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Transition Metal Substituted Acyl Phosphanes and Phosphaalkenes. 28.[1] Reactivity of Metallophosphaalkenes $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CR^1_2$ (R^1 = $SiMe_3$, NMe_2) toward Methyl and Ethyl Propiolate

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The metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ (**1**) undergoes reaction with 2 equiv of alkyl propiolates $HC{\equiv}CCO_2R^2$ (R^2 = Me, Et) to afford the novel bicyclic *P*-metalloylides $\eta^5\text{-}C_5Me_4CH_2CHC(CH{=}CHCO_2R^2){=}C(CO_2R^2)OP[{=}C(SiMe_3)_2]Fe(CO)_2$ [R^2 = Me (**8c**), Et (**8d**)]. In contrast to this, metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2$ (**2**) smoothly adds 3 equiv of the propiolates with formation of the spirobicyclic compounds $(\eta^5\text{-}C_5Me_5)(CO)FeP[CH{=}C(CO_2R^2)C(NMe_2)_2C(CO_2R^2){=}CH]CH{=}C(CO_2R^2)C{=}O$ [R^2 = Me (**10c**), Et (**10d**)]. Treatment of equivalent amounts of methyl propiolate and **2** gave a mixture of *P*-metallo-1-phosphabutadiene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}CHC(CO_2Me){=}C(NMe_2)_2$ (**6c**) and metalloheterocycle $(\eta^5\text{-}C_5Me_5)(CO)FeP[{=}C(NMe_2)_2]CH{=}CH(CO_2Me)C{=}O$ (**5c**). The molecular structure of **8c** was determined by single-crystal X-ray diffraction.

Introduction

Electron-deficient alkynes are valuable and versatile synthons in the organic[2] as well as organometallic chemistry[3] of phosphorus. Recently we studied the reactivity of ferriophosphaalkenes $Cp^*(CO)_2FeP{=}C(SiMe_3)_2$ (**1**)[4] and $Cp^*(CO)_2FeP{=}C(NMe_2)_2$ (**2**)[5] toward electrophilic alkynes. The treatment of **1** with dimethyl acetylenedicarboxylate (**3a**) afforded the five-membered metalloheterocycle 4,[6] which parallels the cycloadditions observed between the alkyne and metallophosphanes,[3a] metallodiphosphenes,[7] or *P*-metallophospholes.[3b] Surprisingly, **2**, upon reaction with **3a**, was converted to *P*-metallo-1-phosphabutadiene **6a**[7] as the main product. Reaction of **2** with methyl butynoate (**3b**) in diethyl ether led to the formation of 2-methylene-1,2-dihydrophosphete 7,[7] whereas **1** remained unaffected by this alkyne (Scheme 1). Clearly, the mode of reaction between metallophosphaalkenes and electron-deficient alkynes is highly governed by the nature of the substituents in both reactants. For a better understanding of these processes we decided to extend our investigation to other alkynes.

Experimental Section

General Experimental Considerations. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Mattson Polaris (FT-IR)/Atari 1040 STF spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were taken in C_6D_6 on Bruker AC 100 (^1H, 100.131 MHz; ^{13}C, 25.180 MHz; ^{31}P, 40.532 MHz), Bruker AM 300 (^1H, 300.1; ^{13}C, 75.5; ^{31}P, 121.7 MHz), and Bruker AC 250 P (^1H, 250.13; ^{13}C, 62.90 MHz) instruments. Spectral standards were $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on varian MAT CH5-DF (70 eV, T = 250 °C) and Finnigan MAT 711 (80 eV) spectrometers.

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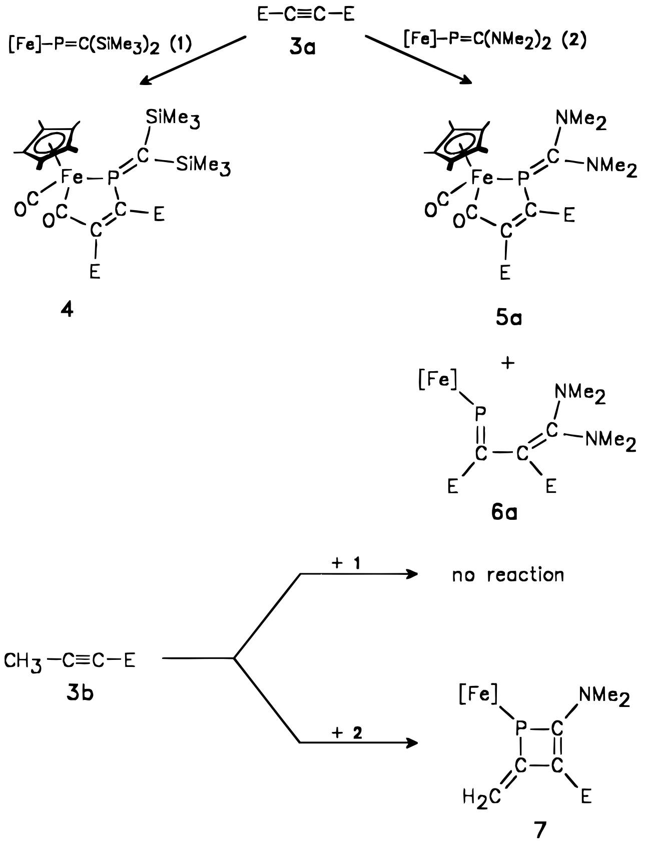
Scheme 1



