Synthesis of 1,3-Dimetallo-1,3-diphosphetane-2,4-diones. X-ray Structure Analysis of $Cp^*(CO)_2FeP[Cr(CO)_5]C(O)P[Fe(CO)_2Cp^*]C(O)$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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Reaction of the lithoxy phosphaalkyne $(DME)_2LiOC{\equiv}P$ (**1**) with 1 equiv of the complexes $(\eta^5\text{-}C_5R_5)(CO)_2FeBr$ (**2**); $C_5R_5 = C_5Me_5$ (**a**), 1,3-t-$Bu_2C_5H_3$ (**b**), 1,2,4-i-$Pr_3C_5H_2$ (**c**)) afforded the 1,3-diferrio-1,3-diphosphetane-2,4-diones $(\eta^5\text{-}C_5R_5)(CO)_2FePC(O)P[Fe(CO)_2(\eta^5\text{-}C_5R_5)]C(O)$ (**3a**−**c**) as red amorphous solids in 32−37% yield. By treatment with ((*Z*)-cyclooctene)-$Cr(CO)_5$, compound **3a** was converted into the red complex $Cp^*(CO)_2FeP[Cr(CO)_5]C(O)P[Fe(CO)_2Cp^*]C(O)$ (**4**). Constitutions and configurations of **3a**−**c** and **4** were determined by elemental analyses and spectra (IR, ^1H, ^{13}C, and ^{31}P NMR, MS). The molecular structure of **4** was established by a single-crystal X-ray analysis.

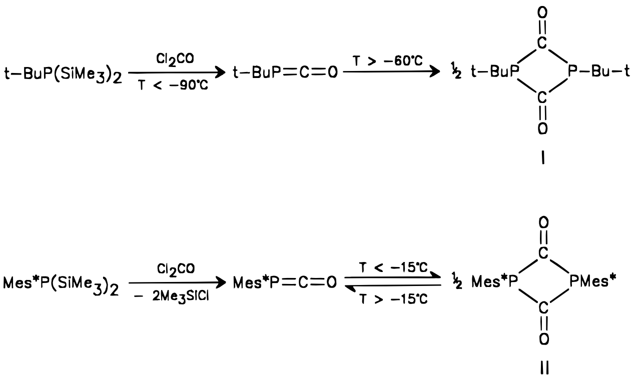
Introduction

1,3-Diphosphetane-2,4-diones are rare compounds, and to date only two representatives have been discussed in the literature. The condensation of *tert*-butyldichlorophosphane with phosgene at temperatures below −90 °C afforded the phosphaketene t-$BuP{=}C{=}O$, which readily dimerized to 1,3-di-*tert*-butyl-1,3-diphosphetane-2,4-dione (**I**) when it was warmed to temperatures above −60 °C.[1] In contrast to t-$BuP{=}C{=}O$ the analogous supermesityl phosphaketene $Mes^*P{=}C{=}O$ ($Mes^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$)[2] partly dimerized in CD_2Cl_2 solution to **II**, when cooled below −15 °C (Scheme 1).[3] The molecular structure of **II** was determined by a single-crystal X-ray crystal structure analysis.[3]

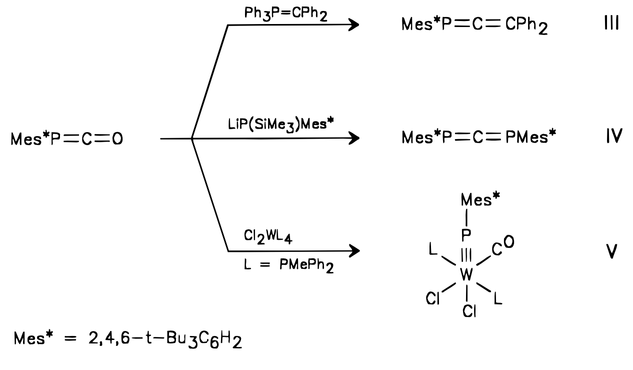
Investigations on the chemistry of **I** were hampered by the thermolability of the ring, whereas the chemical reactivity of **II** is readily explained by its conversion to monomeric $Mes^*P{=}C{=}O$ as the reactive species.[3] The monomeric phosphaketene proved to be useful as a reagent for a number of transformations.

