ture, a value of K_{eq} of 4 × 10^3 for reaction 7 is calculated. This, combined with the equilibrium ratio ($[E]/[Z]$) of 4.7 at −78 °C from NMR data, gives $[Z^+]/[E^+] = 9 \times 10^2$. Thus, while in the neutral molecule the *E* isomer is slightly (2.5 kJ) favored, in the oxidized species the *Z* isomer is favored by 11 kJ. This distribution of isomers in the 17e species is consistent with the observed exclusive product in oxidatively induced CO insertion reactions of the acyl product derived from the *Z* isomer and may have implications for other synthetic chemistry in these compounds.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this project (D. L.R.). We thank Dr. Janet C. Baxter and David G. Garza for the preparation of samples. R.H.P. gratefully acknowledges financial support from Deakin University.

Registry No. Z, 101052-83-9; E, 100946-25-6.

Transition-Metal-Substituted Diphosphenes. 16.[1] [1 + 4] Cycloaddition of a Diphosphene to α,β-Unsaturated Carbonyl Compounds: Synthesis of Dihydro-1,2-λ⁵-oxaphospholes with Exocyclic P=P Bonds and X-ray Structure Analysis of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P[OCH{=}CHC}H_2](=PAr)$ $(Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2)$

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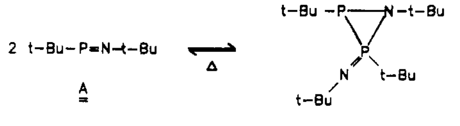
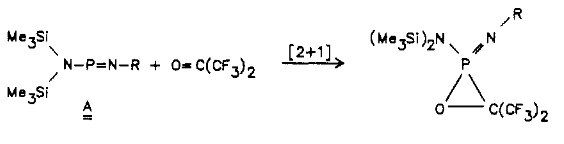
The reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr]$ ($Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) (**1a**) with acrolein (**2a**), methacrolein (**2b**), and buten-3-one-2 (**2c**) in benzene at 20 °C afforded the transition-metal-functionalized dihydro-1,2-λ⁵-oxaphospholes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P[OC(R^1){=}C(R^2)C}H_2](=PAr)$ (**3**) (**a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, $R^2 = CH_3$; **c**; $R^1 = CH_3$, $R^2 = H$) with exocyclic P=P double bonds. The treatment of **1a** with crotonaldehyde (**2d**) at ca. 50 °C during 10 days yielded only an equilibrium mixture of the expected cycloadduct **3d** and the starting materials. A similar product, **3e**, was obtained from the corresponding ruthenium diphosphenyl complex **1b**. The novel heterocycles were characterized by elemental analyses and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR, and mass spectroscopy). The molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P\text{-}(OCH{=}CHC}H_2){=}PAr$ was elucidated by a complete single-crystal diffraction study [$P2_1/n$ space group; $Z = 4$; a = 18.508 (4), b = 9.238 (3), c = 20.577 (5) Å; β = 99.71 (2)°].

Introduction

Low coordinated phosphorus compounds as phosphaalkenes $R^1P{=}CR^2R^3$, iminophosphanes $R^1P{=}NR^2$, and diphosphenes $R^1P{=}PR^2$ are potential candidates for ambident reactivity because they exhibit two high-lying molecular orbitals (π and n(P)) of similar energy.[2,3] Depending on the substitution pattern iminophosphanes tend to react in a carbene-like fashion documented in the [2 + 1] self-dimerization[4]

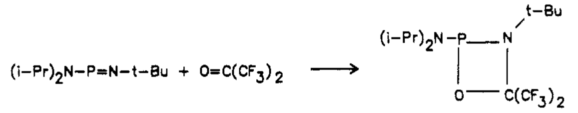


R = ArBu

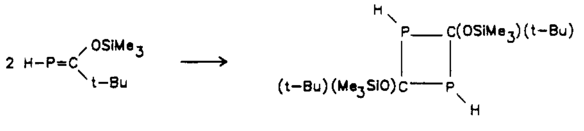


R = Me3Si or Bu

or in an olefinic manner as shown in the [2 + 2] cyclodimerization with hexafluoroacetone[5a]



or its [2 + 2] self-dimerization.[5b] The [2 + 2] cycloaddition is well-documented for kinetically stabilized phosphaalkenes.[6]



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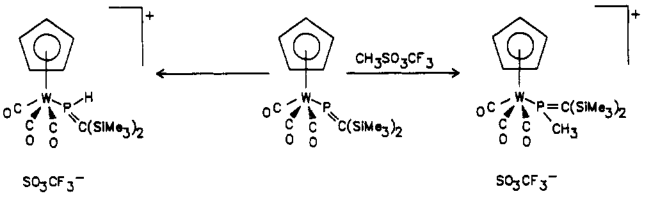
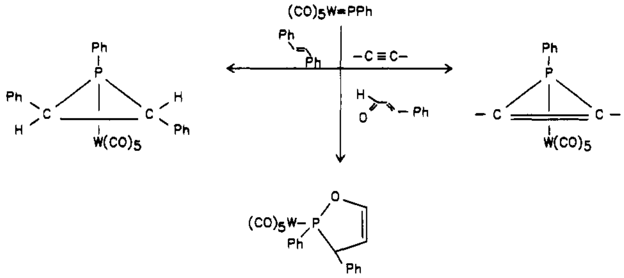
The introduction of an electron-releasing metal fragment at the phosphorus center raises the energy of the n(P) orbital considerably and thus renders a nucleophilic low coordinated P atom.[7]