E = CO_2Me; [Fe] = $Cp^*(CO)_2Fe$

Materials. The complexes (η^5-C_5Me_5)$(CO)_2FeP{=}C(SiMe_3)_2$ (**1**)[4] and (η^5-C_5Me_5)$(CO)_2FeP{=}C(NMe_2)_2$ (**2**)[5] were prepared as described. Methyl and ethyl propiolate were purchased commercially (Aldrich) and used without further purification. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds. η^5-$C_5Me_4CH_2CH{-}C(CH{=}CHCO_2Me){=}C(CO_2Me)O{-}P[{=}C(SiMe_3)_2]Fe(CO)_2$ (8c). A sample of 0.34 g (4.04 mmol) of methyl propiolate (**3c**) was added to a solution of 0.88 g (2.02 mmol) of **1** in 50 mL of *n*-pentane at 20 °C. After 10 min of stirring, all volatiles were removed in vacuo. The residue was extracted with *n*-pentane (4 × 10 mL), and the combined and filtered extracts were stored at −30 °C to afford 0.57 g (48%) of **8c** as a red-brown solid. IR (KBr, cm^{-1}) ν: 2011 s; 1957 s [$\nu(CO)_{term}$], 1740 m, 1712 m [$\nu(CO)_{ester}$], 1595 w [ν(C=C)], 1436 w, 1386 w, 1248 m [$\delta(SiMe_3)$], 1168 w, 1116 w, 1073 w, 842 m [$\varrho(SiMe_3)$], 757 w, 638 w, 595 w, 577 w. ^1H NMR δ: 0.48 (s, 18H, $SiCH_3$), 1.05 (d, $^4J_{PH}$ = 1.3 Hz, 3H, C_5CH_3), 1.08 (s, 3H, C_5CH_3), 1.33 (d, $^4J_{PH}$ = 0.9 Hz, 3H, C_5CH_3), 1.54 (d, $^4J_{PH}$ = 0.6 Hz, 3H, C_5CH_3), 1.95 (ddd, $^2J_{H(A)H(B)}$ = 13.9 Hz, $^3J_{PH(B)}$ = 24.0 Hz, $^3J_{H(B)H(C)}$ = 2.3 Hz, 1H, H_B), 2.15 (dt, $^2J_{H(A)H(B)}$ = 13.9 Hz, $^3J_{H(A)H(C)} \approx {}^3J_{PH(A)}$ = 9.3 Hz, 1H, H_A), 3.36 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 5.29 (ddd, $^3J_{H(A)H(C)} = {}^3J_{PH(C)}$ = 9.3 Hz, $^3J_{H(B)H(C)}$ = 2.3 Hz, 1H, H_c), 5.70 (d, $^3J_{HH}$ = 15.5 Hz, 1H, $1H_E$), 8.36 (d, $^3J_{HH}$ = 15.5 Hz, 1H, H_D). $^{13}C\{^1H\}$ NMR δ: 6.08 [s, $Si(CH_3)_3$], 6.12 [s, $Si(CH_3)_3$], 9.0 (s, C_5CH_3), 9.2 (s, C_5CH_3), 9.3 (s, C_5CH_3), 9.4 (s, C_5CH_3), 23.5 (d, $^2J_{PC}$ = 7.6 Hz, C_5CH_2), 50.7 (s, OCH_3), 55.2 (s, OCH_3), 58.1 (d, $^1J_{PC}$ = 8.7 Hz, P=C), 74.5 (d, $^1J_{PC}$ = 21.7 Hz, PCH), 90.0 (s, C_5Me_4), 92.3 (s, C_5Me_4), 95.5 (d, $^2J_{PC}$ = 3 Hz, C_5Me_4), 98.1 (d, $^2J_{PC}$ = 4 Hz, C_5Me_4), 106.9 (s, C-18), 126.3 (d, $^2J_{PC}$ = 15.4 Hz, C-14), 138.9 (d, $^3J_{PC}$ = 7.2 Hz, C-17), 161.9 (s, C-15), 168.1 (s, C-19), 213.1 (d, $^2J_{PC}$ = 23.2 Hz, FeCO), 216.1 (d, $^2J_{PC}$ = 24.4 Hz, FeCO). $^{31}P\{^1H\}$ NMR δ: 184.5 s. MS/EI: *m*/*z* = 520 (M^+), 492 ($M^+ - CO$), 464 ($M^+ - 2CO$). Anal. Calcd for $C_{23}H_{37}FeO_3PSi_2$ (520.53): C, 53.08; H, 7.11; Fe 10.73. Found: C, 53.02; H, 7.08; Fe, 10.69.

