Transition-Metal-Substituted Diphosphenes. 34.[1] Studies on the Reactivity of Metallodiphosphenes $(\eta^5\text{-}C_5R_5)(CO)_2M{-}P{=}P{-}Mes^*$ of Iron and Ruthenium toward Hexafluoroacetone. X-ray Structure Analyses of $(\eta^5\text{-}C_5Me_5)(CO)M{-}P({=}PMes^*)OC(CF_3)_2C(O)$ (M = Fe, Ru), $(\eta^5\text{-}1,2,4\text{-}iPr_3C_5H_2)(CO)Ru{-}P({=}PMes^*)OC(CF_3)_2C(O)$, and $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{-}P(Mes^*)OC(CF_3)_2$†

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Metallodiphosphenes $(\eta^5\text{-}C_5R_5)(CO)_2M{-}P{=}P{-}Mes^*$ ($C_5R_5 = C_5Me_5, C_5Me_4Et, 1,2,4\text{-}iPr_3C_5H_2, 1,3\text{-}tBu_2C_5H_3, 1,3\text{-}(Me_3Si)_2C_5H_3$; M = Fe, Ru) undergo reaction with anhydrous hexafluoroacetone to afford either the five-membered metallaheterocycles $(\eta^5\text{-}C_5R_5)(CO)M{-}P({=}PMes^*)OC(CF_3)_2C(O)$ or metalated 1-oxa-2,3-diphosphetanes $(\eta^5\text{-}C_5R_5)(CO)_2M{-}P{-}P(Mes^*)OC(CF_3)_2$. It is demonstrated that the 1-oxa-2,3-diphosphetanes result from an intramolecular rearrangement of the metallaheterocycles. The course of the reaction and the nature of the products is largely influenced by the basicity of the cyclopentadienylmetal fragment. The molecular structures of $(\eta^5\text{-}C_5Me_5)(CO)Fe{-}P({=}PMes^*)OC(CF_3)_2C(O)$ (**9a**) ($P2_1/c$, $a = 21.809(4)$ Å, $b = 10.066(2)$ Å, $c = 16.250(3)$ Å, $\beta = 95.87(1)°$, $(\eta^5\text{-}C_5Me_5)(CO)Ru{-}P{=}P(Mes^*)OC(CF_3)_2C(O)$ (**10a**) ($P2_1/c$, $a = 22.308(8)$ Å, $b = 10.174(4)$ Å, $c = 16.014(10)$ Å, $\beta = 96.62(4)°$), $(\eta^5\text{-}1,2,4\text{-}iPr_3C_5H_2)(CO)Ru{-}P({=}PMes^*)OC(CF_3)_2C(O)$ (**10c**) ($P\bar{1}$, $a = 9.416(5)$ Å, $b = 9.784(6)$ Å, $c = 24.40(2)$ Å, $\alpha = 92.74(5)°$, $\beta = 98.42(5)°$, $\gamma = 117.37(4)°$), and $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{-}P(Mes^*)OC(CF_3)_2$ (**11a**) ($C2/c$, $a = 46.79(3)$ Å, $b = 9.316(5)$ Å, $c = 16.611(5)$ Å, $\beta = 101.52(3)°$) were determined by single-crystal X-ray analyses.

Introduction

Metallodiphosphenes are polyfunctional molecules which allow a series of novel chemical transformations.[2] The pronounced nucleophilicity of the metalated phosphorus atom and the presence of electrophilic sites in these molecules are prerequisites for cycloadditions with electron-deficient alkenes,[3] alkynes,[4] and azo compounds.[5]

The extension of our studies to electron-poor heteroalkenes such as hexafluoroacetone (HFA) is obvious. Low-coordinated phosphorus systems such as iminophosphanes are converted by HFA to λ^5-oxaphosphiranes I (for R = Me_3Si)[6] or to λ^3-1-oxa-3-aza-2-phosphetanes II (for R = alkyl).[7] In this report we present our results on the investigation of the chemical reactivity of a number of ferrio- and rutheniodiphosphenes toward HFA. Parts of this study were published in a preliminary 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 ^{13}C, ^1H, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were taken in C_6D_6 solution at 22 °C on Bruker AC 100 (^1H, 100.131; ^{13}C, 25.180; ^{31}P, 40.539 MHz) and Bruker AM 300 (^1H, 300.1; ^{13}C, 75.5; ^{19}F, 282.2; ^{29}Si, 59.595; ^{31}P, 121.7 MHz) spectrometers. Spectral standards were $SiMe_4$ (^1H, ^{13}C, ^{29}Si), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Varian MAT CH5-DF spectrometer (70 eV, T = 250 °C).

Elemental analyses were obtained from the Microanalytical Laboratory of the University of Bielefeld and from the Microanalytical Laboratory Kolbe, Mülheim, Germany.

Materials. The compounds $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}P{-}Mes^*$ (**7a**),[9] $(\eta^5\text{-}C_5Me_4Et)(CO)_2Fe{-}P{=}P{-}Mes^*$ (**7b**),[10] $(\eta^5\text{-}1,3\text{-}$

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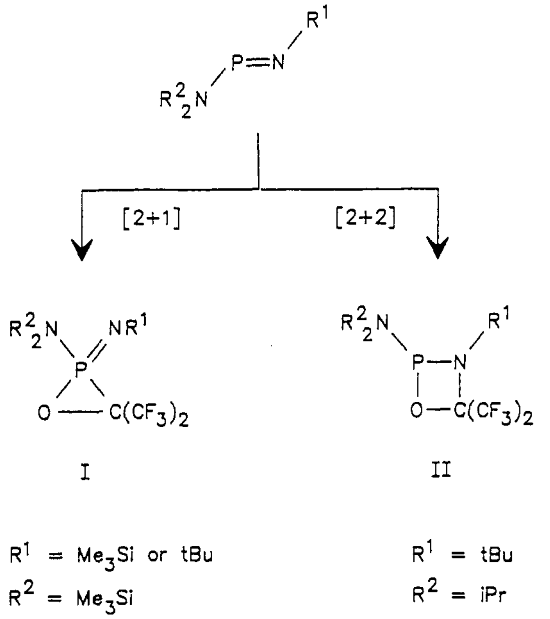
Scheme 1



$tBu_2C_5H_3)(CO)_2Fe—P=P—Mes^*$ (**7d**),[10] $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Fe—P=P—Mes^*$ (**7g**),[9] $(\eta^5\text{-}C_5Me_5)(CO)_2Fe—P=P—C(SiMe_3)_3$ (**7h**),[11] $(\eta^5\text{-}C_5Me_5)(CO)_2Ru—P=P—Mes^*$ (**8a**),[9] $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3](CO)_2FeI$ (**4e**),[12] $Ru_3(CO)_{12}$,[13] 2,3,5-$iPr_3C_5H_3$,[14] 1,3-$tBu_2C_5H_4$,[15] 1,1-$(Me_3Si)_2C_5H_4$,[16] 2,4,6-$tBu_3C_6H_2PCl_2$,[17] and $LiP(SiMe_3)_2{\cdot}DME$[18] were prepared as described in the literature.

Hexafluoroacetone (HFA) and iron pentacarbonyl were commercial products. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds. $[(\eta^5\text{-}1,2,4\text{-}iPr_3C_5H_2)(CO)_2Fe)]_2$ (1c). A mixture of 4.28 g (5.1 mL, 22.3 mmol) of 2,3,5-$iPr_3C_5H_3$ and 29.8 g (20.0 mL, 152.1 mmol) of $Fe(CO)_5$ in 10 mL of *n*-decane was heated under reflux for 10 h. Then 50 mL of benzene was added to the still boiling reaction mixture. The hot burgundy suspension was filtered through a mixture of silica/alumina to remove pyrophoric iron. Removal of all volatiles in vacuo left 4.70 g (69.5%) of **1c** as a dark red powder (mp 110–120 °C dec). IR (KBr): ν 2969 (s), 2932 (m), 2872 (m), 1930 (vs) [ν(CO)], 1754 (vs) [ν(CO)], 1460 (m), 1383 (m), 1274 (m), 873 (m), 633 (s), 610 (m), 597 (m), 532 (m) cm^{-1}. ^{1}H NMR: δ 1.16 (d, $^3J_{HH}$ = 6.3 Hz, 24H, CH_3), 1.22 (d, $^3J_{HH}$ = 5.8 Hz, 12H, CH_3), 2.38 (sept, $^3J_{HH}$ = 5.8 Hz, 2H, $CHMe_2$), 2.55 (sept, $^3J_{HH}$ = 6.3 Hz, 4H, $CHMe_2$), 4.89 (s, 4H, C_5H_2). $^{13}C\{^1H\}$ NMR: δ 22.4 (s, CH_3), 22.9 (s, CH_3), 23.1 (s, CH_3), 24.5 (s, $CHMe_2$), 25.2 (s, $CHMe_2$), 84.2 (s, *C*H ring), 86.1 (s, *C*H ring), 109.8 (s, *C*–iPr ring), 110.1 (s, *C*–iPr ring), 213.7 (s, CO). MS/EI: *m/z* 606 (M^+), 303 (1,2,4-$iPr_3C_5H_2Fe(CO)_2^+$), 247 (1,2,4-$iPr_3C_5H_2Fe^+$), 56 (Fe^+), 43 (iPr^+). Anal. Calcd for $C_{32}H_{46}Fe_2O_4$ (606.4): C, 63.38; H, 7.65. Found: C, 63.12; H, 7.68.

$[(\eta^5\text{-}1,2,4\text{-}iPr_3C_5H_2)Ru(CO)_2]_2$ (2c). A mixture of 3.55 g of $Ru_3(CO)_{12}$ (5.55 mmol) and 4.3 mL of 2,3,5-$iPr_3C_5H_3$ (ca. 10% excess) in 50 mL of *n*-decane was heated under reflux for 16 h. Filtration of the hot solution through a 1:1:1 mixture of sodium sulfate, alumina, and silica resulted in a clear yellow solution, which was stored at −30 °C for 1 day to give 3.20 g (55%) of yellow crystalline **2c**, mp 148–150 °C. IR (KBr): ν 2962 (s), 2872 (m), 1938 (vs) [ν(CO)], 1765 (vs) [ν(CO)], 1470 (m), 1459 (s), 1446 (m), 1384 (m), 1294 (m), 1042 (m), 859 (m), 640 (s, br), 544 (m), 522 (s) cm^{-1}. ^{1}H NMR: δ 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 12H, Me), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Me), 1.3 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Me), 2.81 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHMe_2$), 3.22 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, $CHMe_2$), 4.84 (s, 4H, C*H* ring). $^{13}C\{^1H\}$ NMR: δ 23.3 (s, CH_3), 24.4 (s, CH_3), 24.5 (s, CH_3), 25.5 (s, $CHMe_2$), 25.8 (s, $CHMe_2$), 84.6 (s, *C*H ring), 115.9 (s, *C*–iPr ring), 116.6 (s, *C*–iPr ring), 226.8 (s, CO). MS/EI: *m/z* 697 (M^+), 669 ($M^+ - CO$), 641 ($M^+ - 2CO$), 348 (1,2,4-$iPr_3C_5H_2Ru(CO)_2^+$), 43 ($CHMe_2^+$). Anal. Calcd for $C_{32}H_{46}O_4Ru_2$ (696.8): C, 55.16; H, 6.65. Found: C, 55.12; H, 6.62.

$[(\eta^5\text{-}1,3\text{-}tBu_2C_5H_3)Ru(CO)_2]_2$ (2d). Analogously, 2.20 g (84%) of yellow **2d** (mp 149 °C) was obtained from 1.67 g (2.6 mmol) of $Ru_3(CO)_{12}$ and 1.55 g (8.7 mmol) of 1,3-$tBu_2C_5H_4$. IR (KBr): ν 1974 (vs) [ν(CO)], 1937 (vs) [ν(CO)], 1766 (vs), [ν(CO)], 1744 (vs) [ν(CO)], 1452 (m), 1360 (m), 1248 (m), 1156 (m), 912 (m), 857 (m), 823 (m), 803 (m), 669 (m), 638 (s) cm^{-1}. ^{1}H NMR: δ 1.25 (s, 36H, tBu), 4.48 (d, $^4J_{HH}$ = 2.0 Hz, 4H, H-4,5 ring), 5.37 (t, $^4J_{HH}$ = 2.0 Hz, 2H, H-2 ring). $^{13}C\{^1H\}$ NMR: δ 31.5 (s, $C(CH_3)_3$), 32.0 (s, $C(CH_3)_3$), 80.6 (s, C-2 ring), 86.8 (s, C-4,5 ring), 122.2 (s, C-1,3 ring), 222.2 (s, CO). MS/EI: *m/z* 669 (M^+), 641 ($M^+ - CO$), 611 ($M^+ - 2CO$), 335 (1,3-$tBu_2C_5H_3Ru(CO)_2^+$), 57 (tBu^+). Anal. Calcd for $C_{30}H_{42}O_4Ru_2$ (668.8): C, 53.88; H. 6.33. Found: C, 53.53; H, 6.31.

