Transition Metal Substituted Diphosphenes. 31.[1]
Preparation of the (η¹-1,2-Diphosphaallyl)iron Complex (η⁵-C₅Me₅)(CO)₂FeP(SiMe₃)P=C(SiMe₃)₂ and Reaction with (Z-Cyclooctene)Cr(CO)₅. Formation and Structures of the First η³-Ferradiphosphaallyl and η⁵-1,2-Diphospholyl Complexes

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Reaction of equimolar amounts of (η⁵-C₅Me₅)(CO)₂FeP(SiMe₃)₂ with ClP=C(SiMe₃)₂ furnished the η¹-diphosphaallyl complex (η⁵-C₅Me₅)(CO)₂FeP(SiMe₃)P=C(SiMe₃)₂ (6a) in addition to small amounts of the diphosphirane [(η⁵-C₅Me₅)(CO)₂FeP]₂C(SiMe₃)₂ (7). The isomerization of 6a to the metallodiphosphene (η⁵-C₅Me₅)(CO)₂FeP=PC(SiMe₃)₃ (10a) was accomplished by catalytic amounts of (Z-C₈H₁₄)Cr(CO)₅ whereas an excess of the chromium reagent gave rise to the generation of the η³-ferradiphosphaallyl complex [η³-(η⁵-C₅Me₅)(CO)₂FeP=PC(SiMe₃)₃]Cr(CO)₄ (8) and a few crystals of the 1,2-diphosphaferrocene (η⁵-C₅Me₅){η⁵-1-[(CO)₅Cr]-3,4-(Me₃SiO)₂-5-(Me₃Si)P₂C₃}Fe (9a). The molecular structures of 7 (C2/c, a = 15.803(6) Å, b = 10.905(6) Å, c = 21.056(9) Å, β = 101.20(3)°), 8 (P2₁/n, a = 9.338(5) Å, b = 15.498(13) Å, c = 23.375(14) Å, β = 92.85(5)°), 9a (P2₁/c, a = 11.889(2) Å, b = 18.692(3) Å, c = 16.688(3) Å, β = 103.90(1)°), and 10a (P2₁/c, a = 16.073(16) Å, b = 12.395(9) Å, c = 16.520(16), β = 116.50(7)°) were elucidated by single-crystal X-ray diffraction analysis.

After synthetic and structural studies we focused our interest on the chemical reactivity of metallodiphosphenes (A)[2] and metallophosphaalkenes (B and C).[3] Thus, the
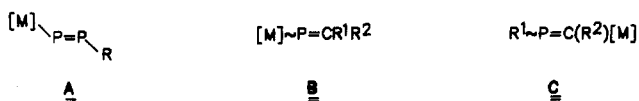

(η³-1-phosphaallyl)iron complex 2[4] was obtained from the
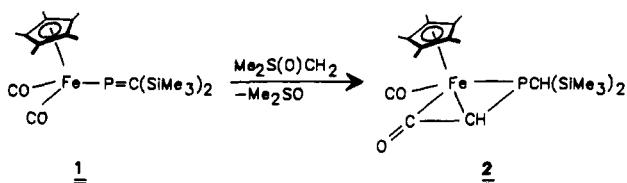
reaction of metallophosphaalkene 1 with the ylide Me₂S-(O)CH₂.[5] Compound 2 was smoothly converted into the metallophosphaalkenes 3a,b by treatment with equimolar amounts of (Z-cyclooctene)Cr(CO)₅[6] or Fe₂(CO)₉,[7] whereas

the employment of an excess of Fe₂(CO)₉ furnished the trinuclear complex 4 featuring a bridging 1-oxa-4-phosphabuta-1,3-diene ligand.[7]
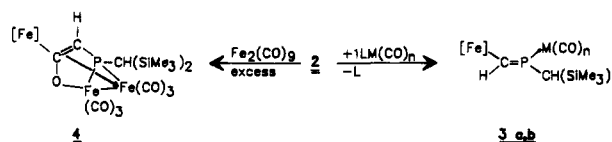
3	L	n
a	Z-C₈H₁₄	5
b	Fe(CO)₅	4

In this paper we describe the preparation and some aspects of the coordination chemistry of the (η¹-1,2-diphosphaallyl)iron complex (η⁵-C₅Me₅)(CO)₂FeP(SiMe₃)-P=C(SiMe₃)₂ (6a). Parts of the work have been published in a brief communication.[8]

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Mattson Polaris (FT-IR)/Atari 1040 STF. The ¹H, ¹³C, and ³¹P NMR spectra were taken in C₆D₆ solution at 22 °C on Bruker AC 100 (¹H, 100.131; ¹³C, 25.180; ³¹P, 40.539 MHz) and Bruker AM 300 (¹H, 300.1; ¹³C, 75.5; ³¹P, 121.7 MHz) spectrometers. Spectral standards were SiMe₄ (¹H, ¹³C) and 85% H₃PO₄ (³¹P). Electron

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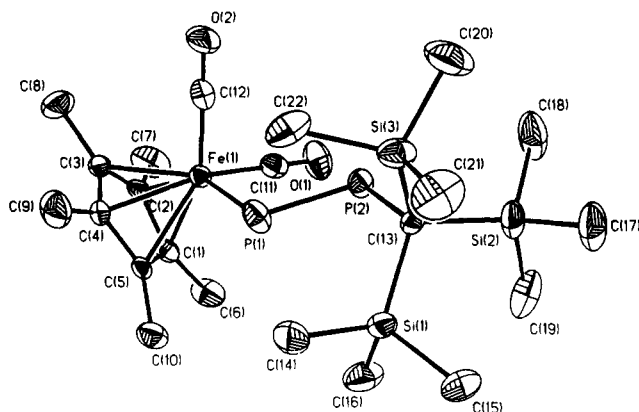(6) Weber, L.; Lücke, E.; Müller, A.; Bögge, H. *Z. Allg. Anorg. Chem.* **1990**, *583*, 91.

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Figure 1. Molecular structure of **10a** in the crystal.

Figure 2. Molecular structure of **8** in the crystal.

impact mass spectra were recorded on a Varian MAT CH5-DF spectrometer (70 eV, T = 250 °C). Elemental analyses were obtained from the Microanalytical Laboratory Dornis and Kolbe, Mülheim, Germany.

Materials. The compounds $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$,[9] (Z-cyclooctene)$Cr(CO)_5$,[10] and $ClP=C(SiMe_3)_2$[11] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds. $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)$-$P=C(SiMe_3)_2$ **(6a)** and $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP]_2C(SiMe_3)_2$ **(7)**. A solution of 1.23 g (5.47 mmol) of $ClP=C(SiMe_3)_2$ in 50 mL of THF was dropwise added to the solution of 2.32 g (5.47 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$ in 100 mL of THF. The obtained mixture was stirred for 4 h at 25 °C, and the course of the reaction was monitored by ^{31}P NMR spectroscopy. Solvent and volatiles were removed in vacuo to give 2.18 g (95%) of **6a** as a black-red oil. The product was spectroscopically pure and may be used for further reactions without additional purification.