η^5-$C_5Me_4CH_2CH{-}C(CH{=}CHCO_2Et){=}C(CO_2Et)OP[{=}C(SiMe_3)_2]Fe(CO)_2$ (8d). Analogously, 0.65 g (56%) of ruby crystalline **8d** resulted from the reaction of 0.80 g (1.83 mmol) of **1** and 0.36 g (3.66 mmol) of **3d** in 50 mL of *n*-pentane. IR (KBr, cm^{-1}) ν: 2010 s, 1954 s [$\nu(CO)_{term}$], 1738 m, 1705 m [$\nu(CO)_{ester}$], 1592 w [ν(C=C)], 1466 w, 1386 w, 1375 w, 1247 m [$\delta(SiMe_3)$], 1179 w, 1112 w, 1030 w, 913 w, 842 m [$\rho(SiMe_3)$], 757 w, 639 w, 595 w, 580 w. ^1H NMR δ: 0.48 (s, 18H, $SiCH_3$), 0.94 (t, $^3J_{PH}$ = 7.0 Hz, 6H, CH_2CH_3), 1.06 (d, $^4J_{PH}$ = 1.5 Hz, 3H, C_5CH_3), 1.09 (s, 3H, C_5CH_3), 1.38 (d, $^4J_{PH}$ = 1.2 Hz, 3H, C_5CH_3), 1.56 (d, $^4J_{PH}$ = 0.9 Hz, 3H, C_5CH_3), 2.04 (m, 1H, C_5CH_2), 2.15 (m, 1H, C_5CH_2), 3.96 (q, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2CH_3), 4.21 (q, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2CH_3), 5.33 (m, 1H, H_c), 5.73 (d, $^3J_{HH}$ = 15.6 Hz, 1H, H_E), 8.43 (d, $^3J_{HH}$ = 15.6 Hz, 1H, H_D). $^{13}C\{^1H\}$ NMR δ: 6.1 [s, $Si(CH_3)_3$], 6.2 [s, $Si(CH_3)_3$], 9.0 (s, C_5CH_3), 9.3 (s, C_5CH_3), 9.4 (s, C_5CH_3), 14.6 (s, CH_2CH_3), 14.9 (s, CH_2CH_3), 23.7 (d, $^2J_{PC}$ = 7.4 Hz, C_5CH_2), 58.4 (d, $^1J_{PC}$ = 8.2 Hz, P=C), 59.5 (s, OCH_2), 65.0 (s, OCH_2), 74.3 (d, $^1J_{PC}$ = 22.5 Hz, PCH), 90.0 (d, $^2J_{PC}$ = 2.5 Hz, C_5Me_4), 92.3 (d, $^2J_{PC}$ = 1.6 Hz, C_5Me_4), 93.2 (d, $^2J_{PC}$ = 1.2 Hz, C_5Me_4), 95.5 (d, $^2J_{PC}$ = 2.8 Hz, C_5Me_4), 98.1 (d, $^2J_{PC}$ = 3.5 Hz, C_5Me_4), 107.6 (s, C-19), 126.5 (d, $^2J_{PC}$ = 14.7 Hz, C-14), 138.7 (d, $^3J_{PC}$ = 7.4 Hz, C-18), 161.5 (d, $^2J_{PC}$ = 3.5 Hz, C-15), 167.7 (s, C-20), 213.1 (d, $^2J_{PC}$ = 22.4 Hz, FeCO), 216.2 (d, $^2J_{PC}$ = 24.4 Hz, FeCO). $^{31}P\{^1H\}$ NMR δ: 181.9 s. L-SIMS (*p*-nitrobenzyl alcohol matrix): *m*/*z* = 633 ($M^+ + H$). Anal. Calcd for $C_{29}H_{45}FeO_6PSi_2$ (632.67): C, 55.06; H, 7.17. Found: C, 54.75; H, 7.35.

Reaction of Equimolar Amounts of (η^5-C_5Me_5)$(CO)_2FeP{=}C(NMe_2)_2$ (2) and $HC{\equiv}CCO_2Me$ (3c) in *n*-Pentane. A sample of 0.13 g (1.55 mmol) of methyl propiolate in 10 mL of *n*-pentane was added dropwise during 1 h to a well-stirred suspension of 0.54 g (1.43 mmol) of **2** in 30 mL of *n*-pentane at −25 °C. A red-brown precipitate separated immediately. After the addition of the ester, stirring was continued at ambient temperature. A 1:1 mixture of **5c** and **6c** was isolated as a red-brown solid (0.39 g, 58%). The separation of the mixture on a preparative scale failed. Repeated recrystallization, however, furnished pure samples of both compounds, albeit in very poor yield (<1%).

