkynes into pyrazole derivatives.[2,3] The treatment of sydnones with alkenes give rise to the formation of Δ^2-pyrazolines as the result of [3 + 2] cycloadditions.[4] Extension of this methodology to phosphaalkynes and suitably functionalized phosphaalkenes provides a useful access to 1,2,4- and 1,2,3-diazaphospholes[5,6] (Scheme 1).

P-Metallophosphaalkenes[7] function as electron-rich heteroalkenes, which undergo [1+2] cycloadditions with isocyanides[8] and [2 + 2] cycloadditions with electron-deficient alkenes[9] and alkynes.[10] The initial step in the formation of *N*-metallo-1,2,3-diazaphospholes from $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2$ and diazoacetates may be considered as a [3 + 2] cycloaddition[11] (Scheme 2). With regard to the rich chemistry displayed by metallophosphaalkenes, we were interested in the reactivity of such compounds toward sydnones, and here we describe the unprecedented insertion of a 1,3-dipole into the P=C double bond of the phosphaalkene.

Scheme 1



Experimental Section

All operations were performed with standard Schlenk techniques in an oxygen-free argon atmosphere. Solvents were dried by standard methods and was freshly distilled under argon. Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer, and the ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in C_6D_6 at 22 °C on Bruker AM Advance DRX 500, Bruker AC 250, and Bruker AC 100 instruments. Standards: $SiMe_4$ (^{1}H, ^{13}C), external 85% H_3PO_4 (^{31}P). Elemental analyses were performed in the microanalytical laboratory of our department. Mass spectra were obtained with a Varian MAT-CH5-DF spectrometer. The metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2$ (**1**)[9] and the sydnones RNNOC(O)CH (R = Ph,[12] 4-FC_6H_4,[13] 4-ClC_6H_4,[14] 4-BrC_6H_4,[15] 4-$MeOC_6H_4$,[16] Me[17]) were prepared according to the literature. Dimethyl fumarate was purchased commercially.

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

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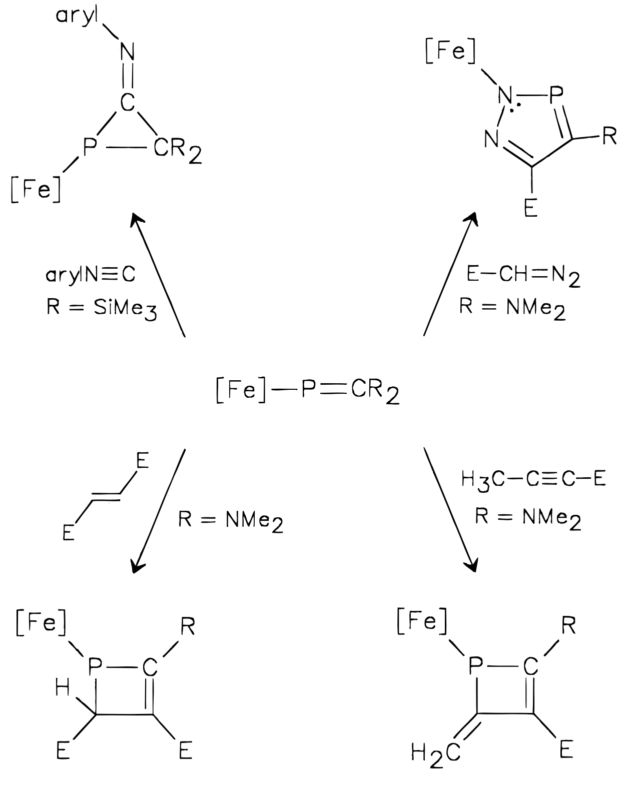
S0276-7333(97)00087-3 CCC: $14.00