Crystalline **6a** may be obtained from a methylcyclohexane solution at -30 °C in only 35% yield: IR (KBr) ν = 2951 m, 2900 m, 1988 vs [ν(CO)], 1940 vs [ν(CO)], 1483 w, 1453 w, 1428 w, 1385 w, 1246 m {δ[Si(CH_3)_3]}, 1052 m, 1032 w, 858 vs {ρ[Si(CH_3)_3]}, 838 vs {ρ[Si(CH_3)_3]}, 685 w, 632 w, 582 m cm^{-1}; ^1H NMR δ 0.45 (d, $^4J_{PH}$ = 2.1 Hz, 9H, C-Si(CH_3)_3), 0.51 (d, $^3J_{PH}$ = 3.5 Hz, 9H, P-Si(CH_3)_3), 0.63 (d, $^4J_{PH}$ = 0.9 Hz, C-Si(CH_3)_3), 1.42 (d, $^4J_{PH}$ = 0.6 Hz, C_5Me_5); $^{13}C\{^1H\}$ NMR δ 3.4 (d, $^2J_{PC}$ = 14.7 Hz, PSi-(CH_3)_3), 3.5 (dd, $^3J_{PC}$ = 10.2, $^4J_{PC}$ = 2.7 Hz, CSi(CH_3)_3), 5.1 (dd, $^3J_{PC}$ = 8.8, $^4J_{PC}$ = 3.0 Hz, CSi(CH_3)_3, 9.5 (dd, $^3J_{PC}$ = 5.8, $^4J_{PC}$ = 1.2 Hz, C_5(CH_3)_5), 96.1 (d, $^2J_{PC}$ = 0.8 Hz, C_5(CH_3)_5), 215.8 (dd, $^1J_{PC}$ = 105.8, $^2J_{PC}$ = 3.1 Hz, P=C), 218.0 (d, $^2J_{PC}$ = 7.4 Hz, Fe-CO); $^{31}P\{^1H\}$ NMR δ -30.3 (d, $^1J_{PP}$ = 295 Hz, Fe-P), 509.2 (d, $^1J_{PP}$ = 295 Hz, P=C); MS m/z = 540 (M$^+$), 512 (M$^+$ - CO), 484 (M$^+$ - 2CO), 411 (M$^+$ - 2CO - SiMe_3), 368 ([Cp*FeP(SiMe_3)_2]$^+$), 338 ([Cp*FePPC(SiMe_3)]$^+$), 293 ([P(SiMe_3)PC(SiMe_3)_2]$^+$), 189 ([PC-(SiMe_3)_2]$^+$), 73 (SiMe_3$^+$).

Anal. Calcd for $C_{22}H_{42}FeO_2P_2Si_3$ (540.6): C, 48.87; H, 7.83; Fe, 10.33. Found: C, 48.98; H, 7.88; Fe, 10.34.

If the reaction mixture was stirred for 2 weeks at 20 °C, small amounts (<1%) of the diphosphirane $[\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{-}P]_2C$-$(SiMe_3)_2$ **(7)** were obtained. Fractional crystallization from pentane at -30 °C afforded a few orange platelets, which were investigated by X-ray analysis: IR (KBr) ν = 2957 m, 2913 m, 1980 vs [ν(CO)], 1930 vs [ν(CO)], 1380 m, 1252 m, 1240 m {δ-[Si(CH_3)_3]}, 1072 w, 1028 w, 856 s {ρ[Si(CH_3)_3]}, 640 w, 574 s, 514 w, 501 w cm^{-1}; ^1H NMR δ 0.64 (s, 18 H, Si(CH_3)_3), 1.60 (s, 30H, C_5Me_5); $^{13}C\{^1H\}$ NMR δ 3.9 (t, J_{PC} = 5.3 Hz, Si(CH_3)_3), 9.2 (t, J_{PC} = 5.4 Hz, C_5(CH_3)_5), 97.9 (s, C_5(CH_3)_5), 218.6 (s, Fe(CO)); $^{31}P\{^1H\}$ NMR δ 0.8 s; MS m/z = 714 (M$^+$), 686 (M$^+$ - CO), 630 (M$^+$ - 3CO), 602 (M$^+$ - 4CO), 529 (M$^+$ - 4CO - SiMe_3), 467 [(Cp*Fe)_2-CSiMe_3]$^+$, 73 (SiMe_3$^+$).

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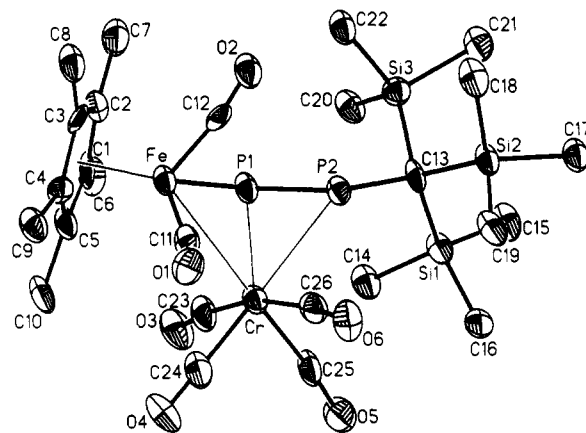(11) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159.

Anal. Calcd for $C_{31}H_{48}Fe_2O_4P_2Si_2$(714.5): C, 52.11; H, 6.77. Found: C, 51.88; H, 6.71.

$[\eta^3\text{-}(\eta^5\text{-}C_5Me_5)(CO)_2FeP=PC(SiMe_3)_3]Cr(CO)_4$ **(8)** and $(\eta^5\text{-}C_5Me_5)\{\eta^5\text{-}1\text{-}[Cr(CO)_5]\text{-}3,4\text{-}(Me_3SiO)_x\text{-}5\text{-}(SiMe_3)P_2C_3\}Fe$ **(9a)**. A solution of 1.29 g of (Z-cyclooctene)$Cr(CO)_5$ in 50 mL of pentane was added dropwise to the stirred solution of 0.800 g (1.48 mmol) of **6a** in 150 mL of pentane at 20 °C. Stirring was continued for 2 h. The reaction was monitored by ^{31}P NMR spectroscopy. Upon disappearance of the ^{31}P NMR signals of **6** the solution was concentrated in vacuo to about 50 mL. Crystallization at -30 °C yielded 0.650 g (62%) of black crystalline **8**. In some cases the ^{31}P NMR spectrum of the reaction mixture displayed the presence of several byproducts. Here a chromatographic workup is recommended. The reaction mixture was concentrated to 3 mL, absorbed on a small amount of Florisil, and dried in vacuo. The dry Florisil was put on the top of a column (l = 40 cm, d = 3 cm), which was filled with Florisil and developed with a 6:1 mixture of *n*-pentane and ether. From the first red fraction a few rhombohedral red crystals of **9a** were obtained by crystallization at 4 °C: $^{31}P\{^1H\}$ NMR δ 11.1 (d, $^1J_{PP}$ = 389.7 Hz, CrP), -87.0 (d, $^1J_{PP}$ = 389.7 Hz, PC); MS m/z 732 (M$^+$), 620 (M$^+$ - 4CO), 592 (M$^+$ - 5CO), 540 (M$^+$ - Cr(CO)_5), 467 (M$^+$ - Cr(CO)_5 - SiMe_3), 191 (FeCp*$^+$, 73 (SiMe_3$^+$).

The black-red fraction was concentrated to 30 mL and stored at -30 °C. After 2 d one obtained 0.430 g (41%) of black crystalline **8**: IR (KBr) ν 2957 m, 2899 m, 2013 vs [ν(CO)], 1989 vs [ν(CO)], 1946 vs [ν(CO)], 1916 vs [ν(CO)], 1894 vs [ν(CO)], 1431 w, 1380 w, 1251 m (δ[Si(CH_3)_3]), 1025 w, 848 vs (ρ[Si(CH_3)_3]), 664 m, 653 m, 621 m, 563 m, 539 w, 511 w, 487 w cm^{-1}; ^1H NMR δ 0.53 (s, 27 H, Si(CH_3)_3), 1.32(s, 15 H, C_5Me_5); $^{13}C\{^1H\}$ NMR δ 5.2 (dd, $^2J_{PC}$ = 5.4 Hz, $^3J_{PC}$ = 3.2 Hz, Si(CH_3)_3), 9.0 (d, $^3J_{PC}$ = 6.9 Hz, C_5(CH_3)_5), 99.3 (s, C_5(CH_3)_5), 211.5 (s, FeCO), 225.5 (s, FeCO), 226.4 (m, CrCO), 227.6 (m, CrCO), 232.7 (m, CrCO); $^{31}P\{^1H\}$ NMR δ 134.9 (d, $^1J_{PP}$ = 524 Hz, PC), 431.5 (d, $^1J_{PP}$ = 524 Hz, Fe-P); MS m/z 540 (M$^+$ - Cr(CO)_4), 512 (M$^+$ - Cr(CO)_4 - CO), 484 (M$^+$ - Cr(CO)_4 - 2CO), 411 (M$^+$ - Cr(CO)_4 - 2CO - SiMe_3), 368 (Cp*FeP(SiMe_3)_2$^+$), 253 (Cp*FeP=P$^+$), 73 (SiMe_3$^+$).