(η^5-C_5Me_5)(CO)$FeP[{=}C(NMe_2)_2]CH{=}C(CO_2Me)C{=}O$ (5c). IR (KBr, cm^{-1}) ν: 1878 s [$\nu(CO)_{term}$], 1712 s [$\nu(CO)_{ester}$], 1571 m [$\nu(CO)_{acyl}$], 1528 m, 1500 w, 1440 w, 1375 m, 1257 m, 1181 m, 1091 m, 1051 w, 802 w, 770 w, 647 w, 643 w, 581 w, 532 w. ^1H NMR δ: 1.86 (d, $^4J_{PH}$ = 0.9 Hz, 15H, C_5Me_5), 2.33 (d, $^4J_{PH}$ = 1.5 Hz, 12H, NMe_2), 3.55 (s, 3H, OMe), 8.03 (d, $^2J_{PH}$ = 12.8 Hz, 1H, CH). $^{13}C\{^1H\}$ NMR δ: 10.5 [d, $^3J_{PC}$ = 3.9 Hz, $C_5(CH_3)_5$], 42.9 (s, NCH_3), 43.1 s (s, NCH_3), 51.0 (s, OCH_3), 92.2 [s, $C_5(CH_3)_5$], 153.1 (d, $^2J_{PC}$ = 32.4 Hz, $=CCO_2Me$), 158.4 (d, $^1J_{PC}$ = 16.7 Hz, PCH), 167.4 (d, $^3J_{PC}$ = 16.7 Hz, CO_2CH_3), 205.4 (d, $^1J_{PC}$ = 45.5 Hz, P=C), 222.1 (d, $^2J_{PC}$ = 12.6 Hz, $FeCO_{term}$), 265.7 (d, $^2J_{PC}$ = 3.0 Hz, $FeCO_{acyl}$). $^{31}P\{^1H\}$ NMR δ: 70.5 s. Anal. Calcd for $C_{21}H_{31}FeN_2O_4P$ (462.30): C, 54.56; H, 6.76; N, 6.06. Found C, 54.87; H, 7.50; N, 6.27.

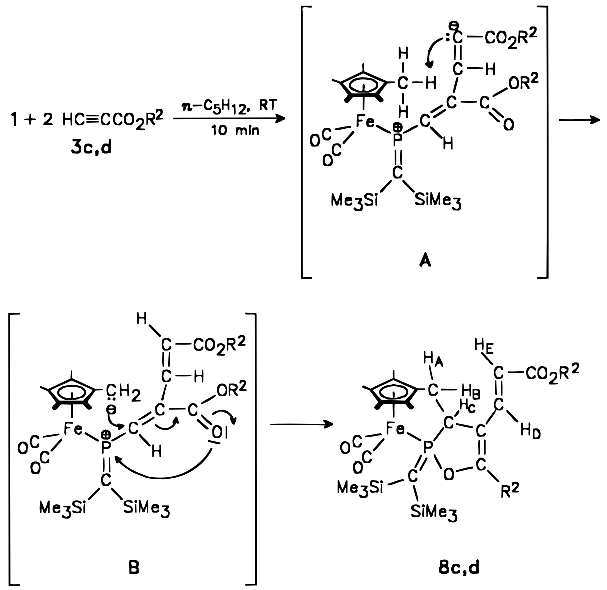
(η^5-C_5Me_5)$(CO)_2FeP{=}CHC(CO_2Me){=}C(NMe_2)_2$ (6c). IR (KBr, cm^{-1}) ν: 1972 s [$\nu(CO)_{term}$], 1924 vs [$\nu(CO)_{term}$], 1645 s [$\nu(CO)_{ester}$], 1543 w, 1511 w, 1460 w, 1398 sh, 1392 m, 1351 w, 1324 m, 1217 s, 1179 w, 1062 m, 996 m, 932 w, 863 w, 822 w, 763 w, 749 w, 708 w, 646 m, 581 s, 509 w, 483 w. ^1H NMR δ: 1.57 (s, 15H, C_5Me_5), 2.54 (s, 12H, NMe_2), 3.67 (s, 3H, OMe), 9.67 (d, $^2J_{PH}$ = 12.6 Hz, 1H, P=CH). $^{13}C\{^1H\}$ NMR δ: 9.4 [d, $^3J_{PC}$ = 7.4 Hz, $C_5(CH_3)_5$], 41.4 (s, NCH_3), 50.2 (s, OCH_3), 92.6 [s, $C_5(CH_3)_5$], 99.0 ($^2J_{PC}$ = 16.6 Hz, P=CC), 166.4 (d, $^3J_{PC}$ = 8.2 Hz, CO_2Me), 167.9 [s, $C(NMe_2)_2$], 186.8 (d, $^1J_{PC}$ = 64.4 Hz, P=CH), 218.4 (s, $FeCO_{term}$). $^{31}P\{^1H\}$ NMR δ: 315.8 s. Anal. Calcd for $C_{21}H_{31}FeN_2O_4P$ (462.30): C, 54.56; H, 6.76; N, 6.06. Found C, 53.50; H, 6.82; N, 5.70.