Scheme 2



[Fe] = $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$

E = CO_2Me, CO_2Et, $CO_2\mathit{t}Bu$

Preparation of Compounds. (*E*)-$(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(Ph)N{=}C(NMe_2)_2$ (3a). A sample of solid 3-phenylsydnone **2a** (0.50 g, 3.06 mmol) was added to a solution of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2$ (**1**) in diethyl ether (40 mL). In order to obtain a homogeneous solution, dichloromethane (10 mL) was added at ambient temperature, whereupon an effervescence and a color change from dark red to orange-red was observed. After the mixture was stirred overnight, solvent and volatiles were removed in vacuo. The remaining red-brown powder was extracted with ether (40 mL) and filtered. The filtrate was stored at −30 °C for 24 h to yield dark red diamond-shaped crystals. Concentration of the mother liquor to *ca.* 10 mL and repeated crystallization furnished a second crop of **3a**. Yield: 0.93 g (61%). IR (Nujol, cm^{-1}): ν 1985 vs [ν(CO)], 1940 s [ν(CO)], 1589 s [ν(CN)], 1551 s, 1490 s, 1422 w, 1365 s, 1305 m, 1264 m, 1218 w, 1176 w, 1151 m, 1137 w, 1105 m, 1074 w, 1063 w, 1041 w, 1027 w, 991 m, 930 m, 899 w, 874 w, 817 m, 776 w, 763 m, 746 s, 690 m, 640 m, 630 m, 578 s, 548 s, 510 m. ^{1}H NMR: δ 1.69 (s, 15H, C_5Me_5), 2.59 (s, 6H, NCH_3), 2.85 (s, 6H, NCH_3), 6.86−7.53 (s, br, 5H, C_6H_5), 9.41 (d, $^2J_{PH}$ = 8.8 Hz, PCH). ^{13}C{^{1}H} NMR: δ 10.1 [s, $C_5(\mathit{C}H_3)_5$], 39.4 (s, NCH_3), 40.0 (s, NCH_3), 94.6 [s, $\mathit{C}_5(CH_3)_5$], 115.6 s, 121.1 s, 129.9 s, 146.9 (s, phenyl C), 166.6 (s, C=N), 176.0 (d, $^1J_{PC}$ = 69.2 Hz, P=C), 219.7 (s, CO). ^{31}P{^{1}H} NMR: δ 204.9 s. MS/CI: *m/z* = 496 (M^+), 440 ($M^+ - 2CO$), 397 ($M^+ - 2CO - MeN{=}CH_2$). Anal. Calcd for $C_{24}H_{33}FeN_4O_2P$ (496.36): C, 58.07; H, 6.70; N, 11.29. Found: C, 57.95; H, 6.88; N, 11.19.

(*E*)-$(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(4\text{-}FC_6H_4)N{=}C(NMe_2)_2$ (3b). A sample of solid 3-(fluorophenyl)sydnone **2b** (0.74 g, 4.15 mmol) was added to a chilled solution (0 °C) of **1** (1.57 g, 4.15 mmol) in 50 mL of ether. The addition of 10 mL of dichloromethane to the slurry was accompanied by effervescence and a color change from dark red to orange. Stirring was continued for 24 h at 20 °C. Volatile compounds were removed *in vacuo*, and the remaining red-brown powder was extracted with 40 mL of ether. The extract was freed from the solvent to yield **3b** as a red-brown powder (1.41 g, 66%). Attempts to crystallize the compound invariably led to decomposition. IR (Nujol, cm^{-1}): ν 1982 vs [ν(CO)], 1934 vs [ν(CO)], 1560 w, 1500 m, 1310 w, 1291 m, 1264 m, 1227 m, 1151 w, 1097 w, 930 w, 844 w, 642 w, 580 m. ^{1}H NMR: δ 1.53 (s, 15H, C_5Me_5), 2.40 (s, 6H, NCH_3), 2.67 (s, 6H, NCH_3), 7.15 (m, 4H, aryl H), 9.14 (d, $^2J_{PH}$ = 9.0 Hz, P=CH). ^{13}C{^{1}H} NMR: δ 9.36 [s, $C_5(\mathit{C}H_3)_5$], 38.8 (s, NCH_3), 39.2 (s, NCH_3), 95.7 [s, $\mathit{C}_5(CH_3)_5$], 114.3 s, 115.6 s, 115.8 s, 144.8 (s, aryl C), 165.8 (s, C=N), 175.1 (d, $^1J_{PC}$ = 69.2 Hz, P=C), 219.0 (s, CO). ^{31}P{^{1}H} NMR: δ 204.4 s. ^{19}F{^{1}H} NMR: δ 97.4 s. MS/CI: *m/z* 514 (M^+), 458 ($M^+ - 2CO$). Anal. Calcd for $C_{24}H_{32}FFeN_4O_2P$ (514.36): C, 56.04; H, 6.27; N, 10.89. Found: C, 54.80; H, 5.98; N, 10.30. Various attempts at purification were unsuccessful due to partial decomposition to $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$ and unidentified components.