$[(\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3)Ru(CO)_2]_2$ (2e). As described before, 3.39 g (76%) of yellow **2e** (mp 170 °C) was prepared from 2.61 g (4.1 mmol) of $Ru_3(CO)_{12}$ and 2.70 g (3.0 mL, 12.8 mmol) of 1,1-$(Me_3Si)_2C_5H_4$ in 15 mL of *n*-octane. IR (*n*-decane): ν 2010 (s) [ν(CO)], 1953 (s) [ν(CO)], 1778 (vs) [ν(CO)] cm^{-1}. ^{1}H NMR: δ 0.34 (s, 36H, $SiMe_3$), 4.75 (d, $^4J_{HH}$ = 1.5 Hz, 4H, H-4,5), 5.60 (t, $^4J_{HH}$ = 1.5 Hz, 2H, H-2). $^{13}C\{^1H\}$ NMR: δ −0.13 (s, $Si(CH_3)_3$), 97.1 (s, C-2), 100.5 (s, C-4,5), 101.3 (s, C-1,3), 222.1 (s, CO). $^{29}Si\{^1H\}$ NMR: δ −5.6 (s, $SiMe_3$). MS/CI: *m/z* 733 (M^+), 705 ($M^+ - CO$), 367 (1,3-$(Me_3Si)_2C_5H_3Ru(CO)_2^+$), 339 ($\eta^5$-1,3-$(Me_3Si)_2C_5H_3RuCO^+$), 311 ($\eta^5$-1,3-$(Me_3Si)_2C_5H_3Ru^+$), 73 ($SiMe_3^+$). Anal. Calcd for $C_{26}H_{42}O_4Ru_2Si_4$ (733.1): C, 42.60; H, 5.77. Found: C, 42.45; H, 5.72.

$(\eta^5\text{-}1,2,4\text{-}iPr_3C_5H_2)Fe(CO)_2I$ (3c). A 3.85-g (6.35-mmol) quantity of **1c** was allowed to react with 1.61 g (6.35 mmol) of iodine in 100 mL of CH_2Cl_2 at 0 °C. Stirring was continued for 12 h at 20 °C. Removal of all volatiles in vacuo left a dark red residue. Extraction into pentane, filtration, and storage at −30 °C resulted in violet-brown crystalline **3c** (3.90 g, 71%, mp 81 °C). IR (KBr): ν 1990 (vs) [ν(CO)], 1955 (vs) [ν(CO)], 1450 (m), 1357 (m), 1263 (m), 1046 (m), 896 (m), 881 (m), 600 (m) cm^{-1}. ^{1}H NMR: δ 0.81 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 0.98 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH_3), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 2.37 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHMe_2$), 2.48 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CHMe_2$), 4.6 (s, 2H, C_5H_2). MS/EI: *m/z* 430 (M^+), 402 ($M^+ - CO$), 374 ($M^+ - 2CO$), 275 ($M^+ - CO - I$), 247 ($M^+ - 2CO - I$), 191 (1,2,4-$iPr_3C_5H_2^+$), 43 (iPr^+). Anal. Calcd for $C_{16}H_{23}FeIO_2$ (430.1): C, 44.68; H, 5.39. Found: C, 44.85; H, 5.33.

$(\eta^5\text{-}1,2,4\text{-}iPr_3C_5H_2)Ru(CO)_2Br$ (4c). A yield of 4.40 g (78% of **4c** (mp 118–119 °C dec) was analogously obtained from 4.59 g (0.66 mmol) of **2c** and 1.05 g (0.66 mmol) of Br_2 in 100 mL of CH_2Cl_2 at −30 °C. IR (KBr): ν 2969 (s), 2921 (m), 2875 (m), 2035 (vs) [ν(CO)], 1980 (vs) [ν(CO)], 1485 (m), 1468 (m), 1460 (m, sh), 1386 (m), 1365 (m), 1296 (m), 580 (m), 552 (s), 502 (m) cm^{-1}. ^{1}H NMR: δ 0.76 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 0.86 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 2.05 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $CHMe_2$), 2.44 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHMe_2$), 4.84 (s, 2H, C_5H_2). $^{13}C\{^1H\}$ NMR: δ 23.3 (s, CH_3), 23.7 (s, CH_3), 24.5 (s, CH_3), 24.6 (s, $CHMe_2$), 26.1 (s, $CHMe_2$), 84.8 (s, CH ring), 106.5 (s, *C*-iPr ring), 115.0 (s, *C*–iPr ring), 197.6 (s, CO). MS/EI: *m/z* 430 ($M^+(^{81}Br/^{102}Ru)$), 428 ($M^+(^{79}Br/^{102}Ru)$), 402 ($M^+ - CO(^{81}Br/^{102}Ru)$), 400 ($M^+ - CO(^{79}Br/^{102}Ru)$), 374 ($M^+ - 2CO(^{81}Br/^{102}Ru)$), 372 ($M^+ - 2CO(^{79}Br/^{102}Ru)$), 43 ($iPr^+$). Anal. Calcd for $C_{16}H_{23}BrO_2Ru$ (428.3): C, 44.77; H, 5.51. Found: C, 44.87; H, 5.41.

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(η^5-1,3-tBu$_2$C$_5$H$_3$)Ru(CO)$_2$Br (4d). Analogously, 1.70 g (68%) of yellow crystalline **4d** (mp 118 °C) was obtained from 2.00 g (3.0 mmol) of **2d** and 0.48 g (0.15 mL; 3.0 mmol) of bromine in 70 mL of CH_2Cl_2 (mp 118 °C). IR (KBr): ν 2010 (vs) [ν(CO)], 1970 (vs) [ν(CO)], 1453 (m), 1247 (s), 1159 (m), 880 (m), 860 (m) cm^{-1}. ^{1}H NMR: δ 0.95 (s, 18H, tBu), 4.6 (d, $^4J_{HH}$ = 1.0 Hz, 2H, H-4,5 ring) 4.9 (t, $^4J_{HH}$ = 1.0 Hz, 1H, H-2 ring). ^{13}C{^{1}H} NMR: δ 30.9 (s, $C(\mathrm{CH_3})_3$), 31.4 (s, $\mathrm{C}(CH_3)_3$), 85.1 (s, C-4,5 ring), 85.4 (s, C-2 ring), 118.1 (s, C-1,3 ring), 198.2 (s, CO). MS/EI: *m/z* 416 (M$^+$ (^{81}Br)), 414 (M$^+$(^{79}Br)), 388 (M$^+$(^{81}Br) – CO), 386 (M$^+$(^{79}Br) – CO), 360 (M$^+$(^{81}Br) – 2CO), 358 (M$^+$(^{79}Br) – 2CO), 57 (tBu$^+$). Anal. Calcd for $C_{15}H_{21}BrO_2Ru$ (414.3): C, 43.49; H, 5.11. Found: C, 43.48; H, 5.01.

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$]Ru(CO)$_2$Br (4e). Analogously, 4.10 g (77%) of **4e** (mp 108 °C) was synthesized from 0.96 g (0.31 mL, 6.0 mmol) of bromine and 4.40 g (6.0 mmol) of **2e**. IR (KBr): ν 2017 (vs) [ν(CO)], 1975 (s) [ν(CO)], 1404 (m), 1245 (s), 1197 (m), 1080 (m), 945 (w), 904 (m), 837 (vs), 758 (m), 696 (m), 630 (m) cm^{-1}. ^{1}H NMR: δ 0.14 (s, 18H, SiMe$_3$), 4.71 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-4,5 ring), 5.38 (t, $^4J_{HH}$ = 1.4 Hz, 1H, H-2 ring). ^{13}C{^{1}H} NMR: δ –0.2 (s, SiMe$_3$), 93.7 (s, C-2 ring), 94.7 (s, C-4,5 ring), 108.6 (s, C-1,3 ring), 197.6 (s, CO). ^{29}Si{^{1}H} NMR: δ –4.1 (s). MS/EI: *m/z* 448 (M$^+$(^{81}Br)), 446 (M$^+$(^{79}Br)), 420 (M$^+$(^{81}Br) – CO), 418 (M$^+$(^{79}Br) – 2CO), 392 (M$^+$(^{81}Br) – 2CO), 390 (M$^+$(^{79}Br) – 2CO), 73 (SiMe$_3^+$). Anal. Calcd for $C_{13}H_{21}BrO_2RuSi_2$ (446.5): C, 34.97; H, 4.74. Found: C, 35.22; H, 4.74.

(η^5-1,2,4-iPr$_3$C$_5$H$_2$)(CO)$_2$FeP(SiMe$_3$)$_2$ (5c). A 0.52-g (1.2-mmol) quantity of **3c** was added to a stirred and –110 °C cold solution of 0.33 g (1.2 mmol) of LiP(SiMe$_3$)$_2$·DME in 30 mL of *n*-hexane. The reaction mixture was allowed to warm to 20 °C over a period of 6 h. Due to the instability of **5c** the dark red solution was directly employed for the synthesis of metallodiphosphene **7c**. ^{31}P{^{1}H} NMR (hexane): δ –231 (s).

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$](CO)$_2$FeP(SiMe$_3$)$_2$ (5e). A 1.55-g (3.46-mmol) sample of **3e** was added to a stirred and –90 °C cold solution of 0.95 g (3.46 mmol) of LiP(SiMe$_3$)$_2$·DME in a mixture of 15 mL of ether and 50 mL of cyclopentane. The reaction mixture was allowed to warm to 20 °C over a period of 16 h. Removal of all volatiles in vacuo left a dark red brown residue. Extraction into *n*-pentane, filtration, and evaporation to dryness resulted in 1.65 g (96%) of crude red-black glassy **5e**. No attempts were made to purify this material prior to its conversion into **7e**. IR (C_6H_6): ν 2002 (s) [ν(CO)], 1957 (s) [ν(CO)], 1249 (m), 985 (m), 839 (s), 727 (s) cm^{-1}. ^{1}H NMR: δ 0.23 (s, 18H, C–SiMe$_3$), 0.43 (d, $^3J_{PH}$ = 3.9 Hz, 18H, PSiMe$_3$), 4.79 (t, $^4J_{HH}$ = 1.4 Hz, 1H, H-2 ring), 4.90 (dd, $^3J_{PH}$ = 4.1, $^4J_{PH}$ = 1.4 Hz, 2H, H-4.5 ring). ^{13}C{^{1}H} NMR: δ –0.09 (d, $^4J_{PC}$ = 2.1 Hz, $\mathrm{CSi}(CH_3)_3$), 4.8 (d, $^2J_{PC}$ = 9.2 Hz, $\mathrm{PSi}(CH_3)_3$), 91.1 (s, C-1,3 ring), 97.1 (s, C-4,5 ring), 98.8 (d, $^2J_{PC}$ = 4.0 Hz, C-2 ring), 217.0 (s, CO). ^{29}Si{^{1}H} NMR: δ –7.8 (d, $^1J_{PSi}$ = 52.5 Hz, PSi), –4.42 (s, C–Si), ^{31}P{^{1}H} NMR (cyclopentane): –264.8 (s).

(η^5-1,2,4-iPr$_3$C$_5$H$_2$)(CO)$_2$RuP(SiMe$_3$)$_2$ (6c). A 1.69-g (3.94-mmol) quantity of **4c** was added to a solution of 1.08 g (3.94 mmol) of LiP(SiMe$_3$)$_2$·DME in a mixture of 30 mL of *n*-pentane and 30 mL of ether at –40 °C. The orange solution was warmed to 20 °C within 5 h and then freed from volatiles in vacuo. The residue was dissolved in 40 mL of *n*-pentane, filtered, and concentrated to ca. 10 mL. Storage at –30 °C afforded yellow crystals. Yield: 1.83 (88%) of **6c** (mp 73 °C). IR (*n*-decane): ν 2009 (s) [ν(CO)], 1957 (s) [ν(CO)] cm^{-1}. ^{1}H NMR: δ 0.49 (d, $^3J_{PH}$ = 4.1 Hz, 18H, SiMe$_3$), 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH$_3$), 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH$_3$), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH$_3$), 2.43 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CHMe$_2$), 2.82 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, CHMe$_2$), 4.67 (s, 2H, C$_5$H$_2$). ^{13}C{^{1}H} NMR: δ 5.4 (d, $^3J_{PC}$ = 11.7 Hz, $\mathrm{Si}(CH_3)_3$), 22.5 (s, $\mathrm{CH}(CH_3)_2$), 24.5 (s, $\mathrm{CH}(CH_3)_2$), 25.0 (s, $\mathrm{CH}(CH_3)_2$), 25.3 (s, $C\mathrm{HMe_2}$), 25.5 (s, $C\mathrm{HMe_2}$), 25.9 (s, $C\mathrm{H(CH_3)_2}$), 79.9 (s, C-3,5 ring), 115.9 (s, C-1,2 ring), 120.3 (s, C-4 ring), 203.1 (s, CO). ^{29}Si{^{1}H} NMR: δ 6.55 (d, $^1J_{PSi}$ = 45.6 Hz). ^{31}P{^{1}H} NMR: δ –231.3 (s). Anal. Calcd for $C_{22}H_{41}O_2PRuSi_2$ (525.8): C, 50.26; H, 7.86. Found: C, 49.44; H, 7.81.

(η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$RuP(SiMe$_3$)$_2$ (6d). A 0.66-g (2.40-mmol) amount of LiP(SiMe$_3$)$_2$·DME was dissolved in a mixture of 10 mL of ether and 20 mL of cyclopentane. Then 1.00 g (2.4 mmol) of **4d** was added to the cold (–20 °C) solution with stirring. The latter was then slowly warmed to 20 °C. After 1 h of stirring at 20 °C the color of the mixture became light yellow. Volatiles were removed in vacuo, the residue was dissolved in 40 mL of *n*-pentane, and the solution was filtered. The filtrate was freed from the solvent to give a yellow oil which resisted crystallization. Yield: 1.2 g (98%) of crude **6d**. This material was used for the preparation of metallodiphosphene **8d** without further purification. IR (hexane): ν 2012 (vs) [ν(CO)], 1961 (vs) [ν(CO)], 1136 (m), 908 (m), 725 (s), 624 (m), 564 (m), 517 (m) cm^{-1}. ^{31}P{^{1}H} NMR: δ –275.6 (s).