Anal. Calcd for $C_{26}H_{42}CrFeO_6P_2Si_3$ (704.7): C, 44.31; H, 6.00; Fe, 7.92. Found: C, 44.26; H, 6.00; Fe, 7.91.

$(\eta^5\text{-}C_5Me_5)(CO)_2FeP=PC(SiMe_3)_3$ **(10a)**. Solid (Z-cyclooctene)$Cr(CO)_5$ (0.30 g, 1.00 mmol) was added to a solution of 7.40 g (13.70 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)P=C(SiMe_3)_2$ **(6a)** in 200 mL of *n*-pentane at 20 °C. The solution was stirred for 2 weeks with ^{31}P NMR monitoring. Then the solvent and all other volatiles were removed in vacuo. The residue was dissolved in 50 mL of pentane. The red filtrate was stored at -30 °C. After 14 days of crystallization, 1.70 g (30.0%) of **10a** was obtained as dark red crystals: IR (KBr) ν 2956 m, 2901 m, 1999 vs [ν(CO)], 1947 vs [ν(CO)], 1491 w. 1429 w, 1378 m, 1249 s [δSi(CH_3)_3], 844 vs ([ρ[Si(CH_3)_3]), 782 w, 662 m, 594 m, 573 cm^{-1}; ^1H NMR δ 0.52 (s, 27 H, Si(CH_3)_3), 1.39 (s, 15 H, C_5Me_5); $^{13}C\{^1H\}$ NMR δ 5.1 (dd, $^2J_{PC}$ = 5.4, $^3J_{PC}$ = 4.1 Hz, Si(CH_3)_3), 9.3 (d, $^3J_{PC}$ = 6.5 Hz, C_5-(CH_3)_5), 97.2 (s, C_5(CH_3)_5), 216.2 (dd, $^2J_{PC}$ = 12.6, $^3J_{PC}$ = 1.4 Hz, FeCO); $^{31}P\{^1H\}$ NMR δ 602.3 (d, $^1J_{PP}$ = 654.8 Hz, PC), 788.2 (d, $^1J_{PP}$ = 654.8 Hz, Fe-P); MS m/z 540 (M$^+$), 512 (M$^+$ - CO), 484

Table I. Crystal Data Collection and Refinement Parameters

	7^a	8^b	$9a^a$	$10a^a$
formula	$C_{31}H_{48}Fe_2O_4P_2Si_2$	$C_{26}H_{42}CrFeO_6P_2Si_3$	$C_{27}H_{42}CrFeO_7P_2Si_3$	$C_{22}H_{42}FeO_2P_2Si_3$
mol wt	714.5	704.7	732.7	540.6
cryst size/mm	0.05 × 0.3 × 0.3	0.29 × 0.12 × 0.08	0.3 × 0.4 × 0.5	0.3 × 0.4 × 0.6
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	15.803(6)	9.338(5)	11.889(2)	16.073(16)
b/Å	10.905(6)	15.498(13)	18.692(3)	12.395(9)
c/Å	21.056(9)	23.375(14)	16.688(3)	16.520(16)
β/deg	101.20(3)	92.85	103.90(1)	116.50(7)
V/Å^3	3560(3)	3378(4)	3600.0(11)	2945(5)
Z	4	4	4	4
D_{calcd}/g cm^{-3}	1.333	1.385	1.352	1.219
$F(000)$	1504	1472	1528	1152
μ(Mo Kα)/mm^{-1}	1.000	0.98	0.920	0.753
temp/K	170	110	297	168
2θ max/deg	55.0	45.0	50.0	50.0
no. of obsd rflns	1376 ($F_o > 5.0\sigma(F)$)	2910 ($F_o > 4\sigma(F)$)	3765 ($F_o > 4.0\sigma(F)$)	3532 ($F_o > 4.0\sigma(F)$)
no. of variables	186	349	372	271
min/max transm		0.09/0.36	0.5280/0.5925	
goodness of fit	1.44	2.16	1.92	1.65
R_f	0.064	0.067	0.055	0.042
R_w	0.044	0.067	0.045	0.036
largest peak in final diff map (e/Å^3)	0.69	0.95	0.38	0.46
abs corr	N/A	empirical	semiempirical	N/A

^{a} Siemens P2$_1$/V diffractometer, Mo Kα (graphite monochromator), λ = 0.710 73 Å. ^{b} Nicolet R 3m/V diffractometer, Mo Kα (graphite monochromator), λ = 0.710 69 Å.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) of 10a

	x	y	z	$U(eqU)^a$
Fe(1)	1484(1)	550(1)	2426(1)	20(1)
Si(1)	4232(1)	−2653(1)	3187(1)	28(1)
Si(2)	2979(1)	−4304(1)	3584(1)	36(1)
Si(3)	2511(1)	−3733(1)	1560(1)	36(1)
P(1)	2454(1)	−766(1)	2415(1)	34(1)
P(2)	2155(1)	−2189(1)	2815(1)	28(1)
O(1)	1016(2)	−463(3)	3754(2)	50(2)
O(2)	28(2)	−488(3)	861(2)	47(1)
C(1)	2178(3)	1810(3)	3326(3)	24(2)
C(2)	1241(3)	2125(3)	2760(3)	26(2)
C(3)	1110(3)	2099(3)	1861(3)	28(2)
C(4)	1973(3)	1780(3)	1868(3)	24(2)
C(5)	2634(2)	1638(3)	2780(3)	19(2)
C(6)	2628(3)	1783(4)	4347(3)	43(2)
C(7)	531(3)	2452(4)	3076(3)	50(2)
C(8)	245(3)	2414(4)	1030(3)	49(2)
C(9)	2173(3)	1705(4)	1060(3)	47(2)
C(10)	3647(3)	1407(3)	3102(3)	34(2)
C(11)	1209(3)	−101(3)	3215(3)	29(2)
C(12)	604(3)	−91(3)	1477(3)	30(2)
C(13)	3001(3)	−3216(3)	2777(2)	20(2)
C(14)	4444(3)	−1921(4)	2305(3)	44(2)
C(15)	5142(3)	−3743(4)	3587(3)	42(2)
C(16)	4582(3)	−1697(3)	4177(3)	47(2)
C(17)	3433(3)	−5645(3)	3421(3)	53(3)
C(18)	1783(3)	−4583(4)	3468(4)	63(3)
C(19)	3674(3)	−3877(4)	4788(3)	54(3)
C(20)	1439(3)	−4578(4)	1248(3)	63(3)
C(21)	3369(3)	−4600(4)	1368(3)	59(3)
C(22)	2162(3)	−2620(4)	706(3)	48(2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(M$^+$ − 2CO), 411 (M$^+$ − 2CO − SiMe$_3$), 368 (Cp*FeP(SiMe$_3$)$_2^+$), 309 (M$^+$ − C(SiMe$_3$)$_3$), 281 (M$^+$ − CO − C(SiMe$_3$)$_3$), 253 (M$^+$ − 2CO − C(SiMe$_3$)$_3$), 73 (SiMe$_3^+$).