(*E*)-$(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(4\text{-}ClC_6H_4)N{=}C(NMe_2)_2$ (3c). Similarly, compound **1** (0.80 g, 2.12 mmol) and 3-(*p*-chlorophenyl)sydnone **2c** (0.43 g, 2.12 mmol) were reacted in a mixture of ether (30 mL) and dichloromethane (10 mL) at 0−10 °C. After 2 h of stirring the solution was evaporated to dryness, and the red-brown solid residue was extracted with ether (40 mL). Filtration of the extract and removal of solvent *in vacuo* yielded **3c** as a red-brown powder (0.81 g, 72%). IR (Nujol, cm^{-1}): ν 1983 vs [ν(CO)], 1934 vs [ν(CO)], 1758 w, 1665 w, 1589 w, 1557 w, 1485 s, 1307 w, 1287 m, 1263 m, 1222 w, 1151 w, 1093 w, 817 m, 797 w, 641 w, 582 m. ^{1}H NMR: δ 1.52 (s, 15H, C_5Me_5), 2.38 (s, 6H, NCH_3), 2.66 (s, 6H, NCH_3), 7.00−7.14 (m, 4H, aryl H), 9.16 (d, $^2J_{PH}$ = 9.2 Hz, P=CH). ^{13}C{^{1}H} NMR: δ 9.34 [s, $C_5(\mathit{C}H_3)_5$], 38.5 (s, NCH_3), 39.2 (s, NCH_3), 95.8 [s, $\mathit{C}_5(CH_3)_5$], 115.6 s, 129.1 s, 144.4 (s, aryl C), 165.9 (s, C=N), 174.5 (d, $^1J_{PC}$ = 67.7 Hz, P=C), 218.8 (s, CO). ^{31}P{^{1}H} NMR: δ 215.4 s. MS/CI: *m/z* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$). Anal. Calcd for $C_{24}H_{32}ClFeN_4O_2P$ (580.82): C, 54.30; H, 6.07; N, 10.56. Found C, 54.43; H, 6.12; N, 10.15.

(*E*)-$(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(4\text{-}BrC_6H_4)N{=}C(NMe_2)_2$ (3d). Analogously, equimolar amounts of **1** (1.76 g, 4.65 mmol) and 3-(*p*-bromophenyl)sydnone **2d** (1.20 g, 4.65 mmol) were reacted in a mixture of ether (40 mL) and dichloromethane (10 mL) in the temperature range of 0−10 °C. Workup as described above afforded 1.79 g (67%) of **3d** as a red-brown powder. IR (Nujol, cm^{-1}): ν 1983 vs [ν(CO)], 1934 vs [ν(CO)], 1583 w, 1481 m, 1262 w, 1148 m, 1073 w, 1031 m, 973 w, 815 m, 801 w, 642 w, 582 m. ^{1}H NMR: δ 1.53 (s, 15H, C_5Me_5), 2.39 (s, 6H, NCH_3), 2.67 (s, 6H, NCH_3), 7.10−7.44 (m, 4H, aryl H), 9.14 (d, $^2J_{PH}$ = 9.4 Hz, P=CH). ^{13}C{^{1}H} NMR: δ 9.30 [s, $C_5(\mathit{C}H_3)_5$], 38.5 (s, NCH_3), 39.2 (s, NCH_3), 95.8 [s, $\mathit{C}_5(CH_3)_5$], 116.2 s, 131.9 s, 144.8 (s, aryl C), 165.9 (s, C=N), 174.5 (d, $^1J_{PC}$ = 68.3 Hz, P=C), 218.8 (s, CO). ^{31}P{^{1}H} NMR: δ 216.7 s. MS/CI: *m/z* = 576 ($M^+ + H$), 548 ($M^+ + H - CO$), 520 ($M^+ + H - 2CO$). Anal. Calcd for $C_{24}H_{32}BrFeN_4O_2P$ (575.27): C, 50.11; H, 5.61; N, 9.74. Found C, 49.35; H, 5.63; N, 9.22. Various attempts at purification were unsuccessful due to partial decomposition.