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$](CO)$_2$RuP(SiMe$_3$)$_2$ (6e). A 0.33-g (1.2-mmol) amount of LiP(SiMe$_3$)$_2$·DME was added to a solution of 0.53 g (1.19 mmol) of **4e** in 25 mL of a cyclopentane/ether mixture (1:1) (–100 °C). With stirring the mixture was warmed to 20 °C over a period of 6 h and then freed from volatiles in vacuo. The residue was dissolved in 50 mL of *n*-pentane and filtered. The filtrate was concentrated to ca. 10 mL and stored at –30 °C. After 1 day poorly soluble **2e** had been precipitated. The mother liquor was decanted. Drying the residue in vacuo for several hours gave a yellow, instable glass, which could not be crystallized: Yield: 0.42 g (65%). ^{31}P{^{1}H} NMR: δ –270.9 (s). This material was immediately converted into the corresponding metallodiphosphene **8e**.

(η^5-1,2,4-iPr$_3$C$_5$H$_2$)(CO)$_2$Fe—P=P—Mes* (7c). A solution of freshly prepared **5c** (1.2 mmol) in *n*-hexane was treated at 0 °C with 0.42 g (1.2 mmol) of Mes*PCl$_2$. After 20 min two dublets with the characteristics of a diphosphene at δ 560 (d, $^1J_{PP}$ = 596 Hz, PC) and δ 688 (PFe) were registered in the ^{31}P NMR spectrum. This diphosphene decomposed over a period of 5 h in solution. Attempts to isolate **7c** failed.

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$](CO)$_2$Fe—P=P—Mes* (7e). A mixture of 2.25 g (4.52 mmol) of **5e** and 1.57 g (4.51 mmol) of Mes*PCl$_2$ in 60 mL of THF was stirred for 3 h at 20 °C. Removal of all volatiles, extraction of the residue into 50 mL of pentane, and filtration gave a red brown solution. Reduction in volume and storage at –75 °C (1 week) afforded brown crystalline **7e**. Recrystallization from *n*-pentane at –30 °C yielded 2.24 g (79%) of orange crystalline **7e** (mp 110 °C dec). IR (KBr): ν 1975 (s) [ν(CO)], 1938 (vs) [ν(CO)], 1582 (w), 1380 (m), 1240 (s), 1068 (s), 830 (vs, br), 747 (s) cm^{-1}. ^{1}H NMR: δ 0.09 (s, 18H, SiMe$_3$), 1.3 (s, 9H, *p*-tBu), 1.71 (s, 18H, *o*-tBu), 4.59 (s, 2H, H-4,5 ring), 4.93 (s, 1H, H-2 ring), 7.64 (s, 2H, *m*-H aryl). ^{13}C{^{1}H} NMR: δ –0.3 (s, Si(CH$_3$)$_3$), 31.5 (s, $p\text{-}\mathrm{C}(CH_3)_3$), 34.7 (s, $o\text{-}\mathrm{C}(CH_3)_3$), 34.9 (s, $p\text{-}C(\mathrm{CH_3})_3$), 38.9 (s, $o\text{-}C(\mathrm{CH_3})_3$), 93.2 (s, C-2 ring), 95.4 (s, C-4,5 ring), 104.0 (s, C-1,3 ring), 122.3 (s, *m*- and *p*-C aryl), 149.1 (s, *o*-C aryl), 152.6 (d, $^1J_{PC}$ = 7.5 Hz, *i*-C aryl), 215.2 (d, $^3J_{PC}$ = 10.4 Hz, CO). ^{29}Si{^{1}H} NMR: δ –4.2 (d, $^3J_{PSi}$ = 67.7 Hz). ^{31}P{^{1}H} NMR: δ 569.1 (d, $^1J_{PP}$ = 599.8 Hz, P—C), 673.4 (d, $^1J_{PP}$ = 599.8 Hz, P—Fe). MS/EI: *m/z* 629 (M$^+$), 516 (M$^+$ – 2CO – C$_4$H$_{10}$), 293 ((Me$_3$Si)$_2$C$_5$H$_3$Fe(CO)$^+$), 73 (SiMe$_3^+$), 57 (tBu$^+$). Anal. Calcd for $C_{31}H_{50}FeO_2P_2Si_2$ (628.7): C, 59.22; H, 8.02. Found: C, 59.17; H, 7.68.

(η^5-1,2,4-iPr$_3$C$_5$H$_2$)(CO)$_2$Ru—P=P—Mes* (8c). A 0.76-g (1.45-mmol) quantity of **6c** was reacted with 0.50 g (1.45 mmol) of Mes*PCl$_2$ in 15 mL of THF at 0 °C. The stirred mixture was allowed to warm to 20 °C within 4 h during which its color changed from yellow to orange. An analgous workup afforded 0.50 g (53%) of yellow crystalline **8c** (mp 127 °C). IR (KBr): ν 2009 (vs) [ν-(CO)], 1958 (vs) [ν-(CO)], 1452 (m, br), 1358 (m), 1261 (s), 876 (m), 802 (s), 752 (m) cm^{-1}. ^{1}H NMR: δ 0.84 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH$_3$), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH$_3$), 1.32 (s, 9H, *p*-tBu), 1.74 (s, 18H, *o*-tBu), 2.23 (sept, $^3J_{HH}$ = 6.8 Hz, 3H, $\mathrm{C}H\mathrm{Me_2}$), 4.91 (s, 2H, C$_5$H$_2$), 7.65 (s, 2H, *m*-H aryl). ^{13}C{^{1}H} NMR: δ 24.2 (s, $\mathrm{CH}(CH_3)_2$), 24.7 (s, $\mathrm{CH}(CH_3)_2$), 26.4 (s, $C\mathrm{HMe_2}$), 31.6 (s, $p\text{-}\mathrm{C}(CH_3)_3$), 34.85 (s, $o\text{-}\mathrm{C}(CH_3)_3$), 34.9 (s, $p\text{-}C(\mathrm{CH_3})_3$), 38.9 (s, $o\text{-}C(\mathrm{CH_3})_3$), 85.5 (s, C-3,5 ring), 112.8 (s, C-4 ring), 115.3 (s, C-1,2 ring), 122.2 (s, *m*- and *p*-C aryl), 148.8 (s, *o*-C aryl), 152.5 (d, $^1J_{PC}$ = 6.9 Hz, *i*-C aryl), 201.6 (d, $^2J_{PC}$ = 13.0 Hz, CO). ^{31}P{^{1}H} NMR: δ 551.9 (d, $^1J_{PP}$ = 593.5, P—C), 652.9 (d, $^1J_{PP}$ = 593.5 Hz, P—Ru). MS/Cl: *m/z* 656 (M$^+$), 599 (M$^+$ – tBu), 571 (M$^+$ – tBu – CO), 543

(M^+ − tBu − 2CO), 293 (Mes^{*+}), 57 (tBu^+). Anal. Calcd for $C_{34}H_{52}O_2P_2Ru$ (655.8): C, 62.27; H, 7.99. Found: C, 62.31; H, 8.23.

(η^5-1,3-$tBu_2C_5H_3$)$(CO)_2$Ru—P=P—Mes* (8d). A 1.0-g (1.95-mmol) sample of **6d** was dissolved in 4 mL of *n*-pentane in a narrow Schlenk tube. After the addition of 0.62 g (1.79 mmol) of solid Mes^*PCl_2, the mixture was shaken vigorously until the complete dissolution of the chlorophosphane. The tube was set aside for 3 h, during which crystalline **8d** separated. A period of 12 h at −30 °C led to completion of the crystallizing process. The supernatant solution was removed with a syringe. Yield: 0.93 g (81%; mp 138 °C, dec). IR (KBr): ν 2962 (s), 2007 (vs) [ν(CO)], 1959 (vs) [ν(CO)], 1360 (m), 1252 (m), 873 (m), 823 (m), 548 (s), 511 (m) cm^{-1}. ^1H NMR: δ 0.96 (s, 18H, tBu-1,3 ring), 1.33 (s, 9H, *p*-tBu), 1.74 (s, 18H, *o*-tBu), 4.75 (d, $^4J_{HH}$ = 2 Hz, 2H, H-4,5 ring), 5.12 (t, $^4J_{HH}$ = 2 Hz, 1H, H-2 ring), 7.65 (s, 2H, m-H aryl). $^{13}C\{^1H\}$ NMR: δ 31.7 (s, C_5—$C(CH_3)_3$), 31.9 (s, C_5—$C(CH_3)_3$), 32.4 (s, *p*-$C(CH_3)_3$), 34.9 (s, *o*-$C(CH_3)_3$), 35.2 (s, *p*-$C(CH_3)_3$), 39.1 (s, *o*-$C(CH_3)_3$), 87.7 (s, C-4,5 ring), 89.8 (s, C-2 ring), 122.2 (s, C-1,3 ring), 122.5 (s, *m*- and *p*-C aryl), 149.0 (s, *o*-C aryl), 152.8 (s, *i*-C aryl), 202.0 (s, CO). $^{31}P\{^1H\}$ NMR: δ 553.4 (d, $^1J_{PP}$ = 596 Hz, PC), 640.6 (d, $^1J_{PP}$ = 596 Hz, PRu). Anal. Calcd for $C_{33}H_{50}O_2P_2Ru$ (641.8): C, 61.76; H, 7.85. Found: C, 60.76; H, 7.77.

[η^5-1,3-$(Me_3Si)_2C_5H_3$]$(CO)_2$Ru—P=P—Mes* (8e). A 0.29-g (0.83-mmol) sample of Mes^*PCl_2 was added to a −130 °C cold solution of 0.45 (0.83 mmol) of **6e** in 20 mL of hexane. A change of color from yellow or orange-red was observed during warm up to 20 °C over a period of 12 h. An analogous workup afforded orange crystalline **8e**. Yield: 0.39 g (70%; mp 100 °C). IR (KBr): ν 2020 (s) [ν(CO)], 1970 (s) [ν(CO)], 1396 (m), 1268 (s), 1082 (s), 913 (m), 845 (vs), 763 (m) cm^{-1}. ^1H NMR: δ 0.07 (s, 18H, $SiMe_3$), 1.30 (s, 9H, *p*-tBu), 1.71 (s, 18H, *o*-tBu), 5.05 (d, $^4J_{HH}$ = 1.4 Hz, 2H, H-4,5 ring), 5.36 (t, $^4J_{HH}$ = 1.4 Hz, 1H, H-2 ring), 7.63 (s, 2H, *m*-H aryl). $^{13}C\{^1H\}$ NMR: δ 0.12 (s, $SiMe_3$), 31.6 (s, *p*-$C(CH_3)_3$), 32.7 (s, *p*-$C(CH_3)_3$), 34.8 (s, *o*-$C(CH_3)_3$), 38.9 (s, *o*-$C(CH_3)_3$, 97.1 (s, C-2 ring), 98.4 (s, C-4,5 ring), 107.4 (s, C-1,3 ring), 122.3 (s, *m*−*p*-C aryl), 149.0 (s, *o*-C aryl), 152.2 (d, *i*-C aryl), 200.6 (d, $^2J_{PC}$ = 13.6 Hz, CO). $^{29}Si\{^1H\}$ NMR: δ −5.13 (s). $^{31}P\{^1H\}$ NMR: δ 562.0 (d, $^1J_{PP}$ = 596 Hz, PC), 628.9 (d, $^1J_{PP}$ = 596 Hz, PRu). Despite several attempts of purification no satisfactory elemental analysis of **8e** could be obtained. The conversion of **8e** into analytical pure **12e**, however, proceeded without difficulties.

(η^5-C_5Me_5)(CO)FeP(=PMes*)OC$(CF_3)_2$C(O) (9a) and (η^5-C_5Me_5)$(CO)_2$Fe—P—P(Mes*)OC$(CF_3)_2$ (11a). A 144.6 mL (6.0-mmol) aliquot of gaseous HFA was condensed on a solution of 1.32 g (2.4 mmol) of **7a** in 40 mL of *n*-pentane at −196 °C. The mixture was stirred under an atmosphere of HFA for 7 days at 20 °C. Volatiles were removed in vacuo and the orange residue was dissolved in 10 mL of *n*-pentane. Storing for 24 h at −40 °C yielded 1.39 g (81%) of orange, crystalline **9a**. If a pentane solution of **9a** was kept under an N_2 atmosphere for 4 weeks at −40 °C red crystals of **11a** were formed. The transformation **9a–11a** stopped at a ratio of ca. 3:1. The complete separation of both components of the mixture failed.