1-Phosphaallene **III** was produced from the phosphaketene by a Wittig reaction,[4] whereas 1,3-diphosphaallene **IV** was isolated from the condensation of $Mes^*P{=}C{=}O$ with a lithiosilylphosphane.[4a] $Mes^*P{=}C{=}O$ also serves as a precursor for the first complex with a linear terminal phosphinidene ligand[5] (Scheme 2). We have been interested in the ligating behavior of the hypothetical phosphaketenide anion $[P{=}C{=}O]^-$, which is preformed in Becker's lithoxy phosphaalkyne $(DME)_2LiOC{\equiv}P$ (**1**).[6] In the present paper we report on the reaction of compound **1** with the bromoiron complexes $Cp^*(CO)_2FeBr$ (**2a**),[7] $(\eta^5\text{-}1,3\text{-}t\text{-}Bu_2C_5H_3)(CO)_2FeBr$ (**2b**),[8] and $(\eta^5\text{-}1,2,4\text{-}i\text{-}Pr_3C_5H_2)(CO)_2FeBr$ (**2c**).[9]

Scheme 1



Scheme 2



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(1) Appel, R.; Paulen, W. *Tetrahedron Lett.* **1983**, *24*, 2639.

(2) Appel, R.; Paulen, W. *Angew. Chem.* **1983**, *95*, 807; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 785.

(3) Fölling, P. Ph.D. Thesis, Universität Bonn, 1988.

(4) (a) Appel, R.; Fölling, P.; Josten, B.; Knoch, F.; Siray, M.; Winkhaus, V. *Angew. Chem.* **1984**, *96*, 620; *Angew. Chem. Int. Ed. Engl.* **1984**, *25*, 619. (b) Appel, R.; Winkhaus, V.; Knoch, F. *Chem. Ber.* **1986**, *119*, 2466.

(5) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734.

(6) Becker, G.; Schwarz, W.; Seidler, N.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **1992**, *612*, 72.

(7) King, R. B.; Douglas, W. M.; Efraty, A. *J. Organomet. Chem.* **1974**, *69*, 131.

(8) Weber, L.; Schumann, I.; Stammler, H.-G.; Neumann, B. *Z. Naturforsch.* **1992**, *47b*, 1134.

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These complexes were chosen because the [(η^5-C_5R_5)(CO)$_2$Fe] group has proved useful as a stabilizing building block in metallodiphosphenes,[10] metallophosphaalkenes,[11] and cycloaddition products thereof.

Experimental Section

General Experimental Considerations. 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 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken in C_6D_6 on Bruker AC 100 (^{1}H, 100.131; ^{13}C, 25.180; ^{31}P, 40.532 MHz), Bruker AM 300 (^{1}H, 300.1; ^{13}C, 75.5; ^{31}P, 121.7 MHz), and Bruker AC 250 P (^{1}H, 250.13; ^{13}C, 62.90 MHz) instruments. Spectral standards were SiMe$_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were obtained from the Microanalytical Laboratory of the University of Bielefeld and the Microanalytical Laboratory H. Kolbe, Mülheim/Ruhr, Germany.

Materials. The complexes Cp*(CO)$_2$FeBr (**2a**),[7] (η^5-1,3-*t*-Bu$_2C_5H_3$)(CO)$_2$FeBr (**2b**),[8] (η^5-1,2,4-*i*-Pr$_3C_5H_3$)(CO)$_2$FeBr (**2c**),[9] and ((*Z*)-cyclooctene)Cr(CO)$_5$[12] as well as (DME)$_2$LiOC≡P (**1**)[6] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled before use. Column chromatography was performed on silanized silica (Merck) as a support.

Preparation of Compounds. Cp*(CO)$_2$FePC(O)P[Fe(CO)$_2$Cp*]C(O) (3a). A solution of 0.66 g (2.03 mmol) of Cp*(CO)$_2$FeBr (**2a**) in 10 mL of 1,2-dimethoxyethane (DME) was added dropwise to a well-stirred solution of 0.50 g (2.03 mmol) of (DME)$_2$LiOC≡P (**1**) in 10 mL of DME. After a few minutes the formation of a red precipitate was observed. Stirring at 20 °C was continued overnight. The reaction mixture was worked up when the ^{31}P NMR resonance of **1** (δ −380) was no longer detectable. The precipitate was filtered off and washed subsequently with 20 mL of DME and 20 mL of pentane. The crude product was purified by chromatography (column $d = 2$ cm, $l = 6$ cm) with CH_2Cl_2 as an eluent. The red zone was completely eluted with 40 mL of solvent. Evaporation to dryness and recrystallization from CH_2Cl_2/pentane gave 0.47 g (38%) of red **3a**. IR (KBr, cm^{-1}): 2982 w, 2965 w, 2923 w, 2853 w, 2014 w, 1993 vs [ν(FeCO)], 1974 w, 1950 vs [ν(FeCO)], 1923 w, 1635 sh, 1600 s [ν(PCO)], 1489 w, 1426 w, 1384 m, 1261 w, 1160 w, 1075 w, 1027 w, 840 w, 821 w, 627 m, 618 m, 581 w, 566 m, 551 m, 542 m, 500 m, 441 w. ^{1}H NMR (CDCl$_3$): δ 1.81 (s, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.87 [s, C$_5$(*C*H$_3$)$_5$], 96.62 [s, *C*$_5$(CH$_3$)$_5$], 213.09 (s, FeCO), 214.09 (s, FeCO), 253.09 (t, $^1J_{PC} = 50.2$ Hz, P$_2$CO). ^{31}P{^{1}H} NMR (DME): δ 110.93 s. MS/FD: *m/z* 612 (M$^+$). Anal. Calcd for $C_{26}H_{30}Fe_2O_6P_2$ (M_r 612.17): C, 51.01; H, 4.90; Fe, 18.25. Found: C, 50.84; H, 4.97; Fe, 18.21.