Reaction of E-$(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHN(Ph)N{=}C(NMe_2)_2$ (3a) with Dimethyl Fumarate. A solution of 0.25 g (1.73 mmol) of dimethyl fumarate in 10 mL of ether was added over 30 min to the chilled solution (−30 °C) of 0.86 g (1.73 mmol) of **3a** in 50 mL of ether. After it was warmed to ambient temperature, the orange solution was stirred for 24 h. Filtration was followed by evaporation of the filtrate to dryness. The solid residue was dissolved in 25 mL of ether and stored at 5 °C for 24 h to yield 0.69 g (63%) of orange crystalline **4a**. IR (Nujol, cm^{-1}): ν 1997 vs [ν(CO)], 1939 vs [ν(CO)], 1723 vs [$\nu(CO)_{ester}$], 1595 m, 1579 m, 1560 m, 1506 m, 1484 w, 1435 w, 1351 w, 1313 w, 1263 w, 1209 m, 1157 w, 1120 w, 1065 w, 1035 w, 993 w, 953 w, 918 w, 754 w, 699 w,

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638 w, 592 w. ^{1}H NMR (500 MHz, 300 K): δ 1.38 (s, 15H, C_5Me_5), 2.60 (s, 6H, NCH_3), 2.86 (s, 6H, NCH_3), 3.32 (s, br, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.56 (s, br, 1H, CHNPh), 4.31 [s, br, 1H, $PCH(CO_2Me)CH$], 5.53 [s, br, 1H, $PCH(CO_2Me)$], 6.76 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-phenyl H), 7.22 (m, 2H, *m*-phenyl H), 7.55 (d, $^3J_{HH}$ = 7.4 Hz, *o*-phenyl H). ^{1}H NMR (100 MHz, 335 K): δ 1.38 (s, 15H, C_5Me_5), 2.56 (s, 6H, NCH_3), 2.81 (s, 6H, NCH_3), 3.31 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.53 (dd, $^3J_{HH}$ = 10.2 Hz, $^2J_{PH}$ = 4.2 Hz, PCHN), 4.43 [dt, $^3J_{HH}$ = 10.4 Hz, $^3J_{PH}$ = 4.1 Hz, $PCH(CO_2Me)CH$], 5.33 (dd, $^3J_{HH}$ = 10.2 Hz, $^2J_{PH}$ = 1 Hz, 1H, $PCH(CO_2Me)$), 6.76 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-phenyl H), 7.22 (m, 2H, *m*-phenyl H), 7.55 (d, $^3J_{HH}$ = 7.4 Hz, *o*-phenyl H). $^{13}C\{^1H\}$ NMR: δ 9.0 [s, $C_5(CH_3)_5$], 34.6 (d, $^1J_{PC}$ = 17.3 Hz, $PCHCO_2Me$), 39.46 [s, $PCH(CO_2Me)C$], 39.51 (s, NCH_3), 48.4 (s, br, OCH_3), 51.2 (s, OCH_3), 62.9 (d, $^1J_{PC}$ = 11.3 Hz, PCHN), 96.5 [s, $C_5(CH_3)_5$], 116.1 s, 118.3 s, 128.8 s, 152.7 s (phenyl C), 165.6 (s, $N{=}CN_2$), 173.0 [s, $C(O)OCH_3$], 175.0 [d, $^2J_{PC}$ = 11.6 Hz, $PCHC(O)OCH_3$], 216.1 (s, CO), 217.5 (s, CO). $^{31}P\{^1H\}$ NMR: δ 113.0 s. MS/CI: *m/z* 641 ($M^+ + H$), 612 ($M^+ - CO$), 584 ($M^+ - 2CO$). Anal. Calcd for $C_{30}H_{41}FeN_4O_6P$ (640.50): C, 56.26; H, 6.45; N, 8.75. Found: C, 56.30; H, 6.40; N, 8.75.