9a: IR (KBr) ν 1960 (vs) [ν(CO) terminal], 1650 (s) [ν(CO) acyl], 1590 (m), 1360 (s), 1270 (vs), 1210 (vs), 1200 (vs), 1140 (m), 1102 (vs), 1030 (m), 965 (s), 875 (m), 825 (vs), 772 (m), 748 (m), 725 (m), 710 (s), 655 (s), 638 (s), 620 (sh), 595 (sh), 570 (sh), 545 (m), 512 (sh), 490 (sh), 458 (sh) cm^{-1}; ^1H NMR δ 1.33 (s, 9H, *p*-tBu), 1.49 (s, 15H, C_5Me_5), 1.65 (s, 9H, *o*-tBu), 1.68 (s, 9H, *o*-tBu), 7.56 (s, 2H, *m*-H aryl); $^{13}C\{^1H\}$ NMR δ 9.28 (d, $^3J_{PC}$ = 6.8 Hz, $C_5(CH_3)_5$), 31.4 (s, *p*-$C(CH_3)_3$), 33.5 (d, $^4J_{PC}$ = 4.9 Hz, *o*-$C(CH_3)_3$), 33.9 (d, $^4J_{PC}$ = 5.1 Hz, *o*-$C(CH_3)_3$), 35.0 (s, *p*-$C(CH_3)_3$), 39.3 (s, *o*-$C(CH_3)_3$), 39.4 (s, *o*-$C(CH_3)_3$), 96.0 (s, $C_5(CH_3)_5$), 122.2 (s, *m*-C aryl), 215.3 (m, FeCO) (the signals for the carbon atoms at the $OC(CF_3)_2$ building block and that of the acyl carbonyl group could not be detected); $^{19}F\{^1H\}$ NMR δ −70.55 (q, $^4J_{FF}$ = 7.3 Hz, CF_3), −71.35 (q, $^4J_{FF}$ = 7.3 Hz, CF_3); $^{31}P\{^1H\}$ NMR δ 180.7 (d, $^1J_{PP}$ = 633.1 Hz, PC), 438.5 (d, $^1J_{PP}$ = 633.1 Hz, PFe); MS/El *m*/*z* 720 (M^+), 554 (M^+ − HFA), 442 ($(CF_3)_2COPMes^{*+}$), 278 ($(C_5Me_5)(CO)_2FeP^+$), 166 (HFA^+), 135 ($C_5Me_5^+$), 57 (tBu^+). Anal. Calcd for $C_{33}H_{44}F_6FeO_3P_2$ (720.5): C, 55.01; H, 6.16; Fe, 7.75. Found: C, 55.18; H, 6.09; Fe, 7.64.

11a: $^{31}P\{^1H\}$ NMR δ 136.0 (dq, $^1J_{PP}$ = 94.0 Hz, $^3J_{PF}$ = 7.3 Hz, PFe), 194.7 (d, $^1J_{PP}$ = 94.0 Hz, PO).

(η^5-C_5Me_4Et)(CO)FeP(=PMes*)OC$(CF_3)_2$C(O)(9b). Analogously, 0.55 g (0.97 mmol) of **7b** was reacted with 53 mL (2.20 mmol) of HFA in 15 mL of toluene at 20 °C to give 0.50 g (70%) of orange crystalline **9b** (mp 172 °C dec). IR (KBr): 2964 (w), 1958 (vs) [ν(CO) terminal], 1656 (s) [ν(CO) acyl], 1261 (s), 1217 (vs), 1096 (s), 1026 (m, br), 960 (m), 823 (s), 800 (s) cm^{-1}. ^1H NMR: δ 0.75 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3), 1.34 (s, 9H, *p*-tBu), 1.51 (s, 3H, CH_3 ring), 1.53 (s, 3H, CH_3 ring), 1.58 (s, 3H, CH_3 ring), 1.59 (s, 3H, CH_3 ring), 1.66 (s, 9H, *o*-tBu), 1.69 (s, 9H, *o*-tBu), 3.25 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CH_3), 7.57 (m, 2H, *m*-H aryl). $^{13}C\{^1H\}$ NMR: δ 9.5 (m, CH_3 ring), 14.2 (d, $^4J_{PC}$ = 0.6 Hz, CH_2CH_3), 18.6 (d, $^3J_{PC}$ = 2.0 Hz, CH_2CH_3), 31.6 (s, *p*-$C(CH_3)_3$), 33.2 (s, *o*-$C(CH_3)_3$), 33.4 (s, *o*-$C(CH_3)_3$), 35.0 (s, *p*-$C(CH_3)_3$), 38.3 (s, *o*-$C(CH_3)_3$), 97.5 (s) and 97.6 (s, CH3,4), 98.5 (d, $^2J_{PC}$ = 1.7 Hz) and 98.7 (d, $^2J_{PC}$ = 1.7 Hz, C-2,5), 102.3 (d, $^2J_{PC}$ = 1.4 Hz, C-1), 122.2 (s, *p*-C aryl), 122.7 (s, *m*-C aryl), 151.6 (s, *o*-C aryl), 151.7 (s, *o*-C aryl), 154.0 (dd, $^2J_{PC}$ = 31.5, $^3J_{PC}$ = 10.7 Hz, *i*-C aryl), 213.5 (dd, $^2J_{PC}$ = 22.0, $^3J_{PC}$ = 5.0 Hz, CO terminal), 236.4 (d, $^2J_{PC}$ = 14.0 Hz, CO acyl). $^{31}P\{^1H\}$ NMR: δ 181.8 (d, 1P, $^1J_{PP}$ = 634.0 Hz, P—C), 483.6 (d, 1P, $^1J_{PP}$ = 634.0 Hz, PFe). $^{19}Fe\{^1H\}$ NMR: δ −71.0 (q, $^4J_{PF}$ = 7.2 Hz, 3F, CF_3), −71.8 (q, $^4J_{PF}$ = 7.2 Hz, 3F, CF_3). MS/Cl: *m*/*z* 735 (M^+), 569 (M^+ − HFA), 456 (M^+ − HFA − 2CO − C_4H_{10}), 166 (HFA^+), 69 (CF_3^+), 57 (tBu^+). Anal. Calcd for $C_{34}H_{46}F_6FeO_3P_2$ (734.5): C, 55.60; H, 6.31. Found: C, 55.66; H, 6.47.

(η^5-C_5Me_5)(CO)RuP(=PMes*)OC$(CF_3)_2$C(O) (10a). An analogous treatment of 0.50 g (0.83 mmol) of **8a** with 20 mL (0.83 mmol) of HFA in 10 mL of toluene at 20 °C during 2 h afforded 0.30 g (47%) of yellow crystalline **10a** (mp 117–119 °C dec). IR (KBr): ν 2964 (s), 1983 (vs) [ν(CO) terminal], 1666 (s) [ν(CO) acyl], 1274 (s), 1215 (s), 1200 (m), 1097 (m), 964 (m), 834 (m) cm^{-1}. ^1H NMR: δ 1.34 (s, 9H, *p*-tBu), 1.42 (s, 15H, C_5Me_5), 1.66 (s, 9H, *o*-tBu), 1.67 (s, 9H, *o*-tBu), 7.58 (m, 2H, *m*-H aryl). $^{13}C\{^1H\}$ NMR: δ 9.9 (s, $C_5(CH_3)_5$), 31.3 (s, p-$C(CH_3)_3$), 33.3 (s, *o*-$C(CH_3)_3$), 35.1 (s, *p*-$C(CH_3)_3$), 38.3 (s, *o*-$C(CH_3)_3$), 101.3 (s, $C_5(CH_3)_5$), 122.6 (s, *m*-C aryl), 122.8 (s, *p*-C aryl), 151.7 (s, *o*-C aryl), 154.2 (dd, $^1J_{PC}$ = 109.2, $^2J_{PC}$ = 11.1 Hz, *i*-C aryl), 200.7 (d, $^2J_{PC}$ = 21.3 Hz, CO terminal), 242.3 (d, $^2J_{PC}$ = 10.2 Hz, CO aryl). $^{19}F\{^1H\}$ NMR: δ −71 (q, $^4J_{FF}$ = 7.0 Hz, 3F, CF_3), −71.4 (q, $^4J_{FF}$ = 7.0 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR: δ 167.0 (d, $^1J_{PP}$ = 638.6 Hz, PC), 451.7 (d, $^1J_{PP}$ = 638.6 Hz, P—Ru). MS/Cl: *m*/*z* 600 (M^+ − HFA), 544 (M^+ − HFA − 2CO), 487 (M^+ − HFA − 2CO − C_4H_{10}), 237 ($C_5Me_5Ru^+$), 57 (tBu^+). Anal. Calcd for $C_{33}H_{44}F_6O_3P_2Ru$ (765.7): C, 51.76; H, 5.79. Found: C, 51.19; H, 5.57.

(η^5-1,2,4-$iPr_3C_5H_2$)(CO)RuP(=PMes*)OC$(CF_3)_2$C(O) (10c). Analogously, the reaction of 0.30 g (0.46 mmol) of **8c** with 50 mL (2.1 mmol) of HFA in 20 mL of methylcyclohexane (12 h, 20 °C) gave 0.33 g (88%) of yellow **10c** (mp 110 °C dec). IR (KBr): ν 1991 (vs) [ν(CO) terminal], 1665 (s) [ν(CO) acyl], 1362 (m), 1268 (s, br), 1217 (s), 1201 (s), 1096 (s), 963 (m), 835 (s), 710 (m), 649 (m), 499 (m), 484 (m) cm^{-1}. ^1H NMR: δ 1.00 (m, 18H, CH_3), 1.34 (s, 9H, *p*-tBu), 1.66 (s, 9H, *o*-tBu), 1.68 (s, 9H, *o*-tBu), 2.5 (sept, $^3J_{HH}$ = 6 Hz, 3H, $CHMe_2$), 4.96 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H ring), 4.99 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H ring), 7.58 (s, 2H, *m*-H aryl). $^{13}C\{^1H\}$ NMR: δ 24.3 (s, $CH(CH_3)_2$), 24.7 (s, $CH(CH_3)_2$), 25.4 (s, $CHMe_2$), 26.7 (s, $CHMe_2$), 31.3 (s, *p*-$C(CH_3)_3$), 33.5 (s, *o*-$C(CH_3)_3$), 35.1 (s, *p*-$C(CH_3)_3$), 38.3 (s, *o*-$C(CH_3)_3$), 86.5 (s, CH ring), 87.7 (s, CH ring), 110.8 (s, C—iPr ring), 114.5 (s, C—iPr ring), 116.6 (s, C—iPr ring), 122.5 (s, *p*-C aryl), 122.8 (s, *m*-C aryl), 151.9 (s, *o*-C aryl), 153.5 (dd, $^1J_{PC}$ = 85.4, $^2J_{PC}$ = 12.2 Hz, *i*-C aryl), 201.6 (d, $^2J_{PC}$ = 13.2 Hz, CO terminal), 238.3 (d, $^2J_{PC}$ = 9.2 Hz, CO acyl). $^{19}F\{^1H\}$ NMR: δ −70.4 (q, $^4J_{FF}$ = 7.2 Hz, 3F, CF_3), −70.6 (q, $^4J_{FF}$ = 7.2 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR (methylcyclohexane): δ 178.0 (d, $^1J_{PP}$ = 642.2 Hz, PC), 446.6 (d, $^1J_{PP}$ = 642.2 Hz, PRu). MS/El:

m/z 656 (M$^+$ – HFA), 599 (M$^+$ – HFA – tBu), 571 (M$^+$ – HFA – tBu – CO), 543 (M$^+$ – HFA – tBu –2CO), 57 (tBu$^+$). Anal. Calcd for C$_{37}$H$_{52}$F$_6$O$_3$P$_2$Ru (821.8): C, 54.08; H, 6.38. Found: C, 54.19; H, 6.61.

(η^5-1,3-tBuC$_5$H$_3$)(CO)RuP(=PMes*)OC(CF$_3$)$_2$C(O) (10d). As described before, 0.41 g (100%) of thermolabile yellow microcrystalline **10d**, which already contained small amounts of **12d**, was obtained from 0.33 g (0.51 mmol) of **8d** and 50 mL (2.10 mmol) of HFA in 20 mL of *n*-hexane (30 min, 20 °C). Due to its lability **10d** was only identified by ^{31}P{^{1}H} NMR data: δ 192 (d, $^1J_{\mathrm{PP}}$ = 643 Hz, PC), 444 (d, $^1J_{\mathrm{PP}}$ = 643 Hz, PRu).

(η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$Fe–P–P(Mes*)OC(CF$_3$)$_2$ (11d). A solution of 0.80 g (1.34 mmol) of **7d** in 25 mL of methylcyclohexane was reacted with 160 mL (6.64 mmol) of HFA at 20 °C for 2 h. Removal of all volatiles, extraction into 75 mL of *n*-pentane, and filtration gave a clear red solution. Reduction in volume to 15 mL and storage at 0 °C furnished 0.55 g (54%) of red microcrystalline **11d** (mp 125–127 °C). IR (KBr): ν 2964 (s), 2008 (vs) [ν(CO)], 1964 (vs) [ν(CO)], 1954 (sh), 1362 (m), 1272 (m), 1258 (m), 1222 (s), 1176 (s), 1078 (s), 756 (m), 617 (m, br), 583 (m) cm^{-1}. ^{1}H NMR: δ 0.96 (s, 9H, tBu ring), 1.05 (s, 9H, tBu ring), 1.30 (s, 9H, *p*-tBu), 1.51 (s, br, 18H, *o*-tBu), 4.41 (m, 1H, H-4 or -5 ring), 4.50 (m, 1H, H-5 or -4 ring), 4.67 (t, $^4J_{\mathrm{HH}}$ = 1.8 Hz, 1H, H-2 ring), 7.41 (d, $^4J_{\mathrm{HH}}$ = 1.7 Hz, 2H, *m*-H aryl). ^{13}C{^{1}H} NMR: δ 30.5 (s, C$_5$*C*(CH$_3$)$_3$), 31.2 (s, C$_5$C(*C*H$_3$)$_3$), 31.3 (s, C$_5$C(*C*H$_3$)$_3$), 31.6 (s, *p*-C(*C*H$_3$)$_3$), 33.5 (s, *o*-C(*C*H$_3$)$_3$), 33.6 (s, *o*-C(*C*H$_3$)$_3$), 34.7 (s, *p*-*C*(CH$_3$)$_3$), 39.4 (s, *o*-*C*(CH$_3$)$_3$), 79.1 (s, C-4 or -5 ring), 83.0 (s, C-5 or -4 ring), 89.0 (s, C-2 ring), 117.1 (s, C-1,3 ring), 122.3 (s, *p*-C aryl), 122.9 (s, *m*-C aryl), 149.3 (s, *o*-C aryl), 154.7 (s, *i*-C aryl), 214.9 (s, CO), 215.3 (s, CO). ^{19}F{^{1}H} NMR: δ –75.1 (m, 3F, CF$_3$), –70.6 (s, br, 3F, CF$_3$). ^{31}P{^{1}H} NMR: δ 112.5 (qqd, $^1J_{\mathrm{PP}}$ = 94.1, $^3J_{\mathrm{PF}}$ = 26.9, 5.9 Hz, PFe), 180.4 (d, $^1J_{\mathrm{PP}}$ = 94.1 Hz, PO). MS/El: *m/z* 763 (M$^+$), 289 (M$^+$ – (P=PMes*)), 57 (tBu$^+$). Anal. Calcd for C$_{36}$H$_{50}$F$_6$FeO$_3$P$_2$ (762.6): C, 56.71; H, 6.61. Found: C, 56.56; H, 6.68.