(η^5-1,3-*t*-Bu$_2C_5H_3$)(CO)$_2$FePC(O)P[Fe(CO)$_2$(η^5-1,3-*t*-Bu$_2C_5H_3$)]C(O) (3b). Analogously 0.35 g (34%) of red solid **3b** was generated by treatment of 0.37 g (1.50 mmol) of **1** with 0.49 g (1.50 mmol) of (η^5-1,3-*t*-Bu$_2C_5H_3$)(CO)$_2$FeBr (**2b**). IR (KBr, cm^{-1}): 2965 m, 2868 w, 2003 vs [ν(FeCO)], 1959 vs [ν(FeCO)], 1645 w, 1593 s, [ν(PCO)], 1496 w, 1463 w, 1366 w, 1256 w, 1166 w, 868 w, 621 w, 579 m, 539 w, 507 w. ^{1}H NMR (CDCl$_3$): δ 1.21 (s, 36H, *t*-Bu), 4.76 (s, 2H, 2-H Cp), 4.83 (s, 4H, 4,5-HCp). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 30.86 [s, C(*C*H$_3$)], 31.39 [s, *C*(CH$_3$)$_3$], 80.99 (s, 4,5-C Cp), 81.64 (s, 2-C Cp), 115.81 (s, 1,3-C Cp), 212.08 (d, $^2J_{PC} = 2.0$ Hz, FeCO), 212.19 (s, FeCO). ^{31}P{^{1}H} NMR (DME): δ 78.06 s. MS/FD: *m/z* 696 (M$^+$). Anal. Calcd for $C_{32}H_{42}Fe_2O_6P_2$ (M$_r$ = 696.33): C, 55.20; H, 6.08. Found: C, 55.20; H, 6.67.

(η^5-1,2,4-*i*-Pr$_3C_5H_2$)(CO)$_2$FePC(O)P[Fe(CO)$_2$(η^5-1,2,4-*i*-Pr$_3C_5H_2$)]C(O) (3c). Analogously 0.42 g (32%) of red solid **3c** was obtained from treatment of 0.45 g (1.82 mmol) of **1** with 0.67 g (1.82 mmol) of (η^5-1,2,4-*i*-Pr$_3C_5H_2$)(CO)$_2$FeBr (**2c**). IR (KBr, cm^{-1}): 2966 m, 2933 w, 2870 w, 2006 vs [ν(FeCO)], 1966 vs [ν(FeCO)], 1934 w, 1596 vs [ν(PCO)], 1491 w, 1460 w, 1385 w, 1368 w, 1299 w, 1275 w, 1059 w, 1025 w, 947 w, 923 w, 900 w, 871 w, 725 w, 704 w, 676 w, 620 w, 547 m, 540 m, 503 w. ^{1}H NMR (CDCl$_3$): δ 1.17 [d, $^3J_{HH} = 9.3$ Hz, 18H, CH(C*H*$_3$)$_2$], 1.20 [d, $^3J_{HH} = 7.8$ Hz, 18H, CH(C*H*$_3$)$_2$], 2.57 [sept, $^3J_{HH} = 6.7$ Hz, 6H, C*H*(CH$_3$)$_2$], 4.87 (s, 4H, H Cp). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 23.48 [s, CH(*C*H$_3$)$_2$], 24.47 (s, CH(*C*H$_3$)$_2$], 25.0 [s, *C*H(CH$_3$)$_2$], 28.14 [s, *C*H(CH$_3$)$_2$], 82.61 (s, 3,5-C Cp), 105.47 (s, 4-C Cp), 109.17 (s, 1,2-C Cp), 212.53 (s, FeCO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 89.25 s. MS/FD: *m/z* 724 (M$^+$). Anal. Calcd for $C_{34}H_{46}Fe_2O_6P_2$ (M_r = 724.04): C, 56.35; H, 6.40; Fe, 15.43. Found: C, 56.25; H, 6.36; Fe, 15.58.