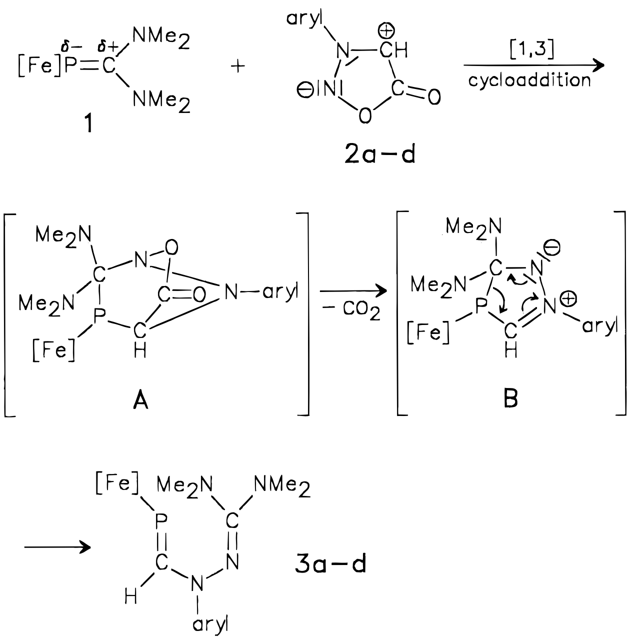
X-ray Crystal Structure Determination of 3a. Single crystals of **3a** were grown from diethyl ether at 5 °C. A dark red crystal with the approximate dimensions 0.60 × 0.50 × 0.40 mm^3 was measured on a Siemens P2$_1$ diffractometer with Mo K$_\alpha$ radiation at 173 K. Crystal data and refinement details (refined from the diffractometer angles of 20 centered reflections): a = 9.020(3) Å, b = 9.104(2) Å, c = 16.155(4) Å, α = 83.73(2)°, β = 76.42(2)°, γ = 74.55(2)°, V = 1241.4(6) Å^3, Z = 2, d_{calcd} = 1.328 g cm^{-3}, μ = 0.699 mm^{-1}, space group $P\bar{1}$, data collection of 5664 unique intensities ($2\Theta_{max}$ = 55°), structure solution by direct methods and anisotropic refinement with full-matrix least-squares methods on F^2 for all non-hydrogen atoms (program used Siemens SHELXTLplus /SHELXL-93), riding groups for hydrogen atoms, 298 parameters, maximum residual electron density 0.3 e/Å^3, R1 = 0.029 based on 4936 reflections with ($I > 2\sigma(I)$), R_w = 0.081 ($w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.6085P]$ with $P = (F_o^2 + 2F_c^2)$ for all data.

Results and Discussion

The metallophosphaalkene (η^5-C_5Me_5)(CO)$_2$FeP=C(NMe_2)$_2$ (**1**) smoothly reacted with equimolar amounts of the sydnones 3-aryl-NNOC(O)CH (aryl = C_6H_5 (**2a**), 4-FC_6H_4 (**2b**), 4-ClC_6H_4 (**2c**), 4-BrC_6H_4 (**2d**)) in an ether/dichloromethane mixture (0−10 °C) to afford the red-brown microcrystalline ferriophosphaalkenes (*E*)-(η^5-C_5Me_5)(CO)$_2$FeP=CHN(aryl)N=C(NMe_2)$_2$ (**3a**−**d**) in good yields (61−72%) (Scheme 3). In contrast to this, the reaction of **1** with the more electron-rich 3-methylsydnone or 3-(*p*-methoxyphenyl)sydnone led to decomposition. Compound **3a** was purified by crystallization from ether, whereas solutions of **3b**−**d** suffer from partial decomposition under similar conditions. The course of the reaction was monitored by ^{31}P NMR spectroscopy. The singlet for compound **1** (δ 140.0) was replaced by a singlet at δ 204.9 −216.7 for the products, which falls in the range of phosphaalkenes.

No intermediates such as the also conceivable bicyclic 1,3-cycloadduct **A** or the heterocycle **B** could be detected. It is remarkable that the reaction of the metallophosphaalkene with the sydnones **2c** and **2d** came to completion after about 3 h, whereas with **2a** and **2b** a reaction time of 24 h was necessary. In the ^{1}H NMR spectra of **3a**−**d** doublets at δ 9.14−9.41 ($^1J_{PH}$ = 8.8−9.4 Hz) were indicative of the presence of a P=CH function. In PhP=CH(NMe_2) the corresponding resonance was observed at δ 8.64 (d, $^2J_{PH}$ = 14.9 Hz).[18] The carbon atom of the P=C bond of the products gave rise to doublets at δ(^{13}C) 174.5−176.0 ($^1J_{PC}$ = 67.7−69.2 Hz) in their $^{13}C\{^1H\}$ NMR spectra. In PhP=C(H)NMe_2 the methylene carbon atom was registered at δ 187.5 (d, $^1J_{PC}$ = 48.0 Hz).