The phosphinidene complex $(CO)_5W{=}PPh$ can also react in a "carbene-like" way with olefins and alkynes.[8] Furthermore the cheletropic [1 + 4] cycloaddition of this complex to cinnamaldehyde has been reported.[8]



Such behavior was previously unknown for diphosphenes. Instead these react in an "olefin-like" fashion with dienes, undergoing [2 + 4] cycloaddition.[9] We report here the cheletropic [1 + 4] cycloaddition of the transition-metal-substituted diphosphene 1 to the α,β-unsaturated carbonyls acrolein (**2a**), methacrolein (**2b**), buten-3-one-2 (**2c**), and crotonaldehyde (**2d**). Part of our results have been reported in a preliminary communication.[10]

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 Perkin-Elmer Model 597 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Varian XL 200 NMR spectrometer in C_6D_6 solution at ambient temperature. Electron-impact mass spectra were recorded on a Varian MAT 312 spectrometer.

Materials. The diphosphenyl complexes $(\eta^5\text{-}C_5Me_5)(CO)_2MP{=}PAr$ (Ar = 2,4,6-t-$Bu_3C_6H_2$, M = Fe, Ru)[11] were prepared as described in the literature, whereas acrolein, methacrolein, methyl vinyl ketone, and crotonaldehyde were purchased commercially. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds. $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P(OCH{=}CHC}H_2){=}PAr$ (3a). A solution (0.7 mL) containing 2 mL of freshly distilled acrolein in benzene (8 mL, 2.95 mmol) was added to a vigorously stirred solution of **1a** (1.50 g, 2.70 mmol) in benzene (10 mL) at 0 °C. The reaction mixture was then stirred for 2 h at 20 °C; the red-brown solution thereby turned deep violet. All volatiles were removed in vacuo, and the violet, oily residue was dissolved in pentane (20 mL). The solution was filtered, and the filter cake was extracted with pentane until the extracts were colorless. The filtrate and combined extracts were concentrated to ca. 10 mL and stored at −28 °C, resulting in the crystallization of 0.77 g (47%) of violet **3a**.

IR (pentane): 2018 (s), 1966 (s), 1929 (m) cm^{-1} [ν(CO)]. IR (Nujol): 2018 (sh), 2010 (vs), 1989 (w), 1962 (vs), 1943 (w), 1932 (w) cm^{-1} [ν(CO)]; 1612 (m), 1589 (w), 1019 (s) cm^{-1}. ^{1}H NMR: δ 1.38 (s, 9 H, p-t-Bu), 1.56 (s, 15 H, $C_5(CH_3)_5$), 1.86 (m, 1 H, CH_2), 1.92 (s, 9 H, o-t-Bu), 2.01 (s, 9 H, o-t-Bu), 2.36 (m, 1 H, CH_2), 4.73 (m, 1 H, $=CHCH_2$), 5.95 (dm, J_{PH} = 13 Hz, 1 H, $=CHO$), 7.47 (d, 2 H, $^4J_{PH}$ = 4.2 Hz, m-phenyl H); $^{13}C\{^1H\}$ NMR: δ 10.0 (d, $^3J_{PC}$ = 5.4 Hz, $C_5(CH_3)_5$), 31.7 (s, p-$C(CH_3)_3$), 33.0 (dd, $^1J_{PC}$ = 18.8, $^2J_{PC}$ = 4.9 Hz, CH_2), 33.8 (dd, J_{PC} = 10.8, 2.7 Hz, o-$C(CH_3)_3$), 34.8 (d, J_{PC} = 6.6 Hz, o-$C(CH_3)_3$), 34.8 (s, p-$C(CH_3)_3$), 39.0 (t, $^3J_{PC}$ = 1.9 Hz, o-$C(CH_3)_3$), 39.5 (t, $^3J_{PC}$ = 1.4 Hz, o-$C(CH_3)_3$), 98.2 (s, $C_5(CH_3)_5$), 103.7 (s, $CH_2CH{=}$), 119.7 (d, J_{PC} = 3.9 Hz, m-aryl-C), 121.0 (d, J_{PC} = 3.9 Hz, m-aryl-C), 138.5 (dd, J_{PC} = 82.0, 20.4 Hz, ipso-aryl-C), 143.6 (dd, J_{PC} = 7.0, 3.5 Hz, $OCH{=}$), 146.9 (d, J_{PC} = 4.5 Hz, p-aryl-C), 157.5 (d, J_{PC} = 9.9 Hz, o-aryl-C), 157.8 (d, J_{PC} = 8.4 Hz, o-aryl-C), 213.5 (dd, J_{PC} = 18.6, 4.8 Hz, FeCO), 215.5 (d, J_{PC} = 22.8 Hz, FeCO). $^{31}P\{^1H\}$ NMR δ 165.1 (d, $|^1J_{PP}|$ = 729.2 Hz, PFe), −28.4 (d, $|^1J_{PP}|$ = 729.2 Hz, P-aryl). MS/EI (70 eV, 70 °C): m/e 610 (M^+).

Anal. Calcd for $C_{33}H_{48}FeO_3P_2$ (610.5): C, 64.92; H, 7.93; Fe, 9.15. Found: C, 64.84; H, 7.88; Fe, 9.21.

$(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P(OCH{=}C(CH_3)C}H_2){=}PAr$ (3b). Analogously a solution of 1.12 g (2 mmol) of **1a** in 10 mL of benzene was reacted with 1.67 mL of a solution of methacrolein in benzene (1:9 v/v) to afford 0.41 g (35%) of dark violet **3b**.