Cp*(CO)$_2$FeP[Cr(CO)$_5$]C(O)P[Fe(CO)$_2$Cp*]C(O) (4). A solution of 0.09 g (0.30 mmol) of ((*Z*)-cyclooctene)Cr(CO)$_5$ in 5 mL of CH_2Cl_2 was added dropwise to the red solution of 0.20 g (0.30 mmol) of **3a** in 10 mL of CH_2Cl_2. When it was stirred at 20 °C, the solution darkened to red-black. After 3 h of reaction at 20 °C, the ^{31}P{^{1}H} NMR resonance of **3a** was no longer detectable and the solution darkened to red-black. Solvents and volatiles were removed in vacuo, and the red-black residue was purified by chromatography as described above for **3a**. A sample of 0.11 g (47%) of red crystalline **4** was isolated. IR (KBr, cm^{-1}): ν 2965 w, 2921 w, 2856 w, 2053 s [ν(CrCO)], 2020 s [ν(FeCO)], 2007 s [ν(FeCO)], 1984 s [ν(FeCO)], 1972 s [ν(FeCO)], 1957 s [ν(CrCO)], 1924 vs [ν(CrCO)], 1906 vs [ν(CrCO)], 1654 w, 1619 s [ν(PCO)], 1473 w, 1456 w, 1426 w, 1381 m, 1160 w, 1074 w, 1030 w, 670 s, 655 s, 581 s, 560 w, 538 w. IR (CH_2Cl_2, cm^{-1}): ν 2057 w, 2024 s, 1980 vs, 1928 vs [ν(CO)]. ^{1}H NMR (CDCl$_3$): δ 1.85 (s, 15H, C$_5$Me$_5$), 1.88 (s, 15H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.71 [s, C$_5$(*C*H$_3$)$_5$], 9.91 [d, $^3J_{PC} = 1.8$ Hz, C$_5$(*C*H$_3$)$_5$], 97.57 [s, *C*$_5$(CH$_3$)$_5$], 97.60 [s, *C*$_5$(CH$_3$)$_5$], 211.21 (d, $^2J_{PC} = 8.7$ Hz, FeCO), 213.06 (d, $^2J_{PC} = 10.1$ Hz, FeCO), 217.11 (d, $^2J_{PC} = 8.7$ Hz, CrCO$_{eq}$), 224.40 (d, $^2J_{PC} = 5.1$ Hz, CrCO$_{ax}$), 236.90 (dd, $^1J_{PC} = 40.3$, 18.6 Hz, P$_2$CO). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 69.85 (d, $^2J_{PP} = 115.8$ Hz, FeP), 158.25 (d, $^2J_{PP} = 115.8$ Hz, PCr). Anal. Calcd for $C_{31}H_{30}CrFe_2O_{11}P_2$ (M_r 804.22): C, 46.30; H, 3.76. Found: C, 46.15; H, 4.01.

X-ray Crystal Structure Determination of 4. Single crystals of **4** were grown from CH_2Cl_2/pentane (3:1) at 5 °C. A red crystal with the approximate dimensions 0.40 × 0.30 × 0.10 mm^3 was measured on a Siemens P2$_1$ diffractometer with Mo Kα radiation at 173 K. Crystal data and refinement details (refined from the diffractometer angles of 11 centered reflections): are $a = 9.365(3)$ Å, $b = 13.117(4)$ Å, $c = 14.947(5)$ Å, $\alpha = 77.30(3)°$, $\beta = 74.15(3)°$, $\gamma = 76.80(3)°$, $V = 1695.1(9)$ Å^3, $Z = 2$, $d_{calcd} = 1.576$ g cm^{-3}, $\mu = 1.311$ mm^{-1}, space group $P\bar{1}$, data collection of 7830 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 SHELXTL plus/SHELXL-93), riding groups for hydrogen atoms, 434 parameters, maximum residual electron density 0.5 e/Å^3, $R_F = 0.050$ based on 5286 reflections with ($I > 2\sigma(I)$, $R_{wF}{}^2 = 0.121$ for all data.

Results and Discussion

The lithoxyphosphaalkyne (DME)$_2$LiOC≡P (**1**) smoothly reacted with equimolar amounts of the bromoiron complexes Cp*(CO)$_2$FeBr (**2a**), (η^5-1,3-*t*-Bu$_2C_5H_3$)(CO)$_2$FeBr (**2b**), and (η^5-1,2,4-*i*-Pr$_3C_5H_2$)(CO)$_2$FeBr (**2c**) in 1,2-dimethoxyethane (DME) (20 °C) to afford the red