Scheme 3



2,3	aryl
a	C_6H_5
b	4-FC_6H_4
c	4-ClC_6H_4
d	4-BrC_6H_4

[Fe] = (η^5-C_5Me_5)(CO)$_2$Fe

Two singlets in the range of δ 2.38−2.59 and 2.66−2.85, each accounting for six protons, agree with two magnetically and chemically different dimethylamino groups. A singlet in the ^{13}C NMR spectra at δ 165.9−166.6 was attributed to the carbon atom of a guanidino unit. The terminal carbonyl groups resonated at δ 218.8−219.7 ppm. The IR spectra of **3a** (Nujol) featured two intense ν(CO) bands at 1985 and 1940 cm^{-1}. In the haloaryl-substituted analogues **3b**−**d** the bands of the stretching modes of the Fe(CO)$_2$ group appear at 1983 and 1934 cm^{-1}. Thus, the electron-withdrawing effect of the halophenyl substituent is only weakly mirrored by the ^{13}C NMR resonances and ν(CO) absorptions of **3b**−**d**. Chemical ionization mass spectra showed that in the products the fragment N−N(aryl)CH was incorporated in **1**. The spectroscopic data are consonant with ferriophosphaalkenes displaying a (C_5Me_5)(CO)$_2$FeP=CHN(aryl) group and a guanidino unit.

X-ray Structure Analysis of 3a. Single crystals of **3a** were grown from diethyl ether at 5 °C. The results of the structural determination are shown in Figure 1. Positional parameters are given in the Supporting Information, and selected bond lengths and angles for the compound are given in Table 1. The analysis confirms the presence of an *E*-configured ferriophosphaalkene with a distorted “piano stool” geometry

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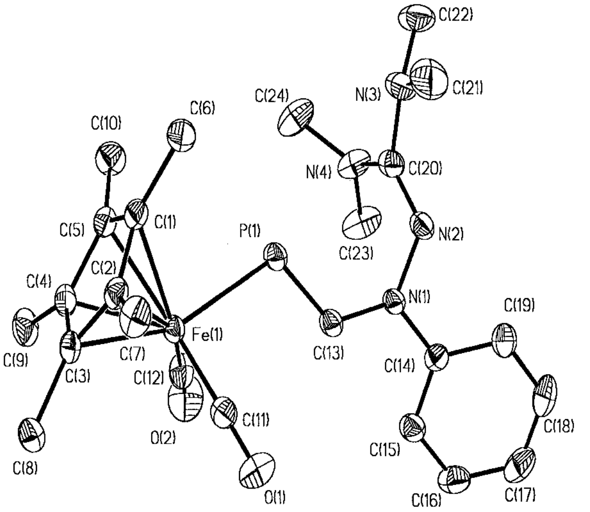

Figure 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a

Fe(1)−C(11)	1.746(2)	Fe(1)−C(12)	1.752(2)
Fe(1)−C(4)	2.101(2)	Fe(1)−C(3)	2.106(2)
Fe(1)−C(5)	2.113(2)	Fe(1)−C(2)	2.120(2)
Fe(1)−C(1)	2.146(2)	Fe(1)−P(1)	2.2956(7)
P(1)−C(13)	1.697(2)	O(1)−C(11)	1.147(2)
O(2)−C(12)	1.149(2)	N(1)−C(13)	1.377(2)
N(1)−C(14)	1.399(2)	N(1)−N(2)	1.420(2)
N(2)−C(20)	1.303(2)	N(3)−C(20)	1.381(2)
N(3)−C(21)	1.447(3)	N(3)−C(22)	1.456(2)
N(4)−C(20)	1.364(2)	N(4)−C(23)	1.454(2)
N(4)−C(24)	1.457(2)		
C(11)−Fe(1)−C(12)	94.23(8)	C(20)−N(4)−C(23)	121.5(2)
C(11)−Fe(1)−P(1)	89.94(6)	C(20)−N(4)−C(24)	122.1(2)
C(12)−Fe(1)−P(1)	87.07(6)	C(23)−N(4)−C(24)	114.5(2)
C(13)−P(1)−Fe(1)	109.67(6)	O(1)−C(12)−Fe(1)	178.7(2)
C(13)−N(1)−C(14)	123.09(13)	O(1)−C(11)−Fe(1)	178.42(14)
C(13)−N(1)−N(2)	117.55(12)	N(1)−C(13)−P(1)	125.00(12)
C(14)−N(1)−N(2)	116.80(12)	C(17)−C(16)−C(15)	120.9(2)
C(20)−N(2)−N(1)	114.22(13)	C(17)−C(18)−C(19)	121.4(2)
C(20)−N(3)−C(21)	118.1(2)	N(2)−C(20)−N(4)	128.1(2)
C(20)−N(3)−C(22)	120.0(2)	N(2)−C(20)−N(3)	116.7(2)
C(21)−N(3)−C(22)	115.0(2)	N(4)−C(20)−N(3)	115.1(2)