Anal. Calcd for $C_{22}H_{42}FeO_2P_2Si_3$ (540.6): C, 48.87; H, 7.83; Fe, 10.33. Found: C, 48.98; H, 7.88; Fe, 10.34.

(12) For reviews on phosphinidene chemistry, see: (a) Mathey, F. *Angew. Chem.* 1987, *99*, 285; *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 257. (b) Mathey, F.; In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Georg Thieme Verlag: Stuttgart, New York, 1990; p 33.

Table III. Selected Bond Lengths (Å) and Angles (deg) of 10a

Fe(1)–P(1)	2.261(3)	Fe(1)–C(1)	2.102(4)
Fe(1)–C(2)	2.113(4)	Fe(1)–C(3)	2.102(4)
Fe(1)–C(4)	2.107(5)	Fe(1)–C(5)	2.148(4)
Fe(1)–C(11)	1.750(5)	Fe(1)–C(12)	1.764(4)
Si(1)–C(13)	1.914(4)	P(2)–C(13)	1.884(5)
Si(2)–C(13)	1.907(5)	O(2)–C(12)	1.137(5)
Si(3)–C(13)	1.913(4)	P(1)–P(2)	2.017(3)
O(1)–C(11)	1.155(7)		

Fe(1)–P(1)–P(2)	111.2(1)	P(1)–Fe(1)–C(11)	94.5(2)
P(1)–Fe(1)–C(12)	87.2(2)	C(11)–Fe(1)–C(12)	94.9(2)
P(1)–P(2)–C(13)	107.4(2)		

Results and Discussion

The reaction of the ferriodisilylphosphane 5 with equimolar amounts of ClP=C(SiMe$_3$)$_2$ yielded the (σ-1,2-diphosphaallyl)iron complex 6a as a black oil which could

[Fe] = (η^5–C$_5$Me$_5$)(CO)$_2$Fe
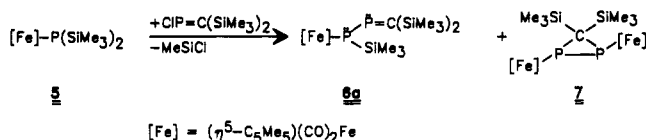
be crystallized from pentane only with a considerable loss of product. The metal-functionalized diphosphirane 7 was also formed in minor quantities, and due to its thermal stability and high tendency for crystallization it was conveniently separated from 6a.

The ^{31}P{^{1}H} NMR spectrum of 6a displays doublets at δ −30.3 and 502.9 ($^1J_{PP}$ = 295 Hz). The carbon atom of the P=C function resonates at δ 215.8 (dd, $^1J_{PC}$ = 105.8, $^2J_{PC}$ = 3.1 Hz). Three distinct absorptions for the protons of the chemically and magnetically different trimethylsilyl groups in the ^{1}H NMR spectrum are in agreement with the proposed structure of the compound. The ^{31}P nuclei of 7 gave rise to a singlet at δ = 0.8. One signal for the methyl protons of the trimethylsilyl group (δ 0.64) underlines the trans geometry of the metal fragments at the diphosphirane ring. The mechanism of the formation of this species from 5 and ClP=C(SiMe$_3$)$_2$ remains unclear. In a formal point of view, it is conceivable that 7 resulted

Table IV.   Atomic Coordinates (×10⁴) and Equivalent
Isotropic Displacement Coefficients (Å² × 10³) of 8

|	x	y	z	$U(eq)^a$
Fe	1049(2)	6894(1)	−43(1)	28(1)
Cr	−878(2)	7980(1)	−773(1)	31(1)
P(1)	1522(3)	7508(2)	−915(1)	30(1)
P(2)	125(3)	6819(2)	−1473(1)	28(1)
Si(1)	189(3)	8113(2)	−2568(1)	33(1)
Si(2)	−531(3)	6119(2)	−2622(1)	31(1)
Si(3)	2605(3)	6753(2)	−2279(1)	30(1)
O(1)	−1935(9)	6559(5)	158(3)	43(3)
O(2)	1268(9)	5203(5)	−566(3)	43(3)
O(3)	955(9)	9569(5)	−525(3)	49(3)
O(4)	−2668(10)	8682(5)	158(3)	55(3)
O(5)	−2309(10)	9292(5)	−1542(3)	58(3)
O(6)	−3450(9)	6855(6)	−1125(3)	50(3)
C(1)	2774(13)	7694(7)	321(4)	36(4)
C(2)	3169(12)	6803(7)	317(4)	35(4)
C(3)	2188(10)	6346(6)	671(4)	28(3)
C(4)	1174(10)	6953(6)	862(4)	26(3)
C(5)	1505(13)	7794(6)	649(4)	35(4)
C(6)	3641(12)	8393(7)	68(4)	43(4)
C(7)	4446(12)	6416(8)	52(4)	48(4)
C(8)	2308(13)	5401(7)	848(4)	43(4)
C(9)	10(13)	6777(7)	1266(4)	40(4)
C(10)	842(13)	8612(7)	824(4)	44(4)
C(11)	−882(13)	6798(6)	7(4)	33(4)
C(12)	1111(10)	5890(7)	−389(4)	27(3)
C(13)	590(12)	7015(6)	−2242(3)	30(3)
C(14)	878(12)	9037(6)	−2126(4)	36(4)
C(15)	944(14)	8272(7)	−3287(4)	45(4)
C(16)	−1781(12)	8265(6)	−2704(4)	40(4)
C(17)	−577(13)	6191(7)	−3423(4)	39(4)
C(18)	115(14)	5023(6)	−2423(4)	43(4)
C(19)	−2460(13)	6116(7)	−2430(4)	40(4)
C(20)	3780(12)	7709(6)	−2143(4)	36(4)
C(21)	3051(13)	6342(6)	−3011(4)	39(4)
C(22)	3264(13)	5907(6)	−1759(4)	38(4)
C(23)	339(13)	8930(7)	−598(4)	38(4)
C(24)	−2009(14)	8400(7)	−191(4)	42(4)
C(25)	−1725(14)	8768(7)	−1269(4)	42(4)
C(26)	−2427(14)	7229(7)	−1000(4)	40(4)

*ᵃ Equivalent isotropic U defined as one-third of the trace of the
orthogonalized U_{ij} tensor.*

from the addition of the phosphinidene [Fe]–P to the
metallophosphaalkene 1.[12]