IR (pentane): 2018 (vs), 1964 (vs) cm^{-1} [ν(CO)]. IR (Nujol): 2009 (vs), 1989 (w), 1961 (vs), 1931 (w) cm^{-1} [ν(CO)]; 1661 (w), 1587 (w), 1190 (m), 1031 (w), 823 (w), 726 (w) cm^{-1}. ^{1}H NMR: δ 1.38 (s, 12 H, p-t-Bu and $HC{=}CCH_3$), 1.57 (s, 15 H, $C_5(CH_3)_5$), 1.95 (s, 9 H, o-t-Bu), 2.04 (s, 9 H, o-t-Bu), 2.33 (m, 2 H, PCH_2), 5.75 (dm, J_{PH} = 12.5 Hz, 1 H, $HC{=}CCH_3$), 7.49 (s, 2 H, m-phenyl-H); $^{13}C\{^1H\}$ NMR: δ 9.9 (d, $^3J_{PC}$ = 5.4 Hz, $C_5(CH_3)_5$), 14.0 (d, $^3J_{PC}$ = 10.1 Hz, $HC{=}CCH_3$), 31.8 (s, p-$C(CH_3)_3$), 33.8 (dd, J_{PC} = 11.0, 2.8 Hz, o-$C(CH_3)_3$), 34.8 (s, p-$C(CH_3)_3$), 34.9 (d, J_{PC} = 6.9 Hz, o-$C(CH_3)_3$), 38.3 (dd, J_{PC} = 21.3, 4.6 Hz, PCH_2), 39.1 (t, J_{PC} = 1.9 Hz, o-$C(CH_3)_3$), 39.6 (s, o-$C(CH_3)_3$), 98.1 (s, $C_5(CH_3)_5$), 113.9 (d, J_{PC} = 3.4 Hz, $HC{=}CCH_3$), 119.6 (d, J_{PC} = 4.2 Hz, m-aryl-C), 120.9 (d, J_{PC} = 4.2 Hz, m-aryl-C), 137.9 (dd, J_{PC} = 8.6, 3.5 Hz, $OCH{=}$), 139.0 (dd, $^1J_{PC}$ = 81.9, $^2J_{PC}$ = 20.1 Hz, ipso-aryl-C), 146.8 (d, J_{PC} = 5.5 Hz, p-aryl-C), 157.6 (t, J_{PC} = 13.5 Hz, o-aryl-C), 157.7 (d, J_{PC} = 24.3 Hz, o-aryl-C), 213.5 (dd, J_{PC} = 16.8, 5.2 Hz, FeCO), 215.9 (d, J_{PC} = 22.6 Hz, FeCO). $^{31}P\{^1H\}$ NMR δ 166.8 (d, $|^1J_{PP}|$ = 727.6 Hz, PFe), −29.4 (d, $|^1J_{PC}|$ = 727.6 Hz, P-aryl). MS/EI (70 eV, 70 °C): m/e 624 (M^+).

Anal. Calcd for $C_{34}H_{50}FeO_3P_2$ (624.3): C, 65.38; H, 8.07; Fe, 8.94. Found: C, 65.03; H, 8.30; Fe, 8.70.

$(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P(OC(CH_3){=}CHC}H_2){=}PAr$ (3c). Analogously a solution of 1.12 g (2 mmol) of **1a** in 10 mL of benzene was allowed to react with 1.70 mL of a solution of buten-3-one-2 in benzene (1:9 v/v) during 2 h at 20 °C to give 0.61 g (49%) of microcrystalline dark violet **3c**.

IR (pentane): 2019 (vs), 1967 (vs) cm^{-1} [ν(CO)]. IR (Nujol): 2011 (vs), 1993 (sh), 1965 (vs), 1929 (w) cm^{-1} [ν(CO)]; 1664 (w), 1587 (w), 1255 (m), 677 (m) cm^{-1}. ^{1}H NMR: δ 1.38 (s, 9 H, p-t-Bu), 1.51 (m, 3 H, $C(CH_3){=}CH$), 1.58 (d, J_{PH} = 0.6 Hz, 15 H, $C_5(CH_3)_5$), 1.92 (s, 9 H, o-t-Bu), 1.99 (s, 9 H, o-t-Bu), 2.51 (m, 2 H, CH_2), 4.42 (dm, 1 H, J_{PH} = 25.5 Hz, $C(CH_3){=}CH$), 7.42 (m, 1 H, m-phenyl-H), 7.47 (m, 1 H, m-phenyl-H). $^{13}C\{H\}$ NMR: δ 10.1 (d, J_{PC} = 5.3 Hz, $C_5(CH_3)_5$), 16.3 (s, $C(CH_3){=}CH$), 31.7 (s, p-$C(CH_3)_3$), 33.8 (dd, J_{PC} = 10.1, 2.9 Hz, o-$C(CH_3)_3$), 34.7 (s, p-$C(CH_3)_3$), 34.9 (d, J_{PC} = 7.0 Hz, o-$C(CH_3)_3$), 35.4 (dd, J_{PC} = 19.0, 4.1 Hz, CH_2), 39.0 (t, J_{PC} = 1.7 Hz, o-$C(CH_3)_3$), 39.4 (t, J_{PC} = 1.7 Hz, o-$C(CH_3)_3$), 98.1 (s, $C_5(CH_3)_5$), 119.6 (d, J_{PC} = 3.8 Hz, m-aryl-C), 120.6 (d, J_{PC} = 3.8 Hz, m-aryl-H), 138.7 (dd, J_{PC} = 82.1, 20.5 Hz, ipso-aryl-C), 146.9 (d, J_{PC} = 4.9 Hz, p-aryl-C), 151.9 (dd, J_{PC} = 6.9, 3.5 Hz, $C(CH_3){=}CH$), 157.6 (dd, J_{PC} = 9.8, 2.4 Hz, o-aryl-C), 157.7 (d, J_{PC} = 17.6 Hz, o-aryl-C), 213.6 (dd, J_{PC} = 18.4, 4.4 Hz, FeCO),