(η^5-C_5Me_5)(CO)FeP[CH═C(CO_2Me)C(NMe_2)$_2$C(CO_2-Me)═CH]CH═C(CO_2Me)C═O (10c). A solution of 0.52 g (6.18 mmol) of methyl propiolate (**3c**) in 20 mL of *n*-pentane was added at 20 °C to a suspension of 0.71 g (1.88 mmol) of **2** in 30 mL of *n*-pentane. Stirring was continued for 2 h. A red-brown precipitate was filtered and extracted by 50 mL of *n*-pentane. Concentration of the extracts to about 5 mL and storage at 0 °C afforded 0.48 g (40%) of red, crystalline **10c**. IR (KBr, cm^{-1}) ν: 1921 vs [$\nu(CO)_{term}$], 1735 s [$\nu(CO)_{ester}$], 1596 m [$\nu(CO)_{acyl}$], 1456 w, 1432 w, 1377 w, 1247 s, 1219 s, 1028 w, 987 w, 956 w, 842 w, 754 w, 670 w, 568 w, 518 w. ^1H NMR δ: 1.61 (d, $^4J_{PH} = 0.5$ Hz, 15H, C_5Me_5), 2.40 (s, 6H, NMe_2), 2.57, (s, 6H, NMe_2), 3.20 (s, 3H, CO_2CH_3), 3.31 (s, 3H, CO_2CH_3), 3.40 (s, 3H, CO_2CH_3), 6.13 [dd, $^2J_{PH} = 24.1$ Hz, $^4J_{HH} = 3.4$ Hz, 1H, PC*H*═C(CO_2Me)CN_2], 6.63 [dd, $^2J_{PH} = 19.0$ Hz, $^4J_{HH} = 3.4$ Hz, 1H, PC*H*═C(CO_2Me)CN_2], 6.99 [d, $^2J_{PH} = 7.9$ Hz, 1H, FePC*H*═C(CO_2Me)C═O]. $^{13}C\{^1H\}$ NMR δ: 10.1 [s, $C_5(CH_3)_5$], 38.1 s and 38.6 (s, NMe_2), 51.5 s, 51.9 s and 52.0 (s, CO_2CH_3), 80.2 (d, $^3J_{PC} = 8.7$ Hz, CN_2), 94.9 [d, $^2J_{PC} = 0.8$ Hz, $C_5(CH_3)_5$], 127.6 (d, $^1J_{PC} = 23.3$ Hz, PCH), 129.7 (d, $^1J_{PC} = 42.6$ Hz, PCH), 140.9 (d, $^1J_{PC} = 35.7$ Hz, PCH), 145.9 (d, $^2J_{PC} = 4.6$ Hz, MeO_2CCCN_2), 148.5 (d, $^2J_{PC} = 6.1$ Hz, MeO_2CCCN_2), 166.8 (d, $^3J_{PC} = 9.1$ Hz, CO_2Me), 167.1 (d, $^3J_{PC} = 10.7$ Hz, CO_2Me), 167.3 (d, $^3J_{PC} = 13.9$ Hz, CO_2Me), 168.0 (d, $^2J_{PC} = 36.6$ Hz, FeC(O)*C*═), 218.7 (d, $^2J_{PC} = 26.4$ Hz, $FeCO_{term}$), 258.7 (d, $^2J_{PC} = 10.0$ Hz; $FeCO_{acyl}$). $^{31}P\{^1H\}$ NMR δ: 48.6 s. MS/CI: m/z = 631 ($M^+ + H$), 588 ($M^+ + H - CO - CH_3$). Anal. Calcd for $C_{19}H_{39}FeN_2O_8P$ (630.47): C, 55.25; H, 6.23; N, 4.44. Found: C, 54.52; H, 6.28; N, 3.93.