We were interested in the ligand properties of compound
6a. Treatment of **6a** with an excess of (Z-C₈H₁₄)Cr(CO)₅
afforded the tetracarbonylchromium complex **8** in 62%
yield as a crystalline dark-red solid. A few crystals of the
1,2-diphosphaferrocene **9a** were also obtained.
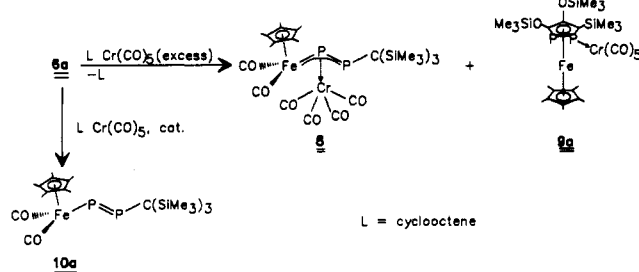
Both compounds **8** and **9a** were isolated by column
chromatography on Florisil with n-pentane as an eluent.
If **6a** is allowed to react with 5 mol % of (Z-cyclooctene)-
Cr(CO)₅ over a period of 3 days, the metallodiphosphene
10a was obtained in 30% yield. The ³¹P{¹H} NMR
spectrum of **10a** was characterized by two doublets at δ
602.3 and 788.2 with the typical coupling $^1J_{PP}$ = 654.8 Hz.
The η^3-coordination of **10a** to the Cr(CO)₄ moiety in **8**
gave rise to significant high-field shifts of $\Delta\delta$ = 356.7 for
the metalated and 467.4 for the alkylated phosphorus atom.
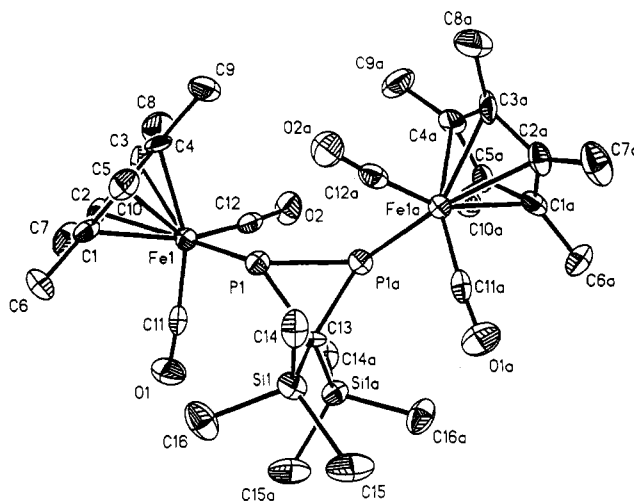
Figure 3. Molecular structure of **7** in the crystal.

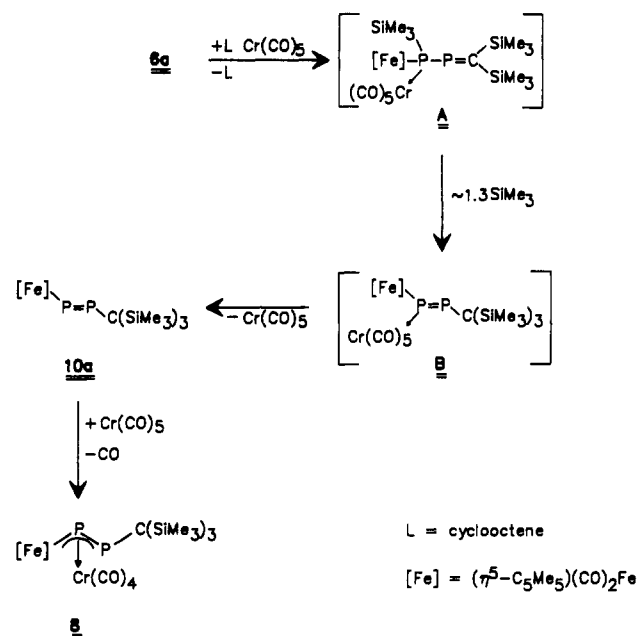Table V.   Selected Bond Lengths (Å) and Bond Angles (deg)
of **8a**

Fe–Cr	2.946(3)	Fe–P(1)	2.314(3)
Fe–C(1)	2.172(11)	Fe–C(2)	2.117(11)
Fe–C(3)	2.111(9)	Fe–C(4)	2.114(9)
Fe–C(5)	2.162(10)	Fe–C(11)	1.818(12)
Fe–C(12)	1.756(11)	Cr–P(1)	2.396(4)
Cr–P(2)	2.635(4)	Cr–C(23)	1.892(12)
Cr–C(24)	1.879(12)	Cr–C(25)	1.837(11)
Cr–C(26)	1.912(13)	P(1)–P(2)	2.090(4)
P(2)–C(13)	1.896(9)	Si(1)–C(13)	1.894(10)
O(2)–C(12)	1.154(13)	Si(2)–C(13)	1.928(10)
O(4)–C(24)	1.133(14)	Si(3)–C(13)	1.931(11)
O(6)–C(26)	1.143(15)	O(1)–C(11)	1.124(14)
		O(3)–C(23)	1.154(14)
		O(5)–C(25)	1.153(13)
Cr–Fe–P(1)	52.5(1)	Cr–Fe–C(11)	60.3(3)
P(1)–Fe–C(11)	108.8(3)	Cr–Fe–C(12)	105.8(3)
P(1)–Fe–C(12)	86.9(3)	C(11)–Fe–C(12)	90.7(4)
Fe–Cr–P(1)	50.1(1)	Fe–Cr–P(2)	75.2(1)
P(1)–Cr–P(2)	48.8(1)	Fe–Cr–C(23)	88.7(3)
P(1)–Cr–C(23)	73.3(4)	P(2)–Cr–C(23)	115.9(4)
Fe–Cr–C(24)	97.4(3)	P(1)–Cr–C(24)	140.3(4)
P(2)–Cr–C(24)	156.3(4)	C(23)–Cr–C(24)	85.8(5)
Fe–Cr–C(25)	167.8(4)	P(1)–Cr–C(25)	119.4(4)
P(2)–Cr–C(25)	102.5(3)	C(23)–Cr–C(25)	81.6(5)
C(24)–Cr–C(25)	89.2(5)	Fe–Cr–C(26)	104.2(3)
P(1)–Cr–C(26)	118.3(4)	P(2)–Cr–C(26)	72.4(4)
C(23)–Cr–C(26)	166.4(5)	C(24)–Cr–C(26)	88.2(5)
C(25)–Cr–C(26)	86.2(5)	Fe–P(1)–Cr	77.4(1)
Fe–P(1)–P(2)	101.5(1)	Cr–P(1)–P(2)	71.6(1)
Cr–P(2)–P(1)	59.6(1)	Cr–P(2)–C(13)	125.8(3)
P(1)–P(2)–C(13)	110.1(3)	Fe–C(11)–O(1)	158.8(9)
Fe–C(12)–O(2)	172.0(8)	Cr–C(23)–O(3)	171.7(10)
Cr–C(24)–O(4)	177.5(10)	Cr–C(25)–O(5)	174.3(9)
Cr–C(26)–O(6)	172.4(11)		

The π-coordination was accompanied by a decrease in the
PP coupling of 130.8 Hz.

The ¹³C{¹H} NMR spectrum of **8** shows five absorptions
in the region of terminal carbonyl ligands. A singlet at δ
211.5 is assigned to the iron carbonyl, which experiences
a coordination shift of 4.7 ppm to high field. This
observation reflects a significant withdrawal of electron
density from the Cp*Fe(CO)₂ fragment as compared to
10a. A similar observation is made in the IR spectra of
both species, where the ν(CO) stretch in the free ligand at
ν = 1998 cm⁻¹ upon coordination is shifted to ν = 2013
cm⁻¹. The novel 1,2-diphosphaferrocene derivative **9a** is
characterized in the ³¹P{¹H} NMR spectrum by two
doublets at δ 11.1 for the chromium-bound phosphorus
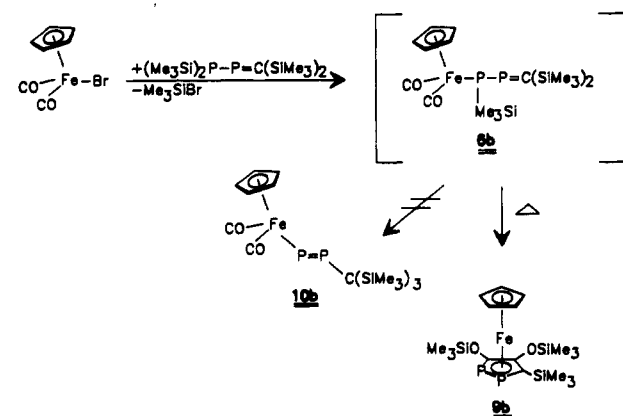atom P1 and δ −87.0 for P2 ($^1J_{PP}$ = 389.7 Hz).