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215.5 (d, J_{PC} = 22.8 Hz, FeCO). $^{31}P\{^1H\}$ NMR: δ 164.1 (d, $|^1J_{PP}|$ = 726.0 Hz, PFe), −26.8 (d, $|^1J_{PP}|$ = 726.0 Hz, P-aryl). MS/EI (70 eV, 70 °C): *m/e* 624 (M^+).

Anal. Calcd for $C_{34}H_{50}FeO_3P_2$ (624.3): C, 65.38; H, 8.07; Fe, 8.94. Found: C, 65.15; H, 8.19; Fe, 8.99.

(η^5-C_5Me_5)(CO)$_2$FeP(OCH=CHCH(CH$_3$))=PAr (3d). A solution of 1.11 g (2 mmol) of **1a** in 10 mL of benzene was reacted with 1.66 mL of a solution of crotonaldehyde in benzene (1:9 v/v) at 50–55 °C for 10 days. Analogous workup yielded 0.075 g (12%) of amorphous, dark violet **3d**.

IR (pentane): 2017 (vs), 1986 (w), 1966 (vs), 1937 (w) cm^{-1} [ν(CO)]. IR (Nujol): 2012 (vs), 1955 (vs), 1913 (w) cm^{-1} [ν(CO)]; 1603 (w), 1266 (w), 1159 (w), 1033 (w), 1014 (w), 806 (br, w), 749 (w), 639 (w), 606 (w), 583 (w) cm^{-1}. ^1H NMR: δ 1.16 (dd, J_{PH} = 18.2, $^3J_{HH}$ = 7.4 Hz, 3 H, CHCH$_3$), 1.37 (s, 9 H, *p*-C(CH$_3$)$_3$), 1.58 (s, 15 H, C$_5$(CH$_3$)$_5$), 1.95 (s, 9 H, *o*-C(CH$_3$)$_3$), 1.98 (s, 9 H, *o*-C(CH$_3$)$_3$), 4.71 (m, 1 H), 6.01 (m, 1 H, olefin H), 7.38 (m, 1 H, *m*-aryl-H), 7.44 (d, J_{PH} = 2.2 Hz, 1 H, *m*-aryl-H). $^{31}P\{^1H\}$ NMR: δ 192.8 (d, $|^1J_{PP}|$ = 733.1 Hz, PFe), −31.2 (d, $|^1J_{PP}|$ = 733.1 Hz, P-aryl). MS/EI (70 eV, 70 °C): *m/e* 624 (M^+).

Anal. Calcd for $C_{34}H_{50}FeO_3P_2$ (624.3): C, 65.38; H, 8.07; Fe, 8.94. Found: C, 65.44; H, 8.55; Fe, 8.80.

(η^5-C_5Me_5)(CO)$_2$RuP(OCH=CHCH$_2$)=PAr (3e). Analogous to the preparation of **3a**, the reaction of 1.21 g (2.0 mmol) of (η^5-C_5Me_5)(CO)$_2$RuP=PAr (**1b**) with 2.0 mmol of acrolein in 10 mL of benzene afforded 0.490 g (42%) of ruby-red crystalline **3e**.