(η^5-C_5Me_5)(CO)FeP[CH═C(CO_2Et)C(NMe_2)$_2$C(CO_2-Et)═CH]CH═C(CO_2Et)C═O (10d). Samples of 0.93 g (2.46 mmol) of **2** and 0.72 g (7.38 mmol) of ethyl propiolate were analogously reacted in 20 mL of *n*-pentane. The crude product was purified by column chromatography (column 15 × 2 cm; Florisil). Elution with ether afforded 1.20 g of red-brown **10d** (72%). IR (KBr, cm^{-1}) ν: 1919 vs [$\nu(CO)_{term}$], 1728 s [$\nu(CO)_{ester}$], 1594 m [$\nu(CO)_{acyl}$], 1463 w, 1384 w, 1365 w, 1233 s, 1208 s, 1098 w, 1041 m, 1027 m, 905 w, 877 w, 858 w, 844 w, 831 w, 754 w, 669 w, 572 w, 518 w. ^1H NMR δ: 0.87 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_2CH_3), 0.92 (t, $^3J_{HH} = 7.0$ Hz, 3H, CH_2CH_3), 0.94 (t, $^3J_{HH} = 7.2$ Hz, 3H, CH_2CH_3), 1.69 (d, $^4J_{PH} = 0.6$ Hz, 15H, C_5Me_5), 2.48 (s, 6H, NMe_2), 2.62 (s, 6H, NMe_2), 3.84 (q, $^3J_{HH} = 7.0$ Hz, 2H, CH_2CH_3), 3.92 (m, 2H, CH_2CH_3), 4.05 (dq, $^3J_{HH} = 7.0$ Hz, $^5J_{PH} = 1.0$ Hz, 2H, CH_2CH_3), 6.21 (dd, $^2J_{PH} = 24.0$ Hz, $^4J_{HH} = 3.3$ Hz, 1H, PCH), 6.79 (dd, $^2J_{PH} = 24.3$ Hz, $^4J_{HH} = 3.3$ Hz, 1H, PCH), 7.04 (d, $^2J_{PH} = 7.9$ Hz, 1H, PCH). $^{13}C\{^1H\}$ NMR δ: 10.1 [s, $C_5(CH_3)_5$], 13.7 s, 13.75 s and 14.2 (s, CH_2CH_3), 38.4 s and 38.8 (s, NMe_2)], 61.1 (s, CH_2CH_3), 61.2 (s, 2 × CH_2CH_3), 80.3 (d, $^3J_{PC} = 8.6$ Hz), 94.9 [d, $^2J_{PC} = 1.0$ Hz, $C_5(CH_3)_5$], 127.5 (d, $^1J_{PC} = 29.3$ Hz, PCH), 129.5 (d, $^1J_{PC} = 42.7$ Hz, PCH), 140.5 (d, $^1J_{PC} = 35.5$ Hz, PCH), 146.3 (d, $^2J_{PC} = 4.8$ Hz, EtO_2CCN_2), 149.0 (d, $^2J_{PC} = 6.0$ Hz, EtO_2CCN_2), 166.6 (d, $^3J_{PC} = 16.5$ Hz, CO_2Et), 166.7 (d, $^3J_{PC} = 15.9$ Hz, CO_2Et), 167.0 (s, CO_2Et), 168.5 [d, $^2J_{PC} = 36.2$ Hz, FeC(O)-*C*═] 218.8 (d, $^2J_{PC} = 26.5$ Hz, $FeCO_{term}$), 259.0 (d, $^2J_{PC} = 10.0$ Hz, $FeCO_{acyl}$). $^{31}P\{^1H\}$ NMR δ: 49.0 s. Anal. Calcd for $C_{32}H_{45}FeN_2O_8P$ (672.53): C, 57.15; H, 6.74; N, 4.16. Found: C, 57.25; H, 6.71; N, 3.65.

X-ray Crystal Structure Determination of 8c. A red crystal with the approximate dimensions of 1.00 × 0.70 × 0.40 mm^3 was measured on a Siemens $P2_1$ diffractometer with Mo Kα radiation at 173 K. Cell dimensions, refined from the diffractometer angles of 38 centered reflections are a = 10.478(5) Å, b = 11.272(5) Å, c = 13.585(6) Å, α = 98.33 (4)°, β = 98.81(4)°, γ = 95.96(4)°, V = 1555.8(12) $Å^3$, Z = 2, d_{calcd} = 1.291 g cm^{-3}, μ = 0.649 mm^{-1}, space group $P\bar{1}$, data collection of 7158 unique intensities ($2\Theta_{max}$ = 55°), structure solution by direct methods and refinement with full-matrix least-squares methods on F^2 (SHELXTL-Plus/SHELXL-93), 346 parameters, riding model for hydrogen atoms; common isotropic U values for each group and ADPs for all other atoms. Maximum residual electron density 0.5 e/A^3. RF = 0.049 for 5205 reflections with $I > 2\sigma(I)$, wRF^2 = 0.142 (all data) $w^{-1} = \sigma^2(F_0{}^2) + (0.0555P)^2$, where $P = (F_0{}^2 + 2F_c{}^2)/3$.