It is reasonable that the generation of **8** was initiated
by the attack of the Cr(CO)₅ fragment at the metalated

phosphorus atom of **6a**. A relief of the steric constraint

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of 7

	x	y	z	$U(eq)^a$
Fe(1)	4329(1)	2191(1)	6121(1)	22(1)
P(1)	5221(2)	2913(3)	7045(1)	23(1)
Si(1)	6017(2)	5232(3)	7513(1)	27(1)
O(1)	3709(5)	4634(7)	5725(3)	47(3)
O(2)	3109(4)	1398(7)	6891(3)	46(3)
C(1)	4977(6)	2070(10)	5320(4)	27(4)
C(2)	4131(6)	1496(9)	5158(4)	27(4)
C(3)	4117(7)	533(10)	5592(5)	31(4)
C(4)	4928(7)	475(9)	6041(5)	31(4)
C(5)	5475(6)	1416(9)	5852(4)	24(4)
C(6)	5297(6)	3093(9)	4966(4)	42(5)
C(7)	3432(6)	1840(9)	4606(4)	48(5)
C(8)	3383(7)	−357(9)	5597(5)	54(5)
C(9)	5205(7)	−418(9)	6590(5)	48(5)
C(10)	6391(6)	1635(9)	6138(4)	36(4)
C(11)	3961(6)	3683(10)	5909(4)	26(4)
C(12)	3591(6)	1768(9)	6586(5)	28(4)
C(13)	5000	4322(10)	7500	17(5)
C(14)	7052(5)	4396(8)	7790(4)	30(4)
C(15)	6103(6)	6658(8)	8027(5)	50(5)
C(16)	5984(6)	5749(9)	6666(4)	45(4)

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

at this position in A was achieved by the 1,3-migration of the Me₃Si group from the phosphorus to the low-coordinated carbon atom rendering the Cr(CO)₅ adduct B of the E-configurated metallodiphosphene **10a**. A similar migratory rearrangement was reported by Markovskii et al., where the reaction of LiP(SiMe₃)Mes* with ClP=C(SiMe₃)₂ yielded Mes*P=PC(SiMe₃)₃.[13] Considerable steric interactions between the cis-oriented (Me₃Si)₃C group and the carbonylchromium moiety in B led to the dissociation of the adduct. In keeping with this, the exclusive formation of **10a** was possible by the employment of only catalytic amounts of (Z-cyclooctene)-Cr(CO)₅. The η²-ligation of Cr(CO)₅ to the P=P bond of **10a** and extrusion of a carbonyl ligand finally gave complex **8**.

The formation of the 1,2-diphosphaferrocene **9a** from **6a** is not clear. Recently Niecke reported the synthesis of the related (η¹-diphosphaallyl)iron species **6b**, which rearranged to the sandwich **9b** by heating. Here no metallodiphosphene such as **10b** was detected.[14]

X-ray Structure Analysis of 10a. The molecular structure of **10a** (Figure 1, Tables II and III) and the first

structurally characterized metallodiphosphene (η⁵-C₅-Me₅)(CO)₂FeP=PMes* (11) (Mes* = 2,4,6-tBu₃C₆H₂) are well comparable.[15] The molecule features an E-configurated PP double bond [2.017(3) Å], which is linked to the metal through an Fe-P single bond [2.261(3) Å]. The respective bond distances in **11** are 2.027(3) and 2.260(1) Å. The carbon–phosphorus separation P(2)–C(13) amounts to 1.884(5) Å, whereas in **11** a value of 1.873(3) Å was found for the corresponding bond. The valence angle at the metalated phosphorus atom in **10a** of 111.2(1)° is markedly widened as compared to the bond angle at the alkylated P atom P(1)–P(2)–C(13) of 107.4(2)°. In **11** a similar situation with angles of 109.8(1) and 102.4(1)°, respectively, was encountered. The E-configurated diphosphene (Me₃Si)₃CP=PC(SiMe₃)₃ features CPP bond angles of 108.2(4) and 108.9(4)° for the two crystallographically independent molecules.[16] As it is also realized in compound **11**, the atoms Fe, P(1), P(2), and C(13) are located in the same plane (torsion angle Fe(1)–P(1)–P(2)–C(13) = 179.9°). The diphosphenyl ligand can be considered as one leg in a distorted three-legged piano-stool arrangement. The distortion is evident by the different angles the ligands form with the iron atom (P(1)–Fe(1)–C(11) = 94.5(2)°; P(1)–Fe(1)–C(12) = 87.2(2)°; C(11)–Fe(1)–C(12) = 94.9-(2)°). Two legs of the piano stool are represented by terminal essentially linear carbonyl groups.

X-ray Structure Analysis of 8. The X-ray structure analysis of **8** (Figure 2; Tables IV and V) displays the picture of a metallodiphosphene which serves as a η³-ligand toward the Cr(CO)₄ moiety. Such a coordination mode of a diphosphene is novel. The complex may also be envisaged as a 42 VE butterfly molecule (arachno cluster) in the sense of the Wade–Mingos rules.[17] Two different chromium–phosphorus bonds [Cr–P(1) = 2.395(4); Cr–P(2) = 2.635(4) Å] underline the unsymmetrical ligation of the PP bond of **10a** to the chromium. The calculated single bond distance Cr⁰–P, resulting from the sum of the

(13) (a) Romanenko, V. D.; Polyachenko, L. K.; Markovskii, L. N. *Phosphorus Sulfur* **1985**, *22*, 365. (b) Ruban, A. V.; Polyachenko, L. K.; Romanenko, V. D.; Markovskii, L. N. *Zh. Obshch. Khim.* **1985**, *55*, 1190.

(14) Niecke, E.; Schmidt, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1659.

(15) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110.

(16) Cowley, A. H.; Kilduff, J. E. Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.

(17) See e.g.: (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
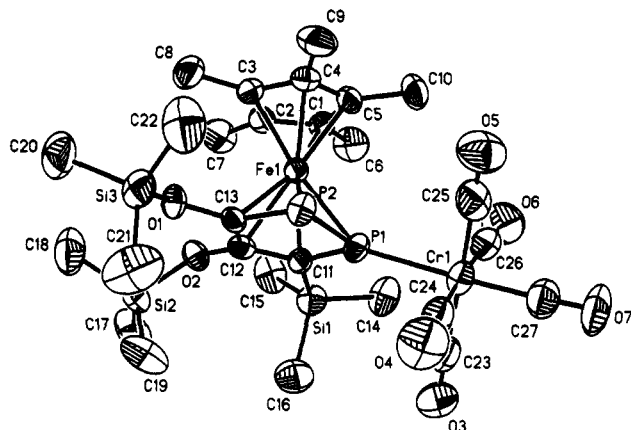
Figure 4. Molecular structure of 9a in the crystal.