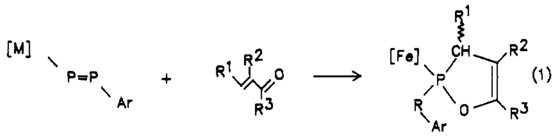
IR (pentane): 2033 (vs), 1977 (vs) cm^{-1} [ν(CO)]. IR (Nujol): 2023 (vs), 1972 (vs), 1940 (w), 1934 (w) cm^{-1} [ν(CO)]: 1611 (m), 1593 (w) cm^{-1} ν[C=C]: 1234 (w), 1193 (w), 1163 (w), 1064 (w), 1034 (sh), 1018 (s), 968 (w), 872 (w), 855 (w), 831 (w), 751 (w), 708 (m), 673 (m), 602 (m), 554 (m), 541 (m) cm^{-1}. ^1H NMR: δ 1.39 (s, 9 H, *p*-*t*-Bu), 1.68 (d, J_{PH} = 1.7 Hz, 15 H, C$_5$Me$_5$), 1.95 (s, 9 H, *o*-*t*-Bu), 2.01 (s, 9 H, *o*-*t*-Bu), 2.44 (m, 1 H, CH$_2$), 2.53 (m, 1 H, CH$_2$), 4.75 (m, 1 H, =C*H*CH$_2$), 5.95 (m, 1 H, OC*H*=), 7.48 (s, 1 H, *m*-aryl-H), 7.50 (t, J_{PH} = 1.1 Hz, 1 H, *m*-aryl-H). $^{13}C\{^1H\}$ NMR: δ 10.3 (d, J_{PC} = 4.6 Hz, C$_5$(*C*H$_3$)$_5$), 31.7 (s, *p*-C(*C*H$_3$)$_3$), 33.2 (dd, J_{PC} = 19.3, 4.8 Hz, CH$_2$), 33.9 (d, J_{PC} = 10 Hz, *o*-C(*C*H$_3$)$_3$), 31.0 (s, *p*-*C*(CH$_3$)$_3$), 34.8 (d, J_{PC} = 6.3 Hz, *o*-C(*C*H$_3$)$_3$), 39.0 (s, *o*-*C*(CH$_3$)$_3$), 39.5 (s, *o*-*C*(CH$_3$)$_3$), 101.7 (s, *C*$_5$(CH$_3$)$_5$), 103.3 (s, CH$_2$=*C*H=), 119.7 (d, J_{PC} = 4.0 Hz, *m*-aryl-C), 120.9 (d, J_{PC} = 4.2 Hz, *m*-aryl-C), 138.5 (dd, J_{PC} = 80.5, 19.1 Hz, ipso-aryl-C), 143.3 (dd, J_{PC} = 6.8, 3.5 Hz, O*C*H=), 146.8 (d, J_{PC} = 4.2 Hz, *p*-aryl-C), 157.7 (dd, J_{PC} = 14.5, 4.4 Hz, *o*-aryl-C), 199.3 (m, RuCO), 201.5 (d, J_{PC} = 13.5, RuCO). $^{31}P\{^1H\}$ NMR: δ 145.2 (d, $|^1J_{PP}|$ = 714.4 Hz, PRu), −45.1 (d, $|^1J_{PP}|$ = 714.4 Hz, P-aryl). MS/EI (70eV, 70 °C): *m/e* 656 (M^+).

Anal. Calcd for $C_{33}H_{48}O_3P_2Ru$ (655.8): C, 60.44; H, 7.38; Found C, 60.61; H, 7.60.

X-ray Structure Determination of (η^5-C_5Me_5)(CO)$_2$FeP[OCH=CHCH$_2$](=PAr) (3a). Crystals of **3a** were grown from *n*-pentane at 5 °C; one with the approximate dimensions 0.28 × 0.23 × 0.17 mm^3 was selected and sealed under nitrogen in a capillary. The cell dimensions were determined on a Nicolet R3 diffractometer with Mo Kα radiation with the angle settings of 25 centered reflections: a = 18.508 (4) Å, b = 9.238 (3) Å, c = 20.577 (5) Å, α = 90°, β = 99.71 (2)°, γ = 90°; V = 3467.9 (14) Å^3; Z = 4; d_{calcd} = 1.1782 g/cm^3; μ = 5.6 cm^{-1}; space group $P2_1/n$. The data collection was taken at room temperature with $2\theta_{max}$ = 45°, resulting in 5248 independent intensities, 3017 of them were regarded as observed ($F_o \geq 3.5\sigma(F)$) and used for structure solution with direct methods and refinement with block-cascade least squares in SHELXTL.[12] The atomic scattering factors were taken from Cromer and Mann.[13] Refinement with 401 parameters converged at R = 0.062 and R_w = 0.058 ($w^{-1} = \sigma^2(F_o) + 0.0029(F_o)$), using rigid groups for hydrogen atoms (C–H = 0.96 Å, H–C–H = 109.5°) and the 1.2-fold isotropic U of the equivalent U_{ij} of the attached carbon atoms. Hydrogen atoms at the phenyl group were located from a difference Fourier map and refined without constraints with an unique isotropic U value. The maximum residual electron density based on the final model was 0.36 e/Å^3.

Results and Discussion

The diphosphenyl complex (η^5-C_5Me_5)(CO)$_2$FeP=PAr (Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) (**1a**) smoothly reacts with equimolar amounts of acrolein (**2a**), methacrolein (**2b**), and buten-3-one-2 (**2c**) in benzene at ambient temperature to give the dark violet microcrystalline dihydro-1,2-λ^5-oxaphospholes **3a–c** in 35–49% yield. Usually the reaction is completed within 2 h. With crotonaldehyde (**2d**) and **1a** no reaction is observed at 20 °C. When the mixture is heated at ca. 50 °C, a sluggish reaction leads to an equilibrium mixture of the desired heterocycle **3d** and **1a**. Workup after 10 days furnishes **3d** in about 12% isolated yield. Prolonged heating resulted in the decomposition of **3d** and **1a**. Similar to the preparation of **3a** the reaction of (η^5-C_5Me_5)(CO)$_2$RuP=PAr (**1b**) with **2a** gave the cyclo adduct **3e** in 42% yield.



1 2 3

[M] = (η^5-C_5Me_5)(CO)$_2$Fe (1a) Ar = 2, 4, 6-t-Bu$_3$C$_6$H$_2$

[M] = (η^5-C_5Me_5)(CO)$_2$Ru (1b)