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$](CO)$_2$Fe–P–P(Mes*)OC(CF$_3$)$_2$ (11e). Analogously, red crystalline **11e** (0.30 g, 39%, mp 120–121 °C) was isolated from the reaction of 0.62 g (0.99 mmol) of **7e** and 60 mL (2.5 mmol) of HFA in 15 mL of methylcyclohexane (20 °C, 24 h). IR (KBr): δ 2962 (m), 2023 (vs) [ν(CO)], 1972 (vs) [ν(CO)], 1392 (w), 1362 (w), 1272 (s), 1257 (s), 1228 (s), 1184 (s), 1077 (s), 946 (w), 909 (m), 879 (w), 841 (s), 758 (m), 581 (m) cm^{-1}. ^{1}H NMR: δ 0.12 (s, 9H, SiMe$_3$), 0.18 (s, 9H, SiMe$_3$), 1.31 (s, 9H, *p*-tBu), 1.46 (s, 9H, *o*-tBu), 1.47 (s, 9H, *o*-tBu), 4.83 (s, 2H, H-4,5 ring), 4.89 (s, 1H, H-2), 7.38 (s, 1H, *m*-H aryl), 7.40 (s, 1H, *m*-H aryl). ^{13}C{^{1}H} NMR: δ –0.85 (s, SiMe$_3$), –0.46 (s, SiMe$_3$), 31.3 (s, *p*-C(*C*H$_3$)$_3$), 33.6 (s, *o*-C(*C*H$_3$)$_3$), 33.7 (s, *o*-C(*C*H$_3$)$_3$), 34.5 (s, *p*-*C*(CH$_3$)$_3$), 39.4 (s, *o*-*C*(CH$_3$)$_3$), 92.1 (s), 92.9 (s), and 94.1 (s, C-2,4,5 ring), 98.7 (s), and 101.6 (s, C-1,3 ring), 122.9 (s, *m*- and *p*-C aryl), 149.4 (s, *o*-C aryl), 154.7 (s, *i*-C aryl), 214.1 (s, CO), 214.4 (s, CO). ^{19}F{^{1}H} NMR: δ –75.9 (ddq, $^3J_{\mathrm{PF}}$ = 27.4, $^4J_{\mathrm{FF}}$ = 10.8, $^4J_{\mathrm{PF}}$ = 3.3 Hz, 3F, CF$_3$), –71.4 (ddq, $^4J_{\mathrm{FF}}$ = 10.8, $^3J_{\mathrm{PF}}$ = 5.7, $^4J_{\mathrm{PF}}$ = 2.8 Hz, 3F, CF$_3$). ^{29}Si{^{1}H} NMR: δ –3.5 (s, 1Si, SiMe$_3$), –5.8 (s, 1Si, SiMe$_3$). ^{31}P{^{1}H} NMR: δ 121.8 (qqd, $^1J_{\mathrm{PP}}$ = 93.0, $^3J_{\mathrm{PF}}$ = 27.4, 5.7 Hz, PFe), 190.1 (d, $^1J_{\mathrm{PP}}$ = 93.0 Hz, PO). MS/El: *m/z* 629 (M$^+$ – HFA), 573 (M$^+$ – HFA –2CO), 516 (M$^+$ – HFA – 2CO – tBu), 265 [((Me$_3$Si)$_2$C$_5$H$_3$)Fe(CO)$_2$$^+$], 73 (SiMe$_3$$^+$), 57 (tBu$^+$). Anal. Calcd for C$_{34}H_{50}F_6FeO_3P_2Si_2$ (794.7): C, 51.39; H, 6.34. Found: C, 51.41; H, 6.16.

(η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$RuP–P(Mes*)OC(CF$_3$)$_2$ (12d). Analogously, 0.26 g (80%) of yellow **12d** (mp 149 °C dec) was prepared from 0.26 g (0.40 mmol) of **8d** and 11 mL (0.46 mmol) of HFA in 20 mL of *n*-hexane (5 h, 20 °C). IR (KBr): ν 2969 (s), 2024 (vs) [ν(CO)], 1973 (vs) [(CO)], 1363 (m), 1276 (s), 1261 (s), 1252 (s), 1221 (s), 1184 (s), 1081 (s), 950 (m), 913 (m), 758 (s), 706 (m), 564 (s) cm^{-1}. ^{1}H NMR: δ 0.91 (s, 9H, C$_5$–tBu), 0.99 (s, 9H, C$_5$–tBu), 1.31 (s, 9H, *p*-tBu), 1.53 (s, br, 18H, *o*-tBu), 4.74 (s, br, 1H, H-4 or -5 ring), 4.95 (m, 1H, H-5 or -4 ring), 5.08 (m, H-2 ring), 7.43 (m, 1H, *m*-H aryl), 7.44 (m, 1H, *m*-H aryl). ^{13}C{^{1}H} NMR: δ 30.7 (s, C$_5$*C*(CH$_3$)$_3$, 31.3 (s, C$_5$C(*C*H$_3$)$_3$), 31.5 (s, C$_5$C(*C*H$_3$)$_3$), 31.8 (s, *p*-C(*C*H$_3$)$_3$), 33.5 (s, *o*-C(*C*H$_3$)$_3$), 33.6 (s, *o*-C(*C*H$_3$)$_3$), 34.5 (s, *p*-*C*(CH$_3$)$_3$, 39.4 (s, *o*-*C*(CH$_3$)$_3$), 82.7 (s) and 83.9 (s, C-4,5 ring), 93.6 (s, C-2 ring), 116.5 (s, C-1,3 ring), 123.0 (s, *m*- and *p*-C aryl), 149.2 (s, *o*-C aryl), 154.6 (s, *i*-C aryl), 201.0 (s, CO). ^{19}F{^{1}H} NMR: δ –70.8 (dq, $^4J_{\mathrm{FF}}$ = 10.0, $^3J_{\mathrm{PF}}$ = 4.6 Hz, CF$_3$), –75.4 (ddq, $^3J_{\mathrm{PF}}$ = 28, $^4J_{\mathrm{FF}}$ = 10, $^4J_{\mathrm{PF}}$ = 3 Hz, CF$_3$). ^{31}P{^{1}H} NMR: δ 94.7 (dqq, $^1J_{\mathrm{PP}}$ = 88.8, $^3J_{\mathrm{PF}}$ = 28.0, 4.6 Hz, PRu), 183.7 (qd, $^1J_{\mathrm{PP}}$ = 88.8, $^4J_{\mathrm{PF}}$ = 3 Hz, PO). MS/El: *m/z* 642 (M$^+$ – HFA), 614 (M$^+$ – HFA – CO), 585 (M$^+$ – HFA – 2CO), 557 (M$^+$ – HFA – CO – tBu), 528 (M$^+$ – HFA – 2CO – tBu), 69 (CF$_3$$^+$), 57 (tBu$^+$). Anal. Calcd for C$_{36}H_{50}F_6O_3P_2$Ru (807.8): C, 53.52; H, 6.24. Found: C, 53.35; H, 6.22.

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$](CO)$_2$RuP–P(Mes*)OC(CF$_3$)$_2$ (12e). Analogously, 0.35 g (56%) of orange crystalline **12e** (mp 120 °C) was obtained from the reaction of 0.50 g (0.74 mmol) of **8e** with 18 mL of HFA (0.75 mmol) at 20 °C (2 h). IR (KBr): ν 2963 (s), 2031 (vs) [ν(CO)], 1982 (vs) [ν(CO)], 1363 (m), 1272 (m), 1257 (s), 1226 (s), 1177 (s), 1079 (s), 840 (s, br), 757 (m), 559 (w) cm^{-1}. ^{1}H NMR: δ 0.09 (s, 9H, SiMe$_3$), 0.14 (s, 9H, SiMe$_3$), 1.30 (s, 9H, *p*-tBu), 1.50 (s, 18H, *o*-tBu), 5.10 (t, $^4J_{\mathrm{HH}}$ = 1.5 Hz, 1H, H-2 ring), 5.27 (d, $^4J_{\mathrm{HH}}$ = 1.5 Hz, 2H, H-4,5 ring), 7.40 (s, 2H, *m*-H aryl). ^{13}C{^{1}H} NMR: δ –0.4 (s, SiMe$_3$), –0.1 (s, SiMe$_3$), 31.3 (s, *p*-C(*C*H$_3$)$_3$), 33.5 (s, *o*-C(*C*H$_3$)$_3$), 33.6 (s, *o*-C(*C*H$_3$)$_3$), 34.5 (s, *p*-*C*(CH$_3$)$_3$), 39.4 (s, *o*-*C*(CH$_3$)$_3$), 94.7 (s) and 95.4 (s, C-4,5 ring), 99.5 (s, C-2 ring), 105.8 (s, C-1,3 ring), 122.9 (s, *m*- and *p*-C aryl), 149.4 (s, *o*-C aryl), 154.6 (s, *i*-C aryl), 200.1 (s, CO). ^{19}F{^{1}H} NMR: δ –70.7 (q, $^4J_{\mathrm{FF}}$ = 10.6 Hz, CF$_3$), –75.3 (ddq, $^3J_{\mathrm{PF}}$ = 28.6, $^4J_{\mathrm{FF}}$ = 10.6, $^4J_{\mathrm{PF}}$ = 3.3 Hz, CF$_3$). ^{29}Si{^{1}H} NMR: δ –4.3 (s, SiMe$_3$), –5.0 (s, SiMe$_3$). ^{31}P{^{1}H} NMR: δ 86.4 (dqq, $^1J_{\mathrm{PP}}$ = 88.0, $^3J_{\mathrm{PF}}$ = 28.6, 3.9 Hz, PRu), 184.9 (d, $^1J_{\mathrm{PP}}$ = 88.0 Hz, PO). Anal. Calcd for C$_{34}$H$_{50}$F$_6$O$_3$P$_2$RuSi$_2$ (839.9): C, 48.62; H, 6.00. Found: C, 48.55; H, 6.08.

Cross Experiment of 10d with 8c. A 0.3-g (0.37-mmol) quantity of freshly prepared **10 d** and 0.24 g (0.37 mmol) of **8c** were dissolved in 3 mL of toluene in an NMR tube. The course of the reaction was monitored by ^{31}P{^{1}H} NMR. **10d** cleanly rearranged to **12d** over a period of 45 min, whereas metallodiphosphene **8c** remained unaffected. No transfer of HFA from **12d** to **8c** was observed.

Results and Discussion

Syntheses and Spectra. A prerequisite for reliable results was the availability of a series of analogously substituted ferrio- and rutheniodiphosphenes. We have chosen the C$_5$Me$_5$ (**a**), C$_5$Me$_4$Et (**b**), 1,2,4-iPr$_3$C$_5$H$_2$ (**c**), 1,3-tBu$_2$C$_5$H$_3$ (**d**), and 1,3-(Me$_3$Si)$_2$C$_5$H$_3$ (**e**) ligands at the metal center with a decreasing σ-donor/π-acceptor capacity along this series and the supermesityl substituent (2,4,6-tBu$_3$C$_6$H$_2$ = Mes*) at the P=P unit.

The missing members in the series were synthesized from the dimers **1** and **2**[19,20] by following literature methods. In some cases slight modifications of these were necessary.

The stability of the ruthenium derivatives in general exceeded that of the iron analogues. Thus the ferriodisilylphosphanes **5c** and **5e** are unstable and had to be converted in situ into the ferriodiphosphenes **7c** and **7e**, whereas the corresponding ruthenium compounds **6c** and **6e** could be isolated in good yields without difficulty. Similarly, **7c** was unstable in contrast to the rutheniodiphosphene **8c**.

The ^{31}P{^{1}H} NMR data for **7a**–**7e** and **8a**–**8e** parallel the decreasing electron donation of the ligands. Thus the resonances of the metalated phosphorus atom in each series was shifted to high field in going from **a**–**e**.