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) of 7

Fe(1)–P(1)	2.309(3)	Fe(1)–C(1)	2.141(10)
Fe(1)–C(2)	2.130(9)	Fe(1)–C(4)	2.118(10)
Fe(1)–C(3)	2.116(10)	Fe(1)–C(11)	1.755(11)
Fe(1)–C(5)	2.171(10)	P(1)–C(13)	1.878(10)
Fe(1)–C(12)	1.724(11)	Si(1)–C(13)	1.884(7)
P(1)–P(1A)	2.162(5)	O(1)–C(11)	1.151(13)
O(2)–C(12)	1.161(13)	C(13)–P(1A)	1.878(10)
C(13)–Si(1A)	1.884(7)		

Fe(1)–P(1)–C(13)	124.4(1)	P(1)–Fe(1)–C(11)	90.9(3)
C(13)–P(1)–P(1A)	54.9(2)	P(1)–Fe(1)–C(12)	89.0(3)
Fe(1)–C(12)–O(2)	175.1(9)	Fe(1)–P(1)–P(1A)	119.8(2)
P(1)–C(13)–P(1A)	70.3(4)	Fe(1)–C(11)–O(1)	175.2(8)
P(1)–C(13)–Si(1A)	131.7(2)	P(1)–C(13)–Si(1)	101.3(2)
P(1A)–C(13)–Si(1A)	101.3(2)	Si(1)–C(13)–P(1A)	131.7(2)
		Si(1)–C(13)–Si(1A)	116.4(6)

covalence radii of Cr^0 (1.48 Å)[18] and P(1.10 Å),[19] is 2.58 Å. The $\eta^1:\eta^1:\eta^2$-diphosphene complex **12** shows considerably

12 **13** **14** **15**
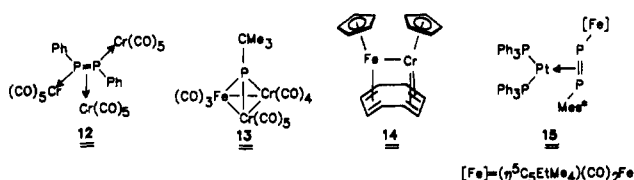
[Fe]=(η^5C₅EtMe₄)(CO)₂Fe

longer Cr–P contacts for the Cr–P π-interaction (2.524-(3)–2.546(5) Å) as compared to the end-on coordinated $Cr(CO)_5$ groups (2.387(4)–2.411(4) Å).[20] The sixth coordination site in the distorted carbonyl chromium octahedron is occupied by the iron atom of the (η^5-C₅-Me₅)(CO)₂Fe unit via a long Cr–Fe bond of 2.945(3) Å. Comparable iron–chromium contacts are present in heterobimetallic carbonyl anions such as [CrFe(CO)₉]²⁻ (2.941(2) Å) or [HCrFe(CO)₉]⁻ (2.956(7) Å).[21] The complex **13** features two different Fe–Cr bonds which are considerably shorter (2.781(2) and 2.846(2) Å),[22] whereas in complex **14** a Fe–Cr distance of only 2.726(8) Å is found.[23]

The π-coordination to the chromium atom is accompanied by an elongation of the P=P bond to 2.090(4) Å.

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(19) Pauling, L. *Principles of Chemistry*; Verlag Chemie: Weinheim, Germany, 1973, p 170.
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Table VIII. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) of 9a

	x	y	z	$U(eq)^a$
Fe(1)	7022(1)	404(1)	6973(1)	31(1)
Cr(1)	7422(1)	-941(1)	9231(1)	48(1)
P(1)	7555(2)	18(1)	8311(1)	36(1)
P(2)	8864(2)	-17(1)	7645(1)	39(1)
Si(1)	6094(2)	1400(1)	8634(1)	48(1)
Si(2)	8488(2)	2703(1)	7707(1)	50(1)
Si(3)	10560(2)	1061(1)	6716(1)	52(1)
O(1)	9259(3)	1255(2)	6884(3)	40(2)
O(2)	7614(3)	2001(2)	7472(3)	40(2)
O(3)	7404(5)	92(3)	10635(3)	85(3)
O(4)	10045(5)	-908(3)	9835(4)	95(3)
O(5)	7669(6)	-1954(3)	7878(4)	95(3)
O(6)	4810(5)	-1099(4)	8704(4)	102(3)
O(7)	7282(6)	-2205(3)	10313(4)	110(3)
C(1)	5285(5)	328(4)	6372(4)	40(3)
C(2)	5841(5)	865(3)	5987(4)	39(2)
C(3)	6740(6)	517(4)	5703(4)	40(3)
C(4)	6730(6)	-210(3)	5911(4)	43(3)
C(5)	5841(6)	-332(4)	6315(4)	44(3)
C(6)	4200(5)	419(4)	6683(4)	68(3)
C(7)	5502(6)	1635(4)	5860(4)	66(3)
C(8)	7486(6)	882(4)	5217(4)	61(3)
C(9)	7490(6)	-787(4)	5674(4)	69(4)
C(10)	5473(6)	-1047(4)	6575(4)	63(3)
C(11)	7123(5)	921(3)	8114(3)	32(2)
C(12)	7814(5)	1294(3)	7659(4)	35(2)
C(13)	8644(5)	902(3)	7365(4)	32(2)
C(14)	5088(6)	774(4)	8984(4)	67(4)
C(15)	5161(6)	2088(4)	7976(5)	65(3)
C(16)	7016(7)	1839(4)	9562(4)	76(4)
C(17)	7594(7)	3403(4)	8052(6)	93(5)
C(18)	8908(7)	3036(4)	6791(5)	90(5)
C(19)	9742(6)	2458(4)	8551(5)	92(4)
C(20)	10720(7)	1693(4)	5914(5)	84(4)
C(21)	11668(6)	1168(6)	7678(5)	106(5)
C(22)	10622(7)	152(4)	6303(5)	90(4)
C(23)	7378(6)	-288(4)	10098(5)	55(3)
C(24)	9068(7)	-923(4)	9600(5)	57(3)
C(25)	7555(7)	-1571(4)	8384(5)	65(4)
C(26)	5776(7)	-1000(5)	8899(5)	62(4)
C(27)	7366(7)	-1719(5)	9908(5)	67(4)

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

This is not unexpected. In **12** the P–P bond was determined to 2.125(6) Å,[20] whereas the η^2-diphosphene complex **15** features a PP separation of 2.140(4) Å.[24] The FeP contact in **8** of 2.313(3) Å also exceeds the corresponding bond distance in the free metallodiphosphene. A significant contraction of the angle Fe(1)–P(1)–P(2) from 111.2(1) to 101.5(1)° is observed in going from **10a** to **8**, whereas the valence angle P(1)–P(2)–C(13) is slightly opened from 107.4(2) to 110.1(3)°. In complex **8** the ligand **10a** is still present in the E-configuration although the atoms Fe, P(1), P(2), and C(13) are no longer arranged coplanarly (torsion angle Fe(1)–P(1)–P(2)–C(13) = -167.0°). In accord with the description of **8** as a $Cr(CO)_4$ complex of **10a** and the latter acting as a η^3-(1-ferra-2,3-diphosphaallyl) ligand, the substituents $C(SiMe_3)_3$ and η^5-C₅Me₅ are present in the syn configuration with the torsion angle P(2)–P(1)–Fe(1)–Cp* = -122.8° to the center of the C₅Me₅ ring (Cp*). The carbonyl ligands at the Fe atom of **8** deviate markedly from linearity [Fe–C(12)–O(2) = 172.2(8)°, Fe–C(11)–O(1) = 158.8(8)°] which might be caused by severe steric interactions between C(2) and the methyl group at C(22) and between C(11)–O(1) and the $Cr(CO)_4$ fragment. The triangles Fe–Cr–P(1) and Cr–P(1)–P(2) include a dihedral angle of 106.8°. The torsion angles Cp*–Fe–Cr–P2 and C(7)–P(2)–Cr–Fe within the

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Table IX. Selected Bond Lengths (Å) and Angles (deg) of 9a