2, 3	R^1	R^2	R^3
a	H	H	H
b	H	CH$_3$	H
c	H	H	CH$_3$
d	CH$_3$	H	H
e	H	H	H

The course of the reaction is conveniently monitored by ^{31}P NMR spectroscopy. The two low-field doublets of the starting material are shifted strongly upfield on cyclization. Possible intermediates of the reaction could not be detected. Compounds **3a–e** are stable at 20 °C under N$_2$ atmosphere. The products **3a–e** were initially characterized by elemental analyses and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR, MS). Mass spectra (EI) revealed the monomeric nature of the compounds in the gas phase. As briefly mentioned above the cyclization results in a significant upfield shift of the ^{31}P NMR resonances of **1a,b** ($\Delta\delta$ (P^1) = 522.4–551.1; $\Delta\delta$(P^2) = 580.3–596.7 ppm). The increase of the coupling constant $^1J_{P1P2}$ from 594.2 (**1a**) and 597.1 (**1b**) to 714.7–733.1 Hz is in agreement with the presence of P=P double bonds in **3a–e**, but its ylidic character is indicated by the marked high-field shift of P^2 (δ −26.8 to −45.1 ppm). Consequently P^1 can also be regarded as a phosphonium center (formula B). Regitz and co-worker recently reported phosphoranylidene phosphines such as mesityl-P=P(*t*-Bu)$_2$(OSiMe$_3$) and mesityl-P=P(OSiMe$_3$)[CMe$_2$CH(Me)CMe$_2$] with coupling constants $^1J_{PP}$ = 429 and 433 Hz.[14]

A B

The presence of an olefinic double bond is evident from multiplet resonances in the ^1H NMR spectra at δ 4.73, 5.95

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Table I. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Factors (Å^2 × 10^3)

	x	y	z	U_{eq}^{a}
Fe	8426 (1)	1865 (1)	399 (1)	55 (1)
P(1)	8951 (1)	1494 (2)	1452 (1)	59 (1)
P(2)	9715 (1)	3084 (2)	1774 (1)	58 (1)
O(1)	9823 (2)	1665 (5)	−49 (2)	91 (2)
O(2)	7991 (3)	−1143 (5)	242 (2)	113 (2)
O(3)	8246 (2)	1273 (7)	1883 (2)	99 (2)
C(1)	9289 (3)	1720 (6)	157 (3)	65 (2)
C(2)	8182 (3)	34 (7)	321 (3)	72 (3)
C(3)	8207 (4)	−178 (10)	2054 (3)	124 (4)
C(4)	8690 (5)	−1057 (9)	1921 (4)	126 (4)
C(5)	9277 (3)	−386 (7)	1635 (3)	84 (3)
C(6)	10216 (3)	2213 (5)	2530 (2)	48 (2)
C(7)	10858 (3)	1376 (6)	2501 (2)	47 (2)
C(8)	11064 (3)	318 (6)	2958 (3)	53 (2)
C(9)	10693 (3)	23 (6)	3482 (3)	56 (2)
C(10)	10156 (3)	999 (6)	3561 (3)	63 (2)
C(11)	9926 (3)	2127 (6)	3127 (2)	51 (2)
C(12)	11355 (3)	1617 (6)	1970 (3)	60 (2)
C(13)	11067 (3)	867 (9)	1328 (3)	101 (3)
C(14)	12133 (3)	1028 (9)	2208 (3)	100 (3)
C(15)	11448 (4)	3237 (7)	1847 (4)	106 (3)
C(16)	10893 (3)	−1254 (7)	3940 (3)	81 (3)
C(17)	10249 (5)	−1852 (9)	4188 (4)	163 (5)
C(18)	11195 (8)	−2443 (11)	3630 (7)	316 (10)
C(19)	11383 (8)	−756 (13)	4523 (7)	382 (10)
C(20)	9408 (3)	3235 (7)	3387 (3)	69 (2)
C(21)	9773 (4)	3734 (8)	4072 (3)	99 (3)
C(22)	9244 (5)	4608 (8)	3000 (4)	120 (4)
C(23)	8676 (3)	2509 (9)	3454 (4)	123 (4)
C(24)	8087 (3)	3283 (6)	−395 (2)	69 (3)
C(25)	8320	4112	185	69 (3)^b
C(26)	7868	3735	655	80 (3)^b
C(27)	7356	2674	365	84 (3)^b
C(28)	7491	2395	−284	75 (3)^b
C(29)	8376 (4)	3409 (8)	−1035 (3)	105 (3)
C(30)	8905 (4)	5262 (7)	258 (4)	108 (4)
C(31)	7850 (5)	4551 (9)	1284 (3)	131 (4)
C(32)	6742 (3)	2005 (11)	667 (5)	148 (5)
C(33)	7039 (4)	1493 (8)	−807 (4)	108 (4)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b} Atoms in rigid groups have standard deviations only for the pivot atom.

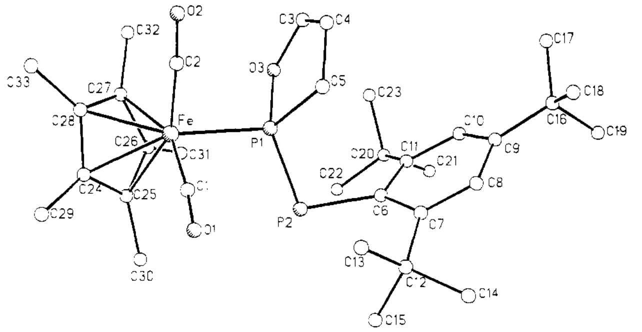

Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P}$-$(OCH{=}CHCH_2)$(=PAr) (**3a**).