(P(1)−Fe(1)−C(11) = 89.94(6)°, P(1)−Fe(1)−C(12) = 87.07(6)°, C(11)−Fe(1)−C(12) = 94.23(8)°). Two legs are represented by nearly linear carbonyls. The phosphaalkenyl ligand is connected via an Fe−P single bond (2.2956(7) Å) to the (η^5-C_5Me_5)(CO)$_2$Fe fragment.[18] In **1** an Fe−P bond distance of 2.325(2) Å was observed.[9] The P=C bond length of 1.697(2) Å compares well with the corresponding bond distance in **1** (1.709(5) Å) and falls into the typical range for amino-substituted phosphaalkenes (1.70−1.76 Å).[19] Shorter P=C bond lengths of 1.65−1.67 Å were observed in nonconjugated phosphaalkenes, which are close to the calculated value of 1.646 Å in $HP{=}CH_2$.[19] The atoms P(1), C(13), N(1), and N(2) are located in a plane (average deviation 0.043 Å), from which the iron atom Fe(1) and the carbon atom C(20) are displaced by 0.3067 and 1.0090 Å, respectively. The dihedral angle between the phenyl group at N(1) and the plane defined by P(1), C(13), N(1), and N(2) amounts to 14.8°, which points to an efficient conjugation of the lone pair at N(1) with the P=C bond and the 6-π-electron system of the aryl group. In keeping with this, the bond lengths C(13)−N(1) (1.377(2) Å) and N(1)−C(14) (1.399(2) Å) are shortened as compared to the single bonds between N(3) and N(4) with the carbon atoms of the methyl substituents (average 1.454 Å). The bond length N(2)−C(20) (1.303(2) Å) agrees with a double bond. The plane defined by the atoms C(20), N(3), and N(4) and the above-mentioned plane with the atoms P(1), C(13), N(1), and N(2) enclose an interplanar angle of 103.0°. The nitrogen atoms N(1) and N(2) are linked by a single bond (1.420(2) Å). From the torsion angles C(11)−Fe(1)−P(1)−C(13) (48.7°) and C(12)−Fe(1)−P(1)−C(13) (−45.6°) it is obvious that the organophosphorus ligand bisects the Fe(CO)$_2$ angle and is oriented trans to the η^5-C_5Me_5 ligand (Figure 2).

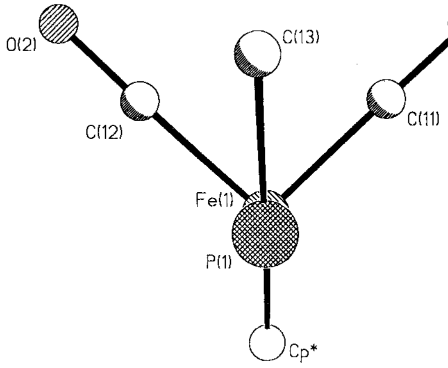

Figure 2.

It is conceivable that the formation of metallophosphaalkenes **3a**−**d** was initiated by a [1,3]-dipolar cycloaddition, resulting in the bicyclic species **A**. In keeping with the precedents in alkyne and alkene chemistry carbon dioxide is extruded to give heterocycle **B**, which undergoes ring opening to the final products. The formation of a stable guanidino function may be one of the driving forces of this process. Accordingly, no reaction was observed between (η^5-C_5Me_5)(CO)$_2$-FeP=C(SiMe$_3$)$_2$ and sydnone **2a**.

The reaction of equimolar amounts of **3a** and dimethyl fumarate led to the formation of an orange crystalline product (**4a**) in 63% yield. Elemental analysis as well as spectroscopic data revealed the compound as a [2 + 2] cycloadduct involving the P=C and C=C bonds of the reactants. Thus, the $^{31}P\{^1H\}$ NMR resonance of **3a** at δ 204.9 was replaced by a singlet at δ 113.0. This resonance compares well with the signal for the metalated phosphorus atom in diphosphetane **5** (δ 124.5)[20] and agrees with the presence of a phosphetanyl ligand in **4a** (Scheme 4).