Fe(1)–P(1)	2.286(2)	Fe(1)–P(2)	2.344(2)
Fe(1)–C(1)	2.072(6)	Fe(1)–C(2)	2.077(6)
Fe(1)–C(3)	2.075(6)	Fe(1)–C(4)	2.069(6)
Fe(1)–C(5)	2.081(7)	Fe(1)–C(11)	2.113(6)
Fe(1)–C(12)	2.110(6)	Fe(1)–C(13)	2.100(6)
Cr(1)–P(1)	2.391(2)	Cr(1)–C(23)	1.904(8)
Cr(1)–C(24)	1.906(8)	Cr(1)–C(25)	1.876(9)
Cr(1)–C(26)	1.905(9)	Cr(1)–C(27)	1.852(9)
P(1)–P(2)	2.119(3)	P(1)–C(11)	1.771(6)
P(2)–C(13)	1.783(6)	Si(1)–C(11)	1.887(7)
O(2)–C(12)	1.364(8)	Si(2)–O(2)	1.662(4)
O(4)–C(24)	1.134(9)	Si(3)–O(1)	1.676(5)
O(6)–C(26)	1.130(10)	O(1)–C(13)	1.377(8)
C(11)–C(12)	1.427(9)	O(3)–C(23)	1.137(10)
		O(5)–C(25)	1.138(11)
		O(7)–C(27)	1.150(11)
		C(12)–C(13)	1.409(9)

P(1)–Cr(1)–C(24)	88.4(2)	P(1)–Cr(1)–C(23)	91.5(3)
P(1)–Cr(1)–C(25)	87.4(3)	C(23)–Cr(1)–C(24)	87.5(3)
C(24)–Cr(1)–C(25)	89.3(4)	C(23)–Cr(1)–C(25)	176.7(4)
C(23)–Cr(1)–C(26)	92.6(3)	P(1)–Cr(1)–C(26)	94.5(3)
C(25)–Cr(1)–C(26)	90.6(4)	C(24)–Cr(1)–C(26)	177.1(4)
C(23)–Cr(1)–C(27)	91.6(4)	P(1)–Cr(1)–C(27)	176.5(3)
C(25)–Cr(1)–C(27)	89.4(4)	C(24)–Cr(1)–C(27)	90.1(4)
Fe(1)–P(1)–Cr(1)	144.9(1)	C(26)–Cr(1)–C(27)	87.0(4)
Cr(1)–P(1)–P(2)	119.0(1)	Fe(1)–P(1)–P(2)	64.2(1)
Fe(1)–P(2)–P(1)	61.4(1)	P(2)–P(1)–C(11)	98.6(2)
P(1)–P(2)–C(13)	91.6(2)	Si(2)–O(2)–C(12)	130.3(4)
Fe(1)–C(11)–Si(1)	136.8(3)	Fe(1)–C(11)–P(1)	71.5(2)
Si(1)–C(11)–C(12)	122.1(5)	P(1)–C(11)–Si(1)	123.9(4)
C(11)–C(12)–C(13)	118.1(6)	P(1)–C(11)–C(12)	112.7(5)
O(1)–C(13)–C(12)	118.0(5)	O(2)–C(12)–C(11)	120.3(6)
Cr(1)–C(24)–O(4)	178.6(8)	O(2)–C(12)–C(13)	121.4(6)
Cr(1)–C(26)–O(6)	173.9(8)	P(2)–C(13)–O(1)	123.3(5)
		P(2)–C(13)–C(12)	118.8(5)
		Cr(1)–C(23)–O(3)	176.7(6)
		Cr(1)–C(23)–O(3)	176.7(6)
		Cr(1)–C(25)–O(5)	178.1(7)
		Cr(1)–C(27)–O(7)	177.1(7)

butterfly skeleton are 147.0 and −143.3°, respectively. The two axial carbonyl groups C(23)–O(3) and C(26)–O(6) experience steric pressure from the metallodiphosphene ligand, which is evident in the marked deviation of the valence angle C(23)–Cr–C(26) [166.3(5)°] from linearity. The corresponding angle C(24)–Cr–C(25) [89.2(5)°] obviously remains unaffected.

X-ray Structure Analysis of 7. The doubly-metalated diphosphirane 7 (Figure 3; Tables VI and VII) is located on a 2-fold crystallographical axis, which bisects the angle P(1)–C(13)–P(1a). The (η^5-C$_5$Me$_5$)(CO)$_2$Fe substituents at the phosphorus centers are trans-oriented with a torsion angle Fe(1)–P(1)–P(1a)–Fe(1a) of 133.7°. The plane defined by the atoms Si(1), C(13), and Si(1a) and the plane P(1)–P(1a)–C13 include a dihedral angle of 61.3°. The corresponding torsion angles Fe(1)–P(1)–C(13)–Si(1) and Fe(1)–P(1)–C(13)–Si(1a) are −124.7 and 17.2°, respectively. The P–P bond distance in 7 [2.162(5) Å] is significantly shorter than the corresponding bond in 16 [2.206(2) Å][25] but agrees well with the P–P bond lengths in 17 [2.163(3) Å[26] and 18 [2.175(2) Å].[27] The standard bond length of a P–P single bond amounts to 2.225 Å.[28]
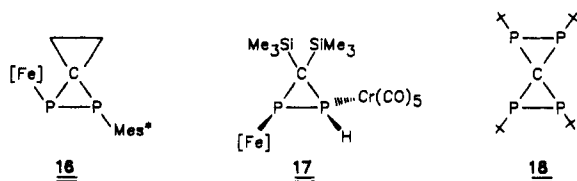
In accordance with the shorter PC distances [1.878(10) Å] the endocyclic valence angles at the P atoms [54.9(2)°]

are more acute than the angle P(1)–C(13)–P(1a) of 70.3-(4)°. Due the steric encumberance of the substituents at the diphosphirane ring the exocyclic angles Fe(1)–P(1)–P(1a) [119.8(2)°] and Fe(1)–P(1)–C(13) [124.4(1)°] are markedly opened in comparison to the situation in 18 where the exocyclic angles C$_{ring}$–P–C$_{tBu}$ and P–P–C$_{tBu}$ are determined to only 110.0(3) and 105.0(4)°. The exocyclic angles P(1)–C(13)–Si(1) and P(1)–C(13)–Si(1a) [101.3(2) and 131.7(2)°] differ significantly and again reflect steric interactions between the cis-oriented metal complex fragment and Me$_3$Si group.

X-ray Structure Analysis of 9a. Compound 9a represents the first example of a 1,2-diphosphaferrocene, whereas 1,1-[29] and 1,3-diphosphaferrocenes[30] are already known. The molecular structure of 9a (Figure 4; Tables VIII and IX) indicates that the novel 1,2-diphospholyl ligand is bonded in an η^5-η^1 fashion to the iron and chromium atoms with the iron atom sandwiched between the two five-membered rings. The 1,2-diphospholyl ring is planar and eclipsed to the C$_5$Me$_5$ ligand with a dihedral angle of 5.7°. The P–P and the P–C bond distances are determined as 2.119(3), 1.771(6), and 1.783(6) Å. They compare well with the corresponding bond lengths in 19 [P–P = 2.098(2); P–C = 1.753(7), 1.764(8) Å][30] and agree with the situation of an η^5-coordinated heteroarene.

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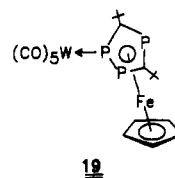
The iron atom is not located under the center of the heterocycle but significantly shifted to the three carbon atoms. Clearly the Fe–C distances of ca. 2.11 Å are not as long as the Fe–P separations. The bond length P(1)–Fe of 2.286(2) Å is markedly shortened as compared to the distance Fe–P(2) [2.344(2) Å]. The bond lengths of both are shorter than that of the to the phosphorus atom coordinated to a Cr(CO)$_5$ moiety [Cr–P(1) = 2.391(2) Å].

Obviously, the CO building blocks of the heterocyclic ligand are derived from the terminal carbonyl ligands in 6a. Me$_3$Si group migrations from phosphorus and carbon in 6a to the oxygen atoms have resulted in the formation of the two Me$_3$SiO substituents of the ring.

Supplementary Material Available: Tables of crystallographic parameters, positional and thermal parameters, and bond distances and angles (30 pages). Ordering information is given on any current masthead page.

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