Scheme 2



3,8	R2
c	Me
d	Et

Results and Discussion

The metallophosphaalkene (η^5-C_5Me_5)$(CO)_2$FeP═C-$(SiMe_3)_2$ (**1**) smoothly reacted with 2 molar equiv of the alkyl propiolates $HC{\equiv}CCO_2R^2$ (**3c**, R^2 = Me; **3d**, R^2 = Et) in *n*-pentane (20 °C) to afford the red, crystalline complexes **8c** and **8d** in moderate yield (Scheme 2). The air- and moisture-sensitive compounds **8c** and **8d** were isolated by crystallization from *n*-pentane. They were stored under an inert atmosphere at ambient temperature without significant decomposition. The reaction of **1** and **3c,d** in equimolar ratio gave a 1:1 mixture of **1** and **8c,d**.

X-ray Analysis of 8c. An X-ray structure analysis was necessary to unambiguously determine the constitution and geometry of the adduct from **1** and 2 equiv of the propiolates. Single crystals of **8c** were grown from acetonitrile at 5 °C. The result of the structural investigation is shown in Figure 1. Positional parameters for the complex are given in Table 1. The analysis showed a bicyclic phosphonium ylide to be present. The tetracoordinate phosphorus atom is part of a 1,2-dihydro-λ^5,σ^4-oxaphosphole, which is bonded to the [$Fe(CO)_2$(η^5-$C_5Me_4CH_2$)] fragment via P(1) and C(13). The Fe–P distance of 2.2399(13) Å compares well with the corresponding bond length in **I**[2.243(2) Å][8]. Normally, Fe–P bond bond distances in low-valent iron carbonyls fall in the range 2.11–2.37 Å.[9] The bond P–O(3) [1.744(2) Å] is significantly longer in comparison to the respective bond length in **I** [1.703(5) Å],[8] whereas the carbon–phosphorus contact P(1)–C(13) of 1.873(3) Å in **8c** resembles the theoretical P–C single-bond

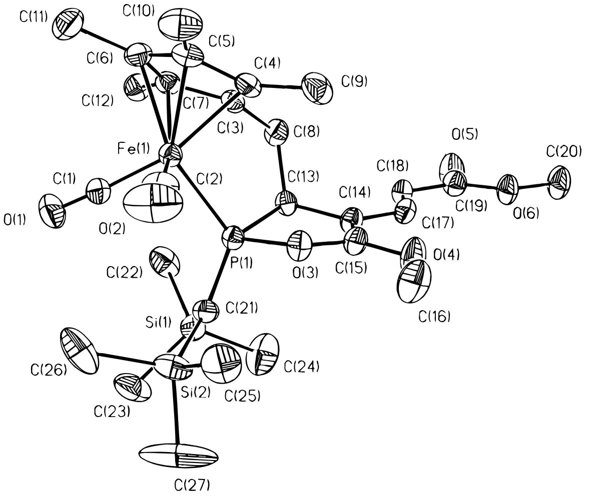


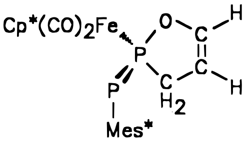
Figure 1. Molecular structure of **8c** in the crystal. Selected bond lengths (Å): Fe−P 2.2399(13), P−O(3) 1.744(2), O(3)−C(15) 1.342(3), C(14)−C(15) 1.356(4), C(13)−C(14) 1.504(4), P−C(13) 1.873(3), C(8)−C(13) 1.548(4), P−C(21) 1.679(3), C(14)−C(17) 1.439(4), C(17)−C(18) 1.343(4), C(18)−C(19) 1.459(4), C(15)−O(4) 1.333(3), C(19)−O(5) 1.214(3), C(19)−O(6) 1.348(4). Selected bond angles (deg): Fe−P−C(21) 125.07(11), C(21)−P−O(3) 108.46(13), C(21)−P−C(13) 114.45(13), O(3)−P−C(13) 92.18(11), Fe−P−O(3) 104.66(8), Fe−P−C(13) 106.59(9), P−C(13)−C(14) 102.3(2), P−O(3)−C(15) 109.4(2), O(3)−C(15)−C(14) 119.2(2), C(13)−C(14)−C(15) 113.0(2), O(3)−C(15)−O(4) 117.5(2), C(14)−C(15)−O(4) 123.4(3), C(13)−C(14)−C(17) 123.7(2), C(15)−C(14)−C(17) 123.0(3), C(14)−C(17)−C(18) 125.4(3), C(17)−C(18)−C(19) 122.9(3), P−C(21)−Si(1) 119.3(2), P-C(21)−Si(2) 117.8(2), Si(1)−C(21)−Si(2) 121.6(2).