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) of 3a

	Bond Lengths		
Fe–P(1)	2.243 (2)	P(1)–O(3)	1.703 (5)
Fe–C(1)	1.750 (6)	P(1)–C(5)	1.852 (7)
Fe–C(2)	1.747 (6)	P(2)–C(6)	1.850 (5)
Fe–C(24)	2.101 (4)	O(1)–C(1)	1.139 (7)
Fe–C(25)	2.119 (5)	O(2)–C(2)	1.143 (8)
Fe–C(26)	2.119 (5)	O(3)–C(3)	1.388 (11)
Fe–C(27)	2.102 (5)	C(3)–C(4)	1.268 (12)
Fe–C(28)	2.090 (4)	C(4)–C(5)	1.455 (11)
P(1)–P(2)	2.064 (2)	Cp^a–Fe	1.726
	Bond Angles		
P(1)–Fe–C(1)	89.7 (2)	Fe–C(1)–O(1)	174.4 (5)
P(1)–Fe–C(2)	90.2 (2)	Fe–C(2)–O(2)	176.1 (5)
C(1)–Fe–C(2)	97.7 (3)	O(3)–C(3)–C(4)	119.6 (7)
Fe–P(1)–P(2)	111.2 (1)	C(3)–C(4)–C(5)	114.4 (7)
Fe–P(1)–O(3)	105.9 (2)	P(1)–C(5)–C(4)	103.9 (5)
P(2)–P(1)–O(3)	117.4 (2)	P(2)–C(6)–C(7)	120.1 (4)
Fe–P(1)–C(5)	114.2 (2)	P(2)–C(6)–C(11)	122.7 (4)
P(2)–P(1)–C(5)	114.7 (2)	Cp^a–Fe–P(1)	126.6
O(3)–P(1)–C(5)	92.0 (3)	Cp^a–Fe–C(1)	121.3
P(1)–P(2)–C(6)	100.3 (2)	Cp^a–Fe–C(2)	122.3
P(1)–O(3)–C(3)	108.8 (5)		

^{a} Centroid of cyclopentadienyl ring.

(**3a**), 5.75 (**3b**), 4.42 (**3c**), 4.71, 6.01 (**3d**), and 4.75, 5.95 (**3e**), respectively. The carbon atoms of the olefinic entity give rise to absorptions in the ^{13}C NMR spectra at δ 103.7 (s), 143.6 (dd, J_{PC} = 7.0, 3.5 Hz), (**3a**), δ 113.9 (d, J_{PC} = 3.4 Hz), 137.9 (dd, J_{PC} = 8.6, 3.5 Hz), (**3b**), and 103.3 (s), 143.3 (dd, J_{PC} = 6.8, 3.5 Hz), (**3e**), respectively. The methylene carbon atoms of the heterocycles are observed in the range of δ 33.0–38.3 as doublet of doublets due to the coupling to both phosphorus nuclei. Complexes **3a–d** display two intense [ν(CO)] bands for the $Fe(CO)_2$ groups at 2018 ± 1 and 1966 ± 1 cm^{-1} in the IR spectra (pentane). The corresponding ν(CO) absorptions in **3e** are observed at 2033 and 1977 cm^{-1}.

X-ray Structure Analysis of 3a. The X-ray structure analysis of **3a** fully confirms the conclusions derived from analyses and spectroscopic data. The result of the structural determinations are shown in Figure 1. Positional parameters for the complex are given in Table I, and derived distances and angles are presented in Tables II and III, respectively. The analysis shows the presence of a dihydrooxaphosphole ring linked to the metal through a Fe–P single bond [2.243 (2) Å]. This distance is comparable with the Fe–P bond length in **1a** [2.260 (1) Å].[11] Usually Fe–P bond distances in low-valent carbonyliron complexes fall in the range of 2.15–2.35 Å.[15] The ligand could be regarded as one leg in a slightly distorted three-legged piano-stool arrangement. The three angles the ligands form with the metal center are (P(1)–Fe–C(1) = 89.7 (2)°; C(1)–Fe–C(2) = 97.7 (3)°; P(1)–Fe–C(2) = 90.2 (2)°).

Two legs of the piano stool are represented by terminal, nearly linear, carbonyl groups. The most interesting structural feature of **3a** is the geometry of the dihydrooxaphosphole ligand containing an exocyclic P=P bond, which is attached to the iron via the tetracoordinate phosphorus atom P(1). The P1–P2-bond length in **3a** [2.064 (2) Å] is significantly longer than that in **1a** [2.027 (1) Å]. The phosphorus atom P1 has the geometry of a distorted tetrahedron as evidenced by bond angles ranging from 92.0 (3) to 117.4 (2)^0 and thus may be regarded formally as a phosphonium center. The P–O bond distance in the ring (1.703 (5) Å) is shorter than the sum of the covalent single bond radii for P (1.10 Å) and O (0.66 Å).[16] P–O distances in P–O–C bonds of tetrahedral phosphorus compounds range from 1.56 to 1.64 Å.[17] For instance for $(CH_3O)Ph_2P{=}S$ a P—O bond length of 1.60 ± 0.2 Å is reported.[18] The endocyclic and exocyclic P–C distances