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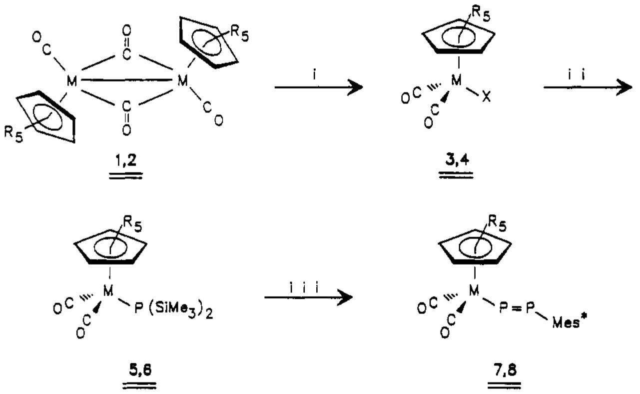
Table 1. $^{31}P\{^1H\}$ NMR Data for the Metallodiphosphenes 7a–e and 8a,c–e (in C_6D_6)

compd	δ(P–M)	δ(P–C)	$^1J_{PP}$/Hz
7a	715.2	553.4	594.2
7b	719.7	553.4	596
7c	688	560	596
7d	678.1	559.1	598
7e	673.4	569.1	599.8
8a	676.5	551.6	597.1
8c	652.6	551.9	593.5
8d	640.6	553.4	596
8e	628.9	562.0	596

Scheme 2



i) X_2 (X=Br, I)[21] ; ii) $LiP(SiMe_3)_2{\cdot}DME$[22,23]; iii) Mes^*PCl_2[9,10]

Compd.	C_5R_5	M	X
1,3,5,7c	1,2,4-$iPr_3C_5H_2$	Fe	I
2,4,6,8c	1,2,4-$iPr_3C_5H_2$	Ru	Br
2,4,6,8d	1,3-$tBu_2C_5H_3$	Ru	Br
3,5,7e	1,3-$(Me_3Si)_2C_5H_3$	Fe	I
2,4,6,8e	1,3-$(Me_3Si)_2C_5H_3$	Ru	Br

The reaction of the ferriodiphosphenes **7a,b** with an excess of HFA in *n*-pentane solution afforded the cycloadducts **9a,b** as orange crystalline solids. These transformations were completed over a period of 1 week. During crystallization experiments in pentane solution at –40 °C pure **9a** rearranged to the 1-oxa-2,3-diphosphetane **11a** within the course of 4 weeks. This conversion stopped at a ratio of **9a**:**11a** = 3:1. Both complexes could not be separated on a preparative scale. In contrast to this no propensity to rearrangement was evident with **9b**. The ferriodiphosphenes **7d,e** and excess of HFA, however, underwent reactions with the exclusive generation of the red microcrystalline 1-oxa-2,3-diphosphetanes **11d,e**. Monitoring by $^{31}P\{^1H\}$ NMR revealed the initial formation of the five-membered rings **9d** (δ 204.9 (d) (PC), 476.8 (d) (PFe), $^1J_{PP}$ = 634.2 Hz) and **9e** (δ 206.2 (d) (PC), 478.2 (d) (PFe), $^1J_{PP}$ = 630.0 Hz), which rapidly rearranged to the final products.

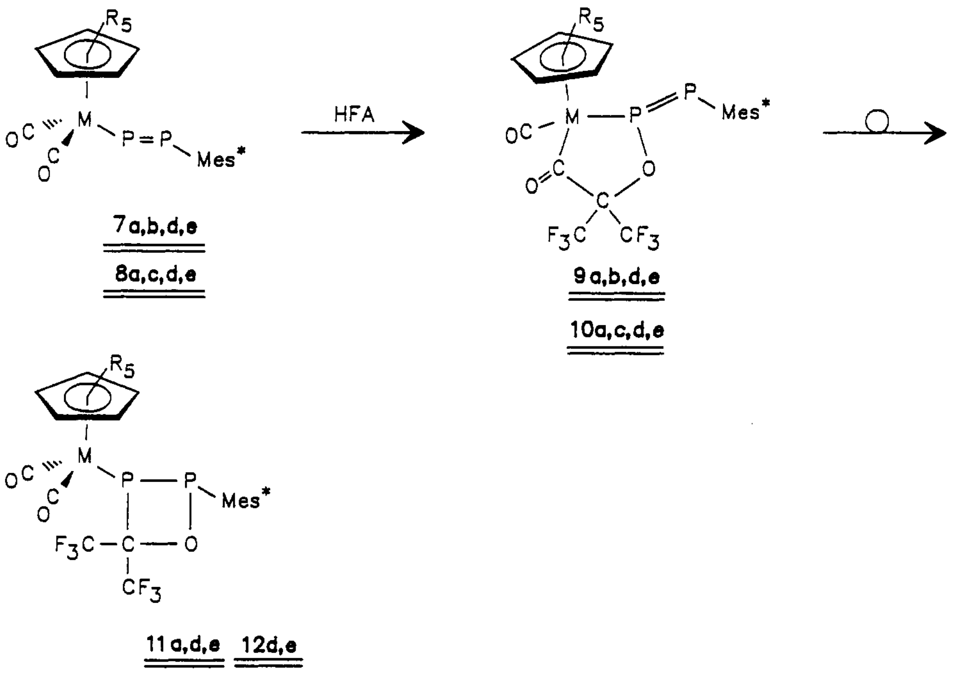
Presumably for steric reasons, metallodiphosphene $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}P{-}C(SiMe_3)_3$ was not affected by HFA, whereas $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Fe{-}P{=}P{-}Mes^*$ was decomposed by the ketone.

The rutheniodiphosphenes **8a,c–e** were also considered as suitable candidates in this study mainly because of their increased metal basicity relative to their Fe analogues. Moreover, due to longer metal–carbon and metal–phosphorus bond lengths steric hindrance may be of minor importance, as in the iron derivatives.

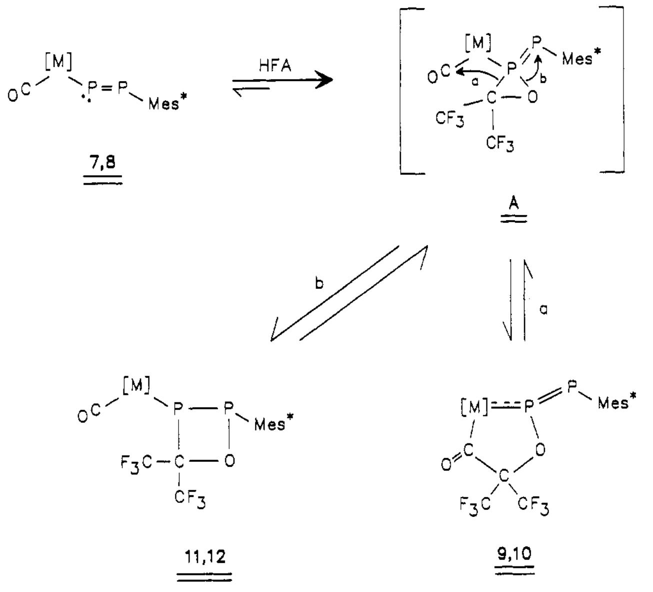
Compounds **8a,c** were cleanly converted into the cycloadducts **10a** and **10c**, which did not show any evidence of rearrangement. The increased thermal stability of **10d** as compared to **9d** is underlined by the fact that **10d** was isolated as a yellow microcrystalline product from the reaction between **8d** and HFA after 30 min.

In toluene solution a quantitative conversion of **10d** to **12d** occurred within 45 min at 20 °C (Scheme 3). The stability of cycloadduct **10e** markedly decreased relative to **10d**. Only at the beginning of the reaction between **8e** and HFA was **10e** briefly detectable by ^{31}P NMR (δ 190.0

Scheme 3



Scheme 4



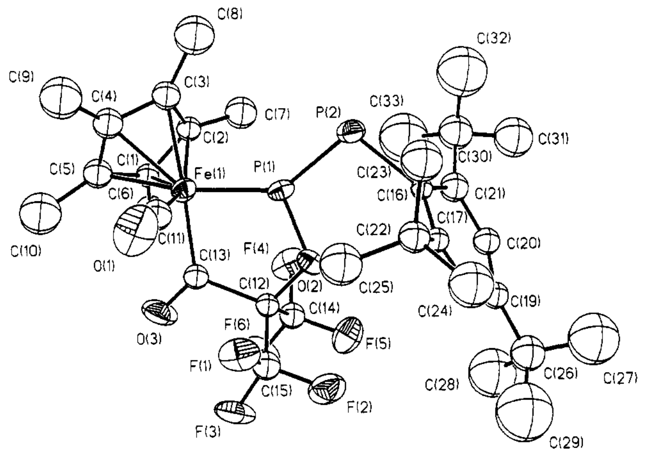


Figure 1. Molecular structure of **9a** in the crystal.

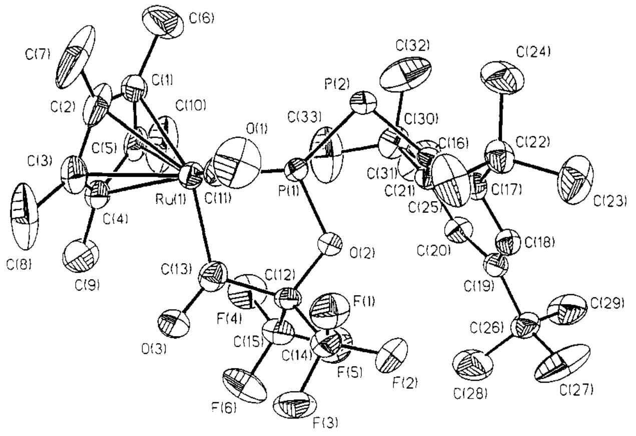


Figure 2. Molecular structure of **10a** in the crystal.

(d) (PC), 441.7 (d) (PRu), ${}^1J_{PP}$ = 642 Hz), before it was transformed into orange-yellow **12e**. In a ${}^{31}P$ NMR experiment equal molar amounts of freshly prepared **10d** and **8c** were allowed to react in toluene. **10d** was cleanly converted into **12d**, whereas metallophosphene **8c** remained unaffected. No trace of **10c**, which would indicate a mechanism for the conversion **10d** → **12d** via free HFA, was detected. The novel compounds **9–12** were diamagnetic solids, which were soluble in most aprotic organic solvents. The structures of the cycloadducts were assigned on the basis of spectral evidence and confirmed by single-crystal X-ray diffraction studies with **9a**, **10a**,**c**, and **11a**. The ${}^{31}P$ NMR spectra of the complexes **9a**,**b**,**d**,**e** display two doublets at δ 478.2–483.6 (FeP) and 180.7–206.2 (PC) with large coupling constants ${}^1J_{PP}$ = 630–633 Hz, suggesting the presence of P=P double bonds. The corresponding data for the Ru analogues are $\delta({}^{31}PRu)$ = 441.7–451.7 and $\delta({}^{31}PC)$ = 167.0–192.0 (${}^1J_{PP}$ = 639–643 Hz).

Table 2. Crystal Data Collection and Refinement Parameters[a]

	9a	**10a**	**10c**	**11a**
formula	$C_{33}H_{44}F_6FeO_3P_2$	$C_{33}H_{44}F_6O_3P_2Ru$	$C_{37}H_{52}F_6O_3P_2Ru$	$C_{33}H_{44}F_6FeO_3P_2$
mol wt	720.5	765.7	821.8	720.5
cryst size/mm	0.1 × 0.45 × 0.5	0.2 × 0.4 × 0.4	0.3 × 0.2 × 0.1	0.1 × 0.35 × 0.5
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
a/Å	21.809(4)	22.308(8)	9.416(5)	46.79(3)
b/Å	10.066(2)	10.174(4)	9.784(6)	9.316(5)
c/Å	16.250(3)	16.014(10)	24.40(2)	16.611(5)
α/deg	90	90	92.74(5)	90
β/deg	95.87(1)	96.62(4)	98.42(5)	101.52(3)
γ/deg	90	90	117.37(4)	90
V/Å^3	3560(2)	3610(3)	1958(2)	7121(6)
Z	4	4	2	8
D_{calcd}/g cm^{-3}	1.344	1.409	1.394	1.344
F(000)	1504	1576	852	3008
μ(Mo Kα)/mm^{-1}	0.571	0.584	0.544	0.571
temp/K	183	177	173	179
2θ max/deg	50.0	55.0	50	45.0
no. of measd rflns	6870	8593	7380	5086
no. of obsd rflns ($F_o > 4\sigma(F_o)$)	2383	5223	4164	2143
no. of variables	232	406	439	254
min/max transm	0.4225/0.4904	0.1943/0.2261		0.2728/0.3101
goodness of fit	2.26	1.90	1.044	1.78
progr used	SHELXTL	SHELXTL	SHELXL-93	SHELXTL
R	0.106	0.059	0.065	0.080
R_w	0.072	0.046	0.100	0.058
based on	F	F	F^2	F
largest peak in diff map/e Å^{-3}	0.88	0.70	0.6	0.50
abs corr	emp (ψ-scan)	emp (ψ-scan)	none	emp (ψ-scan)

[a] Siemens $P2_1$ diffractometer, Mo Kα (graphite monochromator), λ = 0.710 73 Å, full-matrix least-squares refinements.

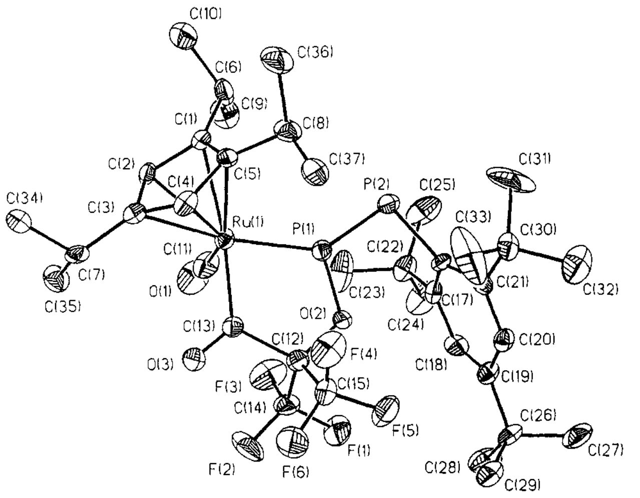


Figure 3. Molecular structure of **10c** in the crystal.