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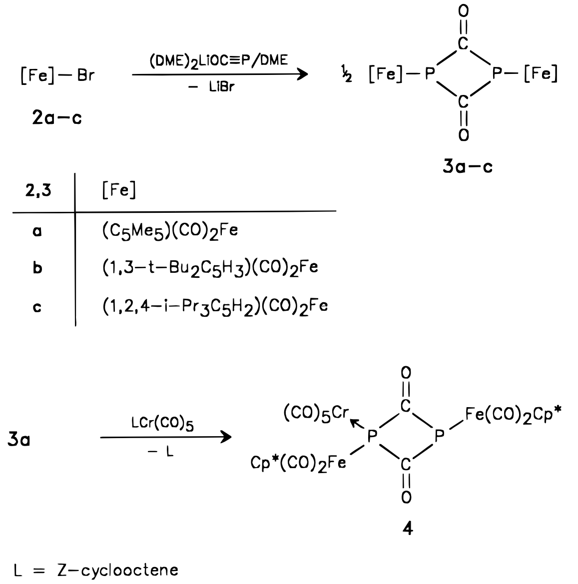
(9) Misiak, H. Ph.D. Thesis, Universität Bielefeld, 1994.
(10) Weber, L. *Chem. Rev.* **1992**, *92*, 1839.
(11) Weber, L. *Angew. Chem.*, in press.
(12) Grevels, F.-W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681.

Scheme 3



2,3	[Fe]
a	$(C_5Me_5)(CO)_2Fe$
b	$(1,3\text{-}t\text{-}Bu_2C_5H_3)(CO)_2Fe$
c	$(1,2,4\text{-}i\text{-}Pr_3C_5H_2)(CO)_2Fe$

L = Z–cyclooctene

microcrystalline 1,3-diferrio-1,3-diphosphetane-2,4-diones **3a**–**c** in moderate yields (Scheme 3).

The air- and moisture-stable compounds **3a**–**c** were purified by column chromatography on silanized silica with CH_2Cl_2 as an eluent. They were quite soluble in polar organic solvents such as CH_2Cl_2, THF, and DME without significant decomposition.

The course of the reactions was monitored by ^{31}P NMR spectroscopy. The singlet for compound **1** (δ −380) was replaced by a singlet at δ 78.60–110.93 for the products. No intermediates such as the also conceivable metallophosphaketenes $(\eta^5\text{-}C_5R_5)(CO)_2FeP{=}C{=}O$ could be detected. The phosphaketene $Mes^*P{=}C{=}O$ displayed a singlet at $\delta(^{31}P)$ −206.62 ($CDCl_3/CH_2Cl_2$ solution, 20 °C).[2,3] In the ^{31}P NMR spectra of the metal-free 1,3-diphosphetanes **I** and **II** singlets were registered at δ +140 (C_6D_6/toluene) and δ −23.6 ($CDCl_3/CH_2Cl_2$), respectively. These data may be taken as an indication for similar connectivities of atoms in **3a**–**c**, **I**, and **II** and eliminate structures with iron–oxygen contacts such as $(\eta^5\text{-}C_5R_5)(CO)_2FeOC{\equiv}P$ and oligomers thereof. The presence of $P_2C{=}O$ units in **II** was underlined by a triplet for the carbonyl carbons at δ 216.2 ($^1J_{PC}$ = 53.8 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The triplet of the respective carbonyls in **3a** was observed at markedly lower field (δ 253.09, $^1J_{PC}$ = 50.2 Hz). In **3b** and **3c** these carbon atoms could not be located unambiguously. The ^{13}C nuclei of the terminal carbonyl ligands in **3a** gave rise to two singlets at δ 213.09 and 214.09, respectively.

The IR spectra (KBr) of **3a**–**c** were characterized by two intense bands at 1993–2006 and 1950–1966 cm^{-1} for the stretching modes of the terminal carbonyl ligands at the iron center. A strong band at 1593–1699 cm^{-1} was assigned to the asymmetric CO stretching mode of the two ring carbonyls. The respective band in the IR spectrum of **II** was registered at 1645 cm^{-1}.

Field desorption mass spectra revealed the molecular ions of **3a**–**c** as peaks with the highest *m*/*z* ratio.

The stability of our 1,3-diphosphetane-2,4-diones allowed thorough investigations of their chemical behavior. The reaction of **3a** with an equimolar amount of ((*Z*)-cyclooctene)$Cr(CO)_5$ in CH_2Cl_2 solution afforded the red diamagnetic **4** in 47% yield (Scheme 2). In **4** both phosphorus atoms are no longer equivalent, which is evidenced by two doublets at δ 69.85 and 158.25 ($^2J_{PP}$ = 115.8 Hz) in the $^{31}P\{^1H\}$ NMR spectrum of the complex. Bearing in mind that coordination of tertiary phosphanes to transition-metal carbonyl units is accompanied by a marked deshielding of the ^{31}P atom, we attribute the resonance at lower field to the tetracoordinate phosphorus atom of complex **4**.