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Table III. Anisotropic Atomic Displacement Factors (Å^2 × 10^3)[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	46 (1)	60 (1)	57 (1)	7 (1)	6 (1)	1 (1)
P(1)	48 (1)	73 (1)	58 (1)	9 (1)	11 (1)	-3 (1)
P(2)	52 (1)	62 (1)	57 (1)	6 (1)	6 (1)	1 (1)
O(1)	63 (3)	135 (4)	79 (3)	11 (3)	24 (2)	18 (3)
O(2)	136 (4)	77 (3)	115 (4)	4 (3)	-9 (3)	-28 (3)
O(3)	67 (3)	159 (5)	76 (3)	15 (3)	27 (2)	-21 (3)
C(1)	54 (3)	82 (5)	60 (4)	6 (4)	9 (3)	14 (3)
C(2)	72 (4)	82 (5)	57 (4)	4 (4)	-4 (3)	-6 (4)
C(3)	111 (6)	179 (9)	85 (5)	15 (6)	28 (5)	-77 (6)
C(4)	170 (8)	107 (6)	100 (6)	32 (5)	17 (6)	-64 (6)
C(5)	91 (5)	71 (5)	82 (5)	20 (4)	-4 (4)	-11 (4)
C(7)	37 (3)	61 (4)	42 (3)	-2 (3)	10 (3)	-4 (3)
C(8)	44 (3)	59 (4)	61 (4)	7 (3)	18 (3)	8 (3)
C(9)	47 (3)	62 (4)	62 (4)	12 (3)	18 (3)	3 (3)
C(10)	56 (4)	78 (4)	60 (4)	10 (3)	27 (3)	5 (3)
C(11)	47 (3)	57 (4)	49 (3)	1 (3)	11 (3)	6 (3)
C(6)	44 (3)	50 (4)	50 (3)	2 (3)	11 (3)	-11 (3)
C(12)	35 (3)	97 (5)	51 (3)	14 (3)	14 (3)	0 (3)
C(14)	46 (4)	176 (7)	84 (5)	42 (5)	29 (4)	10 (5)
C(15)	77 (5)	116 (6)	135 (6)	49 (6)	46 (4)	-15 (5)
C(16)	65 (4)	87 (5)	96 (5)	43 (4)	24 (4)	6 (4)
C(17)	165 (8)	132 (8)	223 (11)	110 (8)	124 (8)	39 (7)
C(18)	447 (19)	185 (11)	419 (18)	216 (12)	373 (17)	228 (12)
C(19)	452 (21)	200 (12)	357 (18)	212 (13)	-327 (16)	-189 (13)
C(20)	69 (4)	80 (5)	59 (4)	-5 (4)	13 (3)	11 (4)
C(21)	105 (6)	117 (6)	75 (5)	-25 (5)	12 (4)	30 (5)
C(22)	170 (8)	102 (6)	96 (6)	0 (5)	41 (6)	70 (6)
C(23)	73 (5)	134 (7)	173 (8)	-45 (6)	57 (5)	5 (5)
C(24)	73 (4)	62 (4)	69 (4)	16 (4)	7 (4)	7 (4)
C(25)	63 (4)	58 (4)	81 (5)	-1 (4)	-5 (4)	5 (4)
C(26)	64 (4)	98 (6)	75 (5)	-4 (4)	5 (4)	33 (4)
C(27)	50 (4)	120 (6)	81 (5)	12 (5)	9 (4)	15 (4)
C(28)	58 (4)	79 (5)	83 (5)	2 (4)	-7 (4)	-1 (4)
C(29)	116 (6)	121 (7)	74 (5)	36 (5)	7 (4)	3 (5)
C(30)	108 (6)	64 (5)	137 (7)	16 (5)	-23 (5)	-5 (4)
C(31)	127 (7)	156 (8)	103 (6)	-42 (6)	-3 (5)	75 (6)
C(32)	58 (5)	226 (10)	164 (8)	63 (8)	33 (5)	-2 (6)
C(33)	78 (5)	121 (7)	107 (6)	-6 (5)	-36 (4)	0 (5)

[a] The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.

of 1.852 (7) and 1.850 (5) Å are normal for such single bonds. The dihydrooxaphosphole ring is slightly tilted along the axis O(3)–C(5) (the dihedral angle is 169.7°). The heterocycle is oriented nearly orthogonally with respect to the (the defined by Fe, P1, and P2 (the interplanar angle is 94.5°). In the starting material **1a** the atoms Fe, P1, P2, and C6 are arranged in the same plane. This is no longer true for **3a** where C6 deviates out of the plane of the remaining atoms by 0.485 Å toward ring atom C5 (torsion angle Fe–P1–P2–C6 = 164.6°).

Conclusion

In P_2H_2 the n^+- and π-orbitals are of comparable energy.[3] The introduction of an electron-releasing and highly nucleophilic transition-metal fragment obviously raises the energy level of the n_+-orbital relative to the π-MO markedly, making "carbene-like" reactions feasible. The oxidation potential of **1a** (in THF vs SCE) is only $E_{ox.} = +0.45$ V,[19] whereas for $[(Me_3Si)_3CP]_2$ the potential $E_{ox.} = +1.14$ V (in CH_3CN vs SCE) was reported.[20] Thus the reaction of diphosphenyl complex **1a** with the α,β-unsaturated carbonyls **2a–d** can be interpreted as a cheletropic [1 + 4] cycloaddition. The small coefficients at the β-carbon atom in the HOMO and LUMO of crotonaldehyde[21] as well as steric hindrance by the methyl group may explain the sluggish formation of **3d** as compared to **3a–c**. From our data we can of course not exclude the initial formation of a carbonyl-substituted phosphirane followed by a very rapid rearrangement into the corresponding dihydrooxaphospholes. Such a carbonyl-substituted phosphirane has been reported from the reaction of the reactive phosphinidene complex $[(CO)_5W{=}PPh]$ with methyl methacrylate.[8]

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Supplementary Material Available: Tables of crystal data, bond distances, bond angles, atomic coordinates, and anisotropic thermal parameters and the molecular structure of **3a** (9 pages); a listing of structure factors (19 pages). Ordering information is given on any current masthead page.

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