In both series the arylated phosphorus atoms were deshielded in going from **9** and **10a–c** to **9** and **10d,e** which parallels the decrease of the donor capacity of the Cp ring. (δ(PO) (**9e**) - δ(PC) (**9a**) = 25.5; δ(PC) (**10e**) - δ(PC) (**10a**) = 23). In the ^{19}F NMR spectra of **9e,b** and **10a,c** two quartets in the range from -70.0 to -71.8 ($^4J_{FF}$ = ca. 7 Hz) agree with two magnetically nonequivalent CF_3 groups with no PF coupling and infer the absence of any direct $PC(CF_3)_2$ contact. The $^{13}C\{^1H\}$ NMR spectra of the five membered cycloadducts largely fulfill the expectations. The resonances of the acylic carbonyl groups in **9b** and **10a,c** were observed as doublets at δ 236.4–242.3 ($^2J_{PC}$ = 9.2–14.0 Hz). A doublet of doublets at δ 213.5 ($^2J_{PC}$ = 22.0; $^3J_{PC}$ = 5.0 Hz) in the spectrum of **9b** and doublets at δ 200.7 ($^2J_{PC}$ = 21.3 Hz, **10a**) and 201.6 ($^2J_{PC}$ = 13.2 Hz, **10c**) were assigned to the remaining terminal CO ligands. The ^{13}C nuclei of the HFA building block in **9** and **10** could not be detected in the spectra. The IR spectra (KBr) of compounds **9** and **10** display only one intense band at ν 1958 (**9b**), 1960 (**9a**), 1983 (**10a**), and 1991 (**10c**) cm^{-1} which parallels the σ-donor/π-acceptor capability of the Cp rings in these molecules. The acylic carbonyl group in these complexes give rise to an absorption at 1650 (**9a**), 1656 (**9b**), and 1665 ± 1 (**10a,c**) cm^{-1} of medium intensity.

The presence of PP single bonds in four-membered rings can be deduced from the ^{31}P NMR parameters of the 1-oxa-2,3-diphosphetanes **11a,d,e** and **12d,e**. The arylated phosphorus atoms are registered as doublets at δ 180.4–194.7 ($^1J_{PP}$ = 93 ± 1 Hz) and δ 183.7–184.9 ($^1J_{PP}$ = 88 Hz), respectively. The linkage between the metalated phosphorus centers and the $C(CF_3)_2$ group is manifested in the PF coupling with one or two CF_3 groups. In **10a** a doublet of quartets at δ 136.0 with a $^3J_{PF}$ coupling of 26 Hz underlines the exclusive interaction of the ^{31}P nucleus with the CF_3 group in cis position to the P lone pair. In **11d,e** and **12d,e** doublets of quartets of quartets feature PF couplings to the cis CF_3 ($^3J_{PF}$ = 26–28.6 Hz) and the trans CF_3 group ($^3J_{PF}$ = 3.9–5.9 Hz). The ^{31}P NMR signals fall in the range δ 86.4–121.8. Due to the multiplicity of the signals and the size of the $^3J_{PF}$ and $^4J_{PF}$ couplings the assignment of the high field resonances at δ(^{19}F) = -75.1 to -75.9 to the CF_3 group which is cis oriented to the lone pair at the metalated P atom is possible. In keeping with this the absorptions of the trans CF_3 groups are measured at δ(^{19}F) = -70.6 to -71.4 ppm in the $^{19}F\{^1H\}$ NMR spectra. The presence of a (η^5–C_5R_5)(CO_2) unit in **11d,e** and **12d,e** is evident from two intense ν(CO) stretches at ν = 2008–2023 and 1964–1972 cm^{-1} and 2024–2031 and 1973–1982 cm^{-1}, respectively.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^3) of 9a

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	6087(1)	1830(2)	3363(1)	28(1)
P(1)	6988(2)	1588(4)	3908(2)	27(1)
P(2)	7532(2)	2128(4)	4929(2)	32(2)
F(1)	6669(3)	-1836(8)	3280(5)	49(3)
F(2)	7569(4)	-1994(8)	2886(5)	55(3)
F(3)	6775(3)	-2034(8)	1992(5)	57(4)
F(4)	7345(3)	1897(8)	1941(5)	56(3)
F(5)	7941(4)	182(8)	2010(5)	56(4)
F(6)	7119(4)	147(9)	1197(4)	63(4)
O(1)	5602(5)	-353(10)	4289(7)	78(6)
O(2)	7349(4)	499(8)	3374(5)	31(4)
O(3)	6000(4)	168(10)	1934(6)	58(5)
C(1)	5777(4)	3169(10)	2402(4)	27(3)
C(2)	6140	3854	3043	29(4)
C(3)	5848	3721	3781	38(4)
C(4)	5305	2954	3596	41(4)
C(5)	5261	2613	2744	41(4)
C(6)	5883(6)	3208(16)	1499(8)	58(5)
C(7)	6687(6)	4691(14)	2933(8)	53(5)
C(8)	6042(7)	4422(15)	4575(9)	72(6)
C(9)	4836(6)	2676(15)	4178(9)	75(6)
C(10)	4745(7)	1848(16)	2301(9)	81(6)
C(11)	5803(7)	474(16)	3933(9)	38(4)
C(12)	7016(6)	46(13)	2626(8)	25(4)
C(13)	6034(6)	593(13)	2526(9)	29(4)
C(14)	7364(7)	560(15)	1931(10)	33(4)
C(15)	6997(7)	-1464(15)	2690(10)	36(4)
C(16)	8249(6)	1241(12)	4722(7)	20(4)
C(17)	8327(6)	-148(13)	4887(8)	25(4)
C(18)	8733(6)	-845(13)	4482(8)	30(4)
C(19)	9107(6)	-262(14)	3959(9)	32(4)
C(20)	9084(6)	1135(14)	3901(8)	34(4)
C(21)	8681(6)	1913(15)	4309(8)	38(4)
C(22)	7967(6)	-897(14)	5540(9)	37(4)
C(23)	7907(7)	-50(15)	6314(8)	62(5)
C(24)	8378(7)	-2135(15)	5874(9)	73(6)
C(25)	7350(6)	-1390(14)	5195(9)	66(5)
C(26)	9537(8)	-1027(17)	3443(10)	58(5)
C(27)	10189(8)	-707(18)	3706(10)	125(8)
C(28)	9379(8)	-759(18)	2535(10)	117(8)
C(29)	9432(10)	-2453(19)	3471(13)	151(10)
C(30)	8769(7)	3512(16)	4224(10)	58(5)
C(31)	9434(7)	3792(15)	4123(9)	81(6)
C(32)	8681(9)	4086(19)	5058(11)	121(8)
C(33)	8354(8)	4003(19)	3535(11)	126(8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Singlets in the $^{13}C\{^1H\}$ NMR spectra of **11d,e** and **12d,e** at δ 215 ± 1 and δ 201 ± 1, respectively, are caused by the terminal CO ligands. Resonances due to the $C(CF_3)_2$ group were not detected in the $^{13}C\{^1H\}$ NMR spectra.

At room temperature solutions of the five-membered rings **9a** and **10c** in benzene decompose within a few weeks to give the metallodiphosphenes and unidentified products.

We suggest that the formation of **9** and **10** as well as **11** and **12** is initiated by a [2 + 1] cycloaddition with the result of the transient adduct **A**, which in no case could be detected spectroscopically. This process, which parallels the formation of **I**, is dependent on the steric encumbrance of the metallodiphosphene, e.g. the very bulky (η^5-Me_5C_5)$(CO)_2$Fe—P=P—C$(SiMe_3)_3$ was inert toward HFA. Subsequent scission of the P—C linkage in **A** and attack of the carbanion at a positively polarized carbon atom of a terminal carbonyl ligand affords the five-membered metallaheterocycles **9** and **10** (path a). Compounds **11** and **12** result from P—O bond rupture in **A** and attack of the oxygen at the arylated P atom. The cross

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å $\times 10^3$) of 10a

	x	*y*	*z*	*U*(eq)[a]
Ru(1)	1099(1)	1846(1)	3418(1)	28(1)
P(1)	2035(1)	1530(1)	3979(1)	25(1)
P(2)	2599(1)	2053(1)	5000(1)	33(1)
F(1)	1696(1)	−1866(3)	3284(2)	49(1)
F(2)	2586(1)	−1975(3)	2889(2)	55(1)
F(3)	1804(2)	−2017(3)	1967(2)	56(1)
F(4)	2345(2)	1888(3)	1959(2)	56(1)
F(5)	2951(1)	246(4)	2029(2)	60(1)
F(6)	2141(2)	169(4)	1190(2)	66(1)
O(1)	639(2)	−418(4)	4387(3)	67(2)
O(2)	2367(1)	455(3)	3411(2)	29(1)
O(3)	1043(2)	179(4)	1913(2)	50(2)
C(1)	834(3)	3897(6)	3776(4)	49(2)
C(2)	318(3)	3155(7)	3616(4)	56(2)
C(3)	270(2)	2748(5)	2748(4)	41(2)
C(4)	760(2)	3288(5)	2392(3)	33(2)
C(5)	1128(2)	3964(5)	3025(4)	39(2)
C(6)	1058(4)	4650(7)	4573(4)	125(4)
C(7)	−152(3)	2896(8)	4189(4)	112(4)
C(8)	−246(3)	2002(7)	2278(5)	92(3)
C(9)	856(3)	3221(7)	1480(3)	67(3)
C(10)	1672(3)	4763(6)	2895(5)	86(3)
C(11)	831(3)	430(6)	4014(4)	41(2)
C(12)	2041(2)	35(5)	2652(3)	28(2)
C(13)	1346(2)	566(5)	2540(3)	35(2)
C(14)	2033(3)	−1468(5)	2696(3)	38(2)
C(15)	2369(3)	563(6)	1947(3)	39(2)
C(16)	3292(2)	1172(5)	4773(3)	27(2)
C(17)	3360(2)	−187(5)	4929(3)	28(2)
C(18)	3771(2)	−866(5)	4488(3)	32(2)
C(19)	4121(2)	−266(5)	3944(3)	31(2)
C(20)	4106(2)	1095(5)	3914(3)	34(2)
C(21)	3714(2)	1849(5)	4327(3)	29(2)
C(22)	3038(2)	−958(6)	5580(3)	38(2)
C(23)	3400(3)	−2174(6)	5891(4)	68(3)
C(24)	2985(3)	−144(6)	6371(3)	65(3)
C(25)	2405(3)	−1445(6)	5216(4)	63(3)
C(26)	4534(2)	−1042(6)	3418(4)	41(2)
C(27)	4451(3)	−2488(7)	3477(5)	98(4)
C(28)	4380(3)	−661(8)	2492(4)	78(3)
C(29)	5190(2)	−676(7)	3687(4)	74(3)
C(30)	3782(3)	3377(5)	4296(4)	46(2)
C(31)	4410(3)	3758(6)	4063(5)	76(3)
C(32)	3752(3)	3973(7)	5170(4)	82(3)
C(33)	3316(3)	3998(7)	3655(5)	91(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

experiment between **8c** and **10d**, which gave only **12d** and no **10c** is in agreement with an intramolecular rearrangement **9**, **10** → **11**, **12**. The intermediacy of free metallodiphosphenes cannot, however, be excluded completely, as the decomposition of **9** and **10** over the period of several days indeed furnished the free metallodiphosphenes. In our opinion, the reluctance of the initially formed five-membered cycloadducts toward conversion into the 1-oxa-2,3-diphosphetanes, is largely determined by the strength of the M—P bond. Scherer, e.g., observed that the thermal stability of the RuP bonds in (η^5-*c*-P_5)Ru complexes markedly exceeds that of the corresponding iron species.[24] The dependency of the stability of **9** and **10** on the electron donating ability (basicity) of the (C_5R_5)(CO)M fragment infers that the M → P back-bonding, and thus π-bond contribution is an important factor for their stability.

One might also envisage steric reasons for the ease of the transformation **9**, **10** → **11**, **12** (e.g. in Ru derivatives **10** steric pressure is relieved by increased RuP and RuC distances). Molecular models of the structurally characterized five-membered cycloadducts, however, showed no significant steric interactions between the heterocycle and the substituents of the cyclopentadienyl ligands.

Table 5. Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Parameters *U*(iso) or *U*(eq)[a] (Å$^2 \times 10^3$) for 10c

	x	*y*	*z*	*U*(eq)
Ru(1)	4690(1)	2268(1)	1472(1)	21(1)
P(1)	4282(2)	1551(2)	2301(1)	22(1)
P(2)	2810(2)	1433(2)	2836(1)	28(1)
F(1)	8840(5)	2121(5)	3076(2)	50(1)
F(2)	9662(5)	2548(6)	2302(2)	59(1)
F(3)	8491(5)	3770(5)	2610(2)	54(1)
F(4)	5235(5)	−1479(4)	1864(2)	48(1)
F(5)	6659(5)	−1010(5)	2685(2)	45(1)
F(6)	7824(5)	−542(5)	1978(2)	55(1)
O(1)	7132(7)	5572(6)	1970(2)	57(2)
O(2)	5690(5)	1126(5)	2580(2)	24(1)
O(3)	7220(5)	1435(5)	1307(2)	35(1)
C(1)	2425(7)	2258(7)	993(3)	23(2)
C(2)	3781(8)	3116(7)	741(2)	23(2)
C(3)	4393(8)	2128(7)	537(3)	23(2)
C(4)	3373(8)	625(7)	673(2)	24(2)
C(5)	2179(7)	681(7)	951(2)	23(2)
C(6)	1383(8)	2873(8)	1209(3)	32(2)
C(7)	5718(7)	2554(7)	211(2)	23(2)
C(8)	823(7)	−694(7)	1143(3)	29(2)
C(9)	2381(9)	4413(8)	1592(3)	48(2)
C(10)	330(9)	3073(10)	712(3)	54(2)
C(11)	6238(9)	4299(8)	1797(3)	36(2)
C(12)	6804(8)	1157(7)	2247(3)	25(2)
C(13)	6428(7)	1581(7)	1624(3)	21(2)
C(14)	8493(8)	2414(9)	2557(3)	34(2)
C(15)	6650(9)	−473(9)	2192(3)	36(2)
C(16)	3875(7)	1054(7)	3457(2)	21(2)
C(17)	5190(8)	2359(7)	3815(3)	25(2)
C(18)	6351(8)	2097(8)	4151(3)	28(2)
C(19)	6248(8)	645(7)	4154(3)	25(2)
C(20)	4837(8)	−613(7)	3865(3)	25(2)
C(21)	3611(8)	−477(7)	3525(2)	23(2)
C(22)	5372(9)	4021(8)	3874(3)	35(2)
C(23)	6100(11)	4924(8)	3398(3)	62(3)
C(24)	6499(10)	4986(8)	4432(3)	55(2)
C(25)	3736(10)	3957(9)	3911(3)	58(2)
C(26)	7597(8)	402(8)	4493(3)	31(2)
C(27)	6943(6)	−568(6)	4958(2)	47(2)
C(28)	9091(6)	1951(6)	4754(2)	51(2)
C(29)	8130(9)	−461(9)	4099(3)	44(2)
C(30)	2042(8)	−1992(7)	3256(3)	30(2)
C(31)	542(9)	−1768(10)	3184(5)	89(4)
C(32)	1703(10)	−3249(8)	3635(3)	62(3)
C(33)	2190(11)	−2589(9)	2700(3)	82(4)
C(34)	5053(8)	2260(8)	−420(3)	31(2)
C(35)	7079(8)	4229(7)	387(3)	36(2)
C(36)	−813(8)	−1167(8)	768(3)	44(2)
C(37)	1145(8)	−2089(7)	1168(3)	35(2)

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

X-ray Structure Analyses of 9a, 10a, and 10c. Crystals of **9a** were grown from pentane solutions at −40 °C; those of **10a** and **10c** were obtained from hexane at −30 °C.