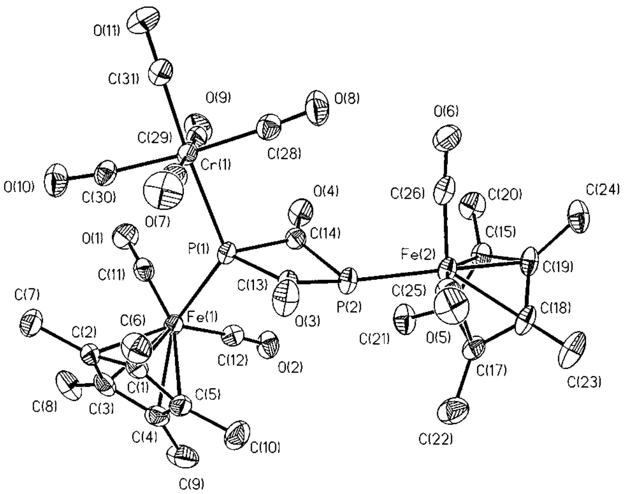


Figure 1. Molecular structure of **4** in the crystal.

Another consequence of two chemically and magnetically different phosphorus atoms is evident in the $^{13}C\{^1H\}$ NMR spectrum of **4**. The carbonyl carbon atoms in **4** give rise to a doublet of doublets at δ 236.90 ($^1J_{PC}$ = 40.3, 18.6 Hz). The significant shielding of this resonance ($\Delta\delta$ = 16 ppm) may be rationalized by the electron withdrawal the $[Cr(CO)_5]$ group exerts on the heterocycle. The coupling of 40.3 Hz is probably caused by the tricoordinate phosphorus, as is obvious by comparison to **3a** and by the information given by the X-ray analysis, that bonding to this atom involves an increased 3s-orbital contribution. The ^{13}C resonances of the carbonyl ligands of the $[Cp^*(CO)_2Fe]$ groups are observed as doublets at δ 211.21 ($^2J_{PC}$ = 8.7 Hz) and δ 213.06 ($^2J_{PC}$ = 10.1 Hz). The doublet at higher field is attributed to the $[Cp(CO)_2Fe]$ substituent at the tetracoordinate phosphorus, in line with the observation that the decrease of electron density at a metal center is accompanied by high-field shifts of the respective carbonyl ligands. One axial and four equatorial carbonyls of the $[Cr(CO)_5]$ fragment are responsible for the doublets at δ 224.40 ($^2J_{PC}$ = 5.1 Hz) and δ 217.11 ($^2J_{PC}$ = 8.7 Hz), respectively.

Adduct formation of **3a** with the $[Cr(CO)_5]$ unit leads to a hypsochromic shift of 19 cm^{-1} in the IR spectrum for the carbonyl stretching vibration of the four-membered heterocycle. In the carbonyl region of the spectrum, eight intense absorptions were found. Those at 2020 and 1972 cm^{-1} we attribute to the $[Fe(CO)_2]$ group at the tetracoordinate phosphorus atom, whereas bands at ν 2007 and 1957 cm^{-1} are due to the remaining $[Fe(CO)_2]$ unit. The $[Cr(CO)_5]$ moiety has a lower local symmetry than that of the point group C_{4v}, evidenced by four carbonyl stretches at 2053, 1984, 1924, and 1906 cm^{-1}.

X-ray Structure Analysis of 4. Single crystals of **4** were grown from CH_2Cl_2/*n*-pentane (3:1) at 5 °C. The results of the structural determination are shown in

Table 1. Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Parameters U(eq)[a] (Å$^2 \times 10^3$) for 4