Further structural information is derived from the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4a**. The ^1H NMR spectrum (500 MHz) at 300 K displays sharp singlets at δ 1.38 (15H), 2.60 (6H), 2.86 (6H), and 3.39 (3H) for the C_5Me_5 group, two distinct $N(CH_3)_2$ groups, and one methyl ester function. The second methyl ester group gives rise to a broad singlet at δ 3.32. Broad singlets at δ 3.56 (1H), 4.31 (1H), and 5.53 (1H) are due to the protons at the four-membered heterocycle. At 335 K both ester methyl groups are observed as sharp singlets. A doublet of triplets ($^3J_{HH}$ = 10.4, $^3J_{PH}$ = 4.1 Hz) at δ 4.43 is attributed to H_A, which experiences $^3J_{HH}$ trans couplings to H_B and H_C, and a $^3J_{PH}$ coupling to the phosphorus atom. In **5** the corresponding couplings are $^3J_{HH}$ = 13 Hz and $^3J_{PH}$ = 4.1 Hz.[20]

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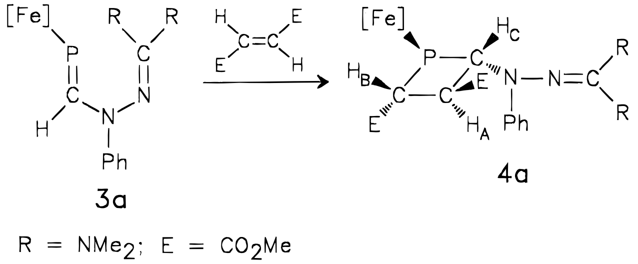
(19) Chernega, A. N.; Ruban, A. V.; Romanenko, V. D.; Markovski, L. N.; Korkin, A. A.; Antipin, M. Yu.; Struchkov, Yu. T. *Heteroat. Chem.* **1991**, *2*, 229.

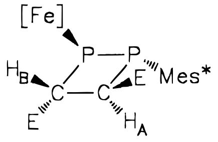
(20) Weber. L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733.

Scheme 4



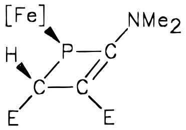
3a

4a



5

The doublet of doublets at δ 5.33 is due to H_B and reflects the coupling $^3J_{AB} = 10.2$ Hz, as well as a small coupling to the phosphorus of 1.0 Hz. A similarly small $^2J_{PH}$ coupling (1.5 Hz) is encountered in the 1,2-dihydrophosphete **6**.[9]



6

The doublet of doublets at δ 3.53 ($^3J_{HC} = 10.2$, $^2J_{PH} = 4.2$ Hz) is assigned to the proton H_C of the nitrogen-substituted CH group. In the 1,3-diphosphetane $(PhPCHNMe)_2$ the respective proton gives rise to a triplet at δ 3.69 (t, $^2J_{PH} = 3.4$ Hz).[18]

The ^{13}C nuclei of the four-membered ring resonate at δ 34.6 (d, $^1J_{PC} = 17.3$ Hz), 39.46 (s), and 62.9 (d, $^1J_{PC} = 11.3$ Hz). Only the carbon atoms adjacent to the phosphorus center experience heteronuclear coupling. For the chemically and magnetically different methyl ester units a broad singlet at δ 48.4 and a sharp singlet at δ 51.2 are seen, whereas a singlet at δ 173.0 and a doublet at δ 175.0 ($^2J_{PC} = 11.6$ Hz) account for the ester carbonyls. Singlets at δ 165.6, 216.1, and 217.5 are assigned to the three-coordinate carbon of the guanidino group and the terminal carbonyl ligands, respectively.

The temperature dependence of the ^1H NMR spectrum may be rationalized by the bending of the four-membered ring about the C−C diagonal.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft, Bonn, Germany, the Fonds der Chemischen Industrie, Frankfurt/M., Germany, and the BASF AG, Ludwigshafen, Germany, which are gratefully acknowledged.

Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **3a** (7 pages). Ordering information is given on any current masthead page.

OM9700876