The compounds **9a**, **10a**, and **10c** display comparable structures (**9a** and **10a** are isomorphous). The most interesting feature of the molecular structures of these species (Figures 1–3 and Table 6) is the geometry of the nearly planar five-membered metallaheterocycle (mean deviation from planarity: **9a**, 0.024 Å; **10a**, 0.024 Å; **10c**, 0.049 Å). The Fe–P bond in **9a** of 2.084(4) Å is remarkably short and strongly suggests multiple-bond contributions. Similarly, short Fe–P bond distances were found for compounds **13** (2.117(2) Å)[25] and **14** (2.112(1) and 2.202(1) Å).[26]

In **7a** the Fe—P contact was determined to be 2.260(1) Å.[9] From the Fe=Fe distance in $(C_5H_5)_2Fe_2(NO)_2$ (2.326

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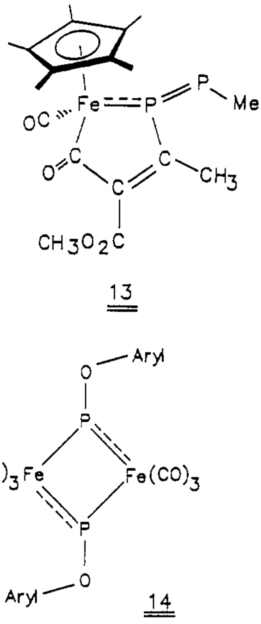
[24] Scherer, O. J. Personal communication.

Table 6. Selected Bond Lengths (Å) and Angles (deg) of 9a, 10a, and 10c

	9a[a]	**10a**[b]	**10c**[b]
M–P(1)	2.084(4)	2.200(2)	2.202(2)
M–C(11)	1.795(16)	1.864(6)	1.884(7)
M–C(13)	1.937(14)	2.038(6)	2.030(6)
P(1)–P(2)	2.014(5)	2.016(2)	2.009(3)
P(1)–O(2)	1.647(9)	1.649(4)	1.632(4)
P(2)–C(16)	1.860(13)	1.859(5)	1.841(6)
O(1)–C(11)	1.128(19)	1.159(8)	1.149(7)
O(2)–C(12)	1.427(15)	1.409(5)	1.408(7)
O(3)–C(13)	1.191(16)	1.210(6)	1.196(7)
C(12)–C(13)	1.640(19)	1.633(7)	1.628(8)
M–P(1)–P(2)	140.3(2)	140.0(1)	138.75(11)
M–P(1)–O(2)	109.5(3)	109.7(1)	109.9(2)
P(2)–P(1)–O(2)	109.0(3)	110.2(1)	111.1(2)
P(1)–O(2)–C(12)	115.6(7)	117.2(3)	117.0(4)
O(2)–C(12)–C(13)	111.8(10)	112.5(4)	112.9(5)
M–C(13)–C(12)	116.3(9)	117.7(3)	117.3(4)
P(1)–M–C(13)	86.4(4)	82.5(2)	82.1(2)

[a] M = Fe. [b] M = Ru.

Chart 1



13

14

(Aryl = 2,6-tBu$_2$-4-MeC$_6$H$_2$)

Å)[27] and the P=P bond length (ca. 2.00 Å),[2] an Fe=P double bond may be estimated to 2.16 Å.

The observed Ru–P distances in **10a** and **10c** of 2.200(2) and 2.202(2) Å, respectively, are also suggestive of a rather substantial M–P π-type interaction. The calculated value for a Ru–P single bond is 2.43 Å,[28] which is about realized in $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{RuP}[\text{C(O)tBu}]_2$ [2.404(1) Å].[29] Observed Ru–P distances in low valent ruthenium–phosphorus compounds range from 2.175 Å in $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}[(\text{F}_5\text{C}_2)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2]$[30] to 2.426(6) in $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+(\text{PF}_6)^-\text{C}_6\text{H}_6$.[31,32]

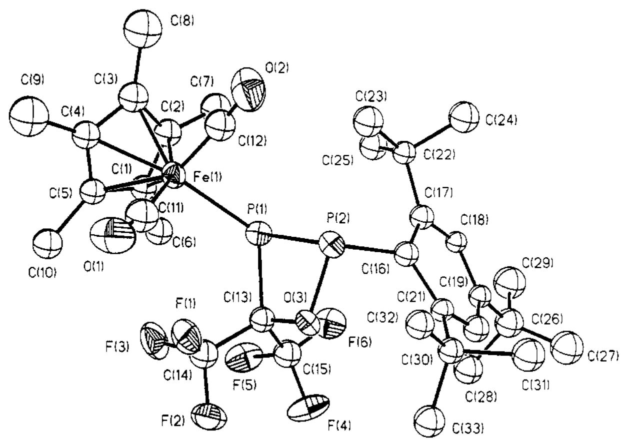


Figure 4. Molecular structure of **11a** in the crystal.

Table 7. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^3) of 11a

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	4432(1)	3024(2)	427(1)	33(1)
P(1)	3994(1)	1892(4)	–124(2)	30(1)
P(2)	3820(1)	2667(4)	–1410(2)	28(1)
F(1)	4450(1)	456(8)	–1267(4)	50(3)
F(2)	4261(2)	–1611(8)	–1357(4)	51(3)
F(3)	4446(2)	–744(8)	–174(4)	59(4)
F(4)	3708(2)	–1782(8)	–1316(4)	58(3)
F(5)	3902(2)	–1628(7)	–26(4)	54(3)
F(6)	3541(2)	–321(8)	–546(4)	49(3)
O(1)	4820(2)	2524(9)	–707(6)	67(5)
O(2)	4263(2)	5686(11)	–423(6)	65(5)
O(3)	3894(2)	917(8)	–1632(4)	26(3)
C(1)	4427(3)	1819(15)	1538(7)	35(3)
C(2)	4341(3)	3223(15)	1628(7)	40(4)
C(3)	4569(3)	4189(15)	1530(8)	44(4)
C(4)	4795(3)	3360(14)	1363(7)	37(4)
C(5)	4712(2)	1905(15)	1356(6)	33(3)
C(6)	4277(3)	498(13)	1669(7)	42(4)
C(7)	4062(3)	3685(14)	1878(7)	53(4)
C(8)	4569(3)	5806(14)	1632(8)	70(5)
C(9)	5094(3)	3863(15)	1279(8)	70(5)
C(10)	4905(3)	623(13)	1288(7)	45(4)
C(11)	4650(3)	2636(15)	–306(8)	48(4)
C(12)	4317(3)	4625(17)	–81(9)	43(4)
C(13)	3999(3)	292(14)	–857(7)	30(3)
C(14)	4285(3)	–426(16)	–909(9)	39(4)
C(15)	3782(3)	–888(16)	–702(9)	40(4)
C(16)	3417(2)	2464(13)	–1576(7)	30(3)
C(17)	3246(2)	2899(14)	–1002(6)	31(3)
C(18)	2987(2)	2166(12)	–991(6)	24(3)
C(19)	2880(3)	1121(13)	–1544(7)	28(3)
C(20)	3023(3)	920(13)	–2186(7)	35(4)
C(21)	3281(2)	1580(12)	–2248(7)	25(3)
C(22)	3316(3)	4144(13)	–391(7)	29(3)
C(23)	3586(3)	4980(13)	–448(7)	45(4)
C(24)	3070(3)	5250(13)	–661(7)	48(4)
C(25)	3323(2)	3673(13)	491(7)	44(4)
C(26)	2609(3)	196(15)	–1475(8)	47(4)
C(27)	2397(6)	164(35)	–2258(17)	62(10)
C(28)	2725(5)	–1357(27)	–1220(15)	51(10)
C(29)	2478(6)	630(30)	–752(16)	64(11)
C(27′)	2492(7)	–678(36)	–2277(18)	35(11)
C(28′)	2334(7)	1343(34)	–1530(19)	53(13)
C(29′)	2652(7)	–461(39)	–662(21)	62(13)
C(30)	3384(3)	1415(13)	–3079(7)	29(4)
C(31)	3121(2)	1882(14)	–3772(6)	46(4)
C(32)	3636(2)	2316(12)	–3222(6)	33(4)
C(33)	3437(3)	–171(13)	–3242(7)	42(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The exocyclic P–P bond lengths in **9a**, **10a**, and **10c** (2.014(5) Å; 2.016(2) Å; 2.009(3) Å) are comparable to the P–P bond in **7a** (2.027(3) Å). The bond lengths P(1)–O(2) [**9a**, 1.647(9) Å; **10a**, 1.649(4) Å; **10c**, 1.632(4) Å] are shorter

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Table 8. Selected Bond Lengths (Å) and Angles (deg) of 11a

Fe–P(1)	2.327(4)	P(1)–C(13)	1.927(13)
Fe–C(11)	1.779(15)	P(2)–O(3)	1.722(8)
Fe–C(12)	1.744(15)	O(3)–C(13)	1.409(13)
P(1)–P(2)	2.249(5)	O(1)–C(11)	1.139(18)
P(2)–C(16)	1.865(11)	O(2)–C(12)	1.144(18)

Fe–P(1)–P(2)	110.7(2)	O(3)–P(2)–C(16)	96.6(5)
Fe–P(1)–C(13)	118.5(4)	P(1)–Fe–C(11)	103.0(4)
P(1)–P(2)–C(16)	105.9(4)	P(1)–Fe–C(12)	92.0(5)
P(1)–C(13)–O(3)	102.2(8)	C(11)–Fe–C(12)	90.4(7)
P(2)–O(3)–C(13)	104.2(7)		

than the sum of the covalent single-bond radii for P (1.10 Å) and O (0.66 Å).[33]

In the complexes **9a** and **10a** the atoms P(2) and C(16) are located in the ring plane, as evidenced by the deviations of P(2) (0.07 Å) and C(16) (0.01 and 0.07 Å, respectively). In **10c**, the deviation of the ipso-carbon atom from the plane of the five-membered ring amounts to 0.174 Å. The *E* configuration of the educts **7a**,**8a**, and **8c** has been maintained throughout the cycloaddition. The internal ring distances C(12)–C(13) are conspicuously long [**9a**, 1.640(19) Å; **10a**, 1.633(7) Å; **10c**, 1.628(8) Å] as compared to the standard value of a C–C single bond (1.54 Å).

X-ray Structure Analysis of 11a. Red crystals of **11a** were obtained from crystallization experiments with pentane solutions of **9a** at −40 °C after a period of 4 weeks. The X-ray diffraction analysis (Figure 4 and Table 8) shows the presence of an essentially planar 1-oxa-2,3-diphosphetane (mean deviation from planarity 0.01 Å) which is linked to the (η^5-C_5Me_5)$(CO)_2$Fe fragment via an Fe–P single bond of 2.327(4) Å. The P–P bond of 2.249(5) Å reveals a bond order of unity.[34] In the four-membered ring the oxygen atom of the ketone is added to the arylated P atom [P(2)–O(3) = 1.722(8) Å]. In keeping with this, the $(CF_3)_2C$ fragment in **11a** is connected to the metalated phosphorus via a long P–C single bond [P(1)–C(13) = 1.927(13) Å], which is quite common for diphosphetane derivatives.[35,36]

Due to the longer distance P(1)–P(2) the bond angles at the phosphorus atoms are markedly more acute [C(13)–P(1)–P(2) = 72.3(4)°, P(1)–P(2)–O(3) = 81.3(3)°] as compared to the angles at carbon and oxygen (102.2(9) and 104.2(7)°, respectively). Like in **7a** and **9a** the P–P bond is *E* configurated.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, anisotropic displacement coefficients, and H-atom coordinates for **9a**, **10a**, **10c**, and **11a** (28 pages). Ordering information is given on any current masthead page.

OM940062W

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[34] The standard bond length of a P–P single bond amounts to 2.225 Å: Tebbe, K. F. *Z. Anorg. Allg. Chem.* **1980**, *468*, 202 and literature cited therein.

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