	x	*y*	*z*	*U*(eq)
Fe(1)	2670(1)	7847(1)	8740(1)	22(1)
Fe(2)	1493(1)	4502(1)	6571(1)	24(1)
Cr(1)	−562(1)	9271(1)	7167(1)	25(1)
P(1)	1327(1)	7823(1)	7664(1)	22(1)
P(2)	1778(1)	5799(1)	7217(1)	27(1)
O(1)	−81(3)	8875(2)	9913(2)	39(1)
O(2)	2302(3)	5690(2)	9639(2)	36(1)
O(3)	3227(3)	7318(2)	5915(2)	40(1)
O(4)	−685(3)	6408(2)	8649(2)	37(1)
O(5)	3477(4)	5235(2)	4774(2)	47(1)
O(6)	−1257(3)	5600(2)	5986(2)	41(1)
O(7)	1679(4)	9997(3)	5364(2)	52(1)
O(8)	−1483(4)	7833(2)	6159(2)	46(1)
O(9)	−2674(3)	8636(2)	9057(2)	45(1)
O(10)	−2(4)	10909(2)	8120(2)	43(1)
O(11)	−3088(4)	10958(2)	6616(3)	56(1)
C(1)	4392(4)	8559(3)	7676(3)	26(1)
C(2)	3872(4)	9135(3)	8439(3)	27(1)
C(3)	4124(4)	8425(3)	9280(3)	30(1)
C(4)	4831(4)	7417(3)	9034(3)	31(1)
C(5)	4958(4)	7480(3)	8044(3)	28(1)
C(6)	4478(5)	9038(3)	6663(3)	38(1)
C(7)	3380(5)	10312(3)	8358(3)	40(1)
C(8)	3830(5)	8729(4)	10234(3)	43(1)
C(9)	5466(5)	6466(3)	9664(3)	48(1)
C(10)	5722(5)	6598(3)	7486(3)	44(1)
C(11)	998(4)	8480(3)	9436(3)	27(1)
C(12)	2406(4)	6544(3)	9274(3)	26(1)
C(13)	2412(4)	7046(3)	6663(3)	26(1)
C(14)	426(4)	6587(3)	8036(3)	25(1)
C(15)	308(4)	3404(3)	7570(3)	28(1)
C(16)	1569(5)	3472(3)	7895(3)	28(1)
C(17)	2915(4)	3202(3)	7191(3)	29(1)
C(18)	2471(5)	2903(3)	6446(3)	32(1)
C(19)	860(5)	3032(3)	6677(3)	29(1)
C(20)	−1317(5)	3580(3)	8110(3)	40(1)
C(21)	1504(5)	3716(3)	8844(3)	39(1)
C(22)	4491(5)	3161(3)	7261(3)	45(1)
C(23)	3505(5)	2471(3)	5603(3)	46(1)
C(24)	−83(5)	2770(3)	6126(3)	39(1)
C(25)	2720(5)	4963(3)	5485(3)	31(1)
C(26)	−162(5)	5210(3)	6222(3)	30(1)
C(27)	858(5)	9701(3)	6038(3)	33(1)
C(28)	−1109(5)	8347(3)	6548(3)	31(1)
C(29)	−1877(4)	8834(3)	8339(3)	31(1)
C(30)	−145(5)	10264(3)	7759(3)	29(1)
C(31)	−2113(5)	10312(3)	6816(3)	37(1)

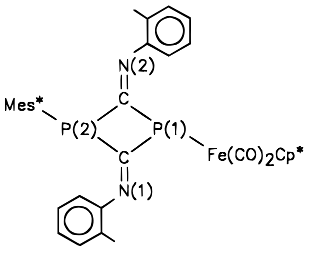
[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Fe(1)−C(11)	1.766(4)	Fe(1)−C(12)	1.762(4)
Fe(2)−C(25)	1.786(4)	Fe(2)−C(26)	1.763(4)
Fe(1)−P(1)	2.3057(13)	Fe(2)−P(2)	2.2296(12)
Cr−P(1)	2.4197(14)	P(1)−C(13)	1.917(4)
P(1)−C(14)	1.902(4)	P(2)−C(13)	1.815(4)
P(2)−C(14)	1.812(4)	C(13)−O(3)	1.201(4)
C(14)−O(4)	1.213(4)	Cr−C(27)	1.906(4)
Cr−C(28)	1.903(4)	Cr−C(29)	1.902(4)
Cr−C(30)	1.887(4)	Cr−C(31)	1.856(4)
Fe(1)−C(Cp*)	2.102(4)−2.153(4)		
Fe(2)−C(Cp*)	2.101(4)−2.146(4)		

P(1)−Fe(1)−C(11)	88.98(13)	P(1)−Fe(1)−C(12)	89.89(13)
C(11)−Fe(1)−C(12)	95.4(2)	Fe(1)−P(1)−Cr	124.90(5)
Cr−P(1)−C(13)	111.63(12)	Cr−P(1)−C(14)	106.56(12)
Fe(1)−P(1)−C(13)	115.24(13)	Fe(1)−P(1)−C(14)	109.14(12)
C(13)−P(1)−C(14)	79.1(2)	P(1)−C(13)−P(2)	96.7(2)
P(1)−C(14)−P(2)	97.3(2)	C(13)−P(2)−C(14)	84.3(2)
P(1)−C(13)−O(3)	130.7(3)	P(2)−C(13)−O(3)	132.5(3)
P(1)−C(14)−O(4)	129.7(3)	P(2)−C(14)−O(4)	139.9(3)
Fe(2)−P(2)−C(13)	130.13(13)	Fe(2)−P(2)−C(14)	130.19(13)
P(2)−Fe(2)−C(25)	90.60(13)	P(2)−Fe(2)−C(26)	94.75(13)
C(25)−Fe(2)−C(26)	94.0(2)		

Figure 1. Positional parameters and selected bond lengths and angles for the complex are given in Tables 1 and 2, respectively. The analysis confirms the presence of a nearly planar 1,3-diphosphetane-2,4-dione ring which is ligated to a [Cr(CO)$_5$] group via a chromium−phosphorus single bond of 2.4197(14) Å. This bond distance is markedly shortened as compared to the sum of the covalent radii of Cr (1.48 Å)[13] and P (1.10 Å),[14] and it compares well with the Cr−P bond lengths in [(menthyl)−P=P−(menthyl)][Cr(CO)$_5$]$_2$ (2.403(2) and 2.412(2) Å).[15] The [Cp*(CO)$_2$Fe] groups are oriented trans to each other, featuring two different iron−phosphorus single bonds (Fe(1)−P(1) = 2.3057(13) Å and Fe(2)−P(2) = 2.2296(12) Å). The longer Fe−P bond is quite comparable to the Fe−P separations in the 2,4-diimino-1,3-diphosphetane **5** (2.303(1) Å).[16] Usually, Fe−P bond distances in low-valent iron carbonyls fall in the range 2.11−2.37 Å.[17]



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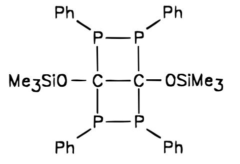

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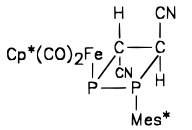

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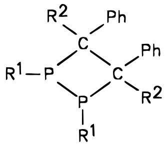

8: R^1 = i-Pr; R^2 = Me$_3$SiO
9: R^1 = CH$_2$Ph; R^2 = Me$_3$SiO

In contrast to compound **II**, where the endocyclic carbon−phosphorus bonds range from 1.796(5) to 1.838(6) Å (average 1.812 Å),[3] being equidistant within the 3-fold standard deviation, these bonds in **4** significantly differ in length. The P−C single-bond distances to the tricoordinate phosphorus atom P(2) are markedly shortened (1.812(4) and 1.815(3) Å) as compared to the ones involving the tetracoordinate atom P(1) (1.902(4) and 1.917(4) Å). This bond shortening may be rationalized by an increased 3s orbital constribution in the three bonds formed by P(2). This assumption is further confirmed by the geometry at P(2) in comparison to that of the phosphorus atoms in **II**. P(2) displays the

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[13] Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1986**, *5*, 1851.

[14] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

[15] Hinke, A.-M.; Hinke, A.; Kuchen, W.; Hönle, W. *Z. Naturforsch.* **1986**, *41B*, 629.

[16] Weber, L.; Buchwald, S.; Lentz, D.; Stamm, O.; Preugschat, D.; Marschall, R. *Organometallics* **1994**, *13*, 4406.

[17] (a) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem.* **1984**, *96*, 708; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739. (b) Lal De, R.; Vahrenkamp, H. *Z. Naturforsch.* **1986**, *41B*, 273. (c) Arif, A. M.; Cowley, A. H.; Pakulsky, M. *J. Am. Chem. Soc.* **1985**, *107*, 2553. (d) Huttner, G.; Mohr, G.; Friedrich, P.; Schmid, H. G. *J. Organomet. Chem.* **1978**, *169*, 59. (e) Williams, G. D.; Geoffroy, G. J.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729. (f) Weber, L.; Frebel, M.; Boese, R. *New J. Chem.* **1989**, *13*, 303.

configuration of a considerably flat trigonal pyramid (sum of angles 344.6°), whereas in **II** the respective sum of angles ranges from 332.1 to 336.6°.[3]

Phosphorus−carbon bond distances, which are lengthened beyond 1.90 Å, are encountered in the ring compounds **6** (1.887(6) and 1.950(6) Å),[18] **7** (1.889(3) and 1.934(3) Å),[19] **8** (1.918(3) and 1.930(3) Å),[20] and **9** (1.931(12)−1.967(12) Å).[20] Expectedly the endocyclic bond angles at P(1) (79.1(2)°) and P(2) (84.3(2)°) are more acute than those at the trigonal-planar carbonyl carbon atoms C(13) (96.7(2)°) and C(14) (97.3(2)°). Due to steric interactions the [Cr(CO)$_5$] group is slightly distorted, as evidenced by the angles P(1)−Cr−C(30) (95.25(12)°), P(1)−Cr−C(29) (86.43(13)°), C(27)−Cr−C(29) (176.1(2)°), C(28)−Cr−C(30) (175.7(2)°), Cr−C(30)−O(10) (174.7(4)°), and Cr−C(29)−O(9) (175.5(3)°).

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Supporting Information Available: Tables of crystal data and structure refinement details, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positional parameters for **4** (7 pages). Ordering information is given on any current masthead page.

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(18) Appel, R.; Barth, V.; Halstenberg, M.; Huttner, G.; von Seyerl, J. *Angew. Chem.* **1979**, *91*, 935; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 872.

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

(20) Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur Relat. Elem.* **1983**, *14*, 267.