distance of 1.87 Å.[10] The sum of the covalent single bond radii of P(1.10 Å) and O (0.66 Å) is 1.76 Å.[11] The length of the exocyclic double bond of 1.679(3) Å is comparable to the P═C bond distances in **1** [1.680(9) Å]. The theoretical PC double-bond length is 1.667 Å.[10] Inspection of the structural data for a number of ylides reveals P═C linkages ranging from 1.640 to 1.78 Å with the majority of the lengths near 1.71 Å.[12] The dihydrooxaphosphole ring is slightly bent along the O(3)−C(13) axis with a dihedral angle of 161.5° between the planes defined by the atoms P(1), C(13), O(3) and C(13), C(14), C(15), O(3), respectively. The heterocycle is oriented nearly perpendicular to the plane defined by the atoms Fe(1), P(1), and C(21). The Fe(1)−P(1) vector and the plane defined by Si(1), C(21), and Si(2) enclose an angle of 118.9°. From structural evidence **8c** and **8d** may be regarded as *P*-metalloylides. Singlets at δ 184.5 (**8c**) and 181.9 (**8d**) in the $^{31}P\{^1H\}$ NMR spectra are comparable to the resonance of the λ^5,σ^4-phosphorus atom in **I** (δ 165.1)[8]. Two singlets for the methoxy groups at δ 3.36 and 3.58 in the ^1H NMR spectrum of **8c** support the incorporation of two molecules of the propiolate into the product. The trans-configured alkene unit in **8c** gives rise to doublets at δ 5.70 (H_E) and 8.36 (H_D) ($^3J_{HH}$ = 15.5 Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the carbonyl ligands were observed as doublets at δ 213.1 ($^2J_{PC}$ = 23.3 Hz) and 216.1 ($^2J_{PC}$ = 24.4 Hz), respectively. A doublet at δ 58.1 ($^1J_{PC}$ = 8.7 Hz) is assigned to the carbon atom of the ylidic P═C bond.

Table 1. Atomic Coordinates (×10⁴) and Isotropic Displacement Parameters *U*(iso) or *U*(eq)[a] (×10³ Å²) of 8c

	x	*y*	*z*	*U*(eq)
Fe(1)	1817(1)	4864(1)	2761(1)	23(1)
P(1)	1924(1)	2898(1)	2264(1)	23(1)
Si(1)	4191(1)	1562(1)	2931(1)	32(1)
Si(2)	3946(1)	2738(1)	898(1)	42(1)
O(1)	4600(2)	5359(2)	3535(2)	49(1)
O(2)	1820(3)	5575(3)	791(2)	71(1)
O(3)	689(2)	2468(2)	1216(1)	29(1)
O(4)	−975(2)	944(2)	573(2)	44(1)
O(5)	−1671(2)	−1429(2)	4445(2)	53(1)
O(6)	−2715(2)	−1461(2)	2868(2)	36(1)
C(1)	3515(3)	5150(3)	3201(2)	32(1)
C(2)	1849(3)	5259(3)	1552(2)	39(1)
C(3)	532(3)	4204(2)	3638(2)	25(1)
C(4)	−169(3)	4690(3)	2836(2)	29(1)
C(5)	312(3)	5952(3)	2959(2)	32(1)
C(6)	1305(3)	6242(2)	3824(2)	30(1)
C(7)	1439(3)	5160(3)	4250(2)	26(1)
C(8)	384(3)	2908(2)	3809(2)	30(1)
C(9)	−1328(3)	4072(3)	2069(2)	41(1)
C(10)	−201(4)	6813(3)	2296(3)	50(1)
C(11)	2005(4)	7478(3)	4250(3)	44(1)
C(12)	2327(3)	5078(3)	5210(2)	34(1)
C(13)	991(3)	2048(2)	3070(2)	25(1)
C(14)	−9(3)	1211(2)	2297(2)	27(1)
C(15)	−107(3)	1522(3)	1363(2)	29(1)
C(16)	−989(4)	1354(3)	−385(2)	51(1)
C(17)	−871(3)	258(2)	2538(2)	28(1)
C(18)	−828(3)	−76(2)	3451(2)	28(1)
C(19)	−1752(3)	−1031(3)	3657(2)	33(1)
C(20)	−3648(3)	−2429(3)	3011(3)	46(1)
C(21)	3265(3)	2315(2)	1997(2)	29(1)
C(22)	4229(3)	2278(4)	4275(2)	46(1)
C(23)	5964(3)	1630(4)	2831(3)	58(1)
C(24)	3563(4)	−77(3)	2825(3)	64(1)
C(25)	2675(4)	2875(4)	−192(2)	59(1)
C(26)	5038(4)	4222(4)	1198(3)	64(1)
C(27)	4913(7)	1587(6)	364(4)	124(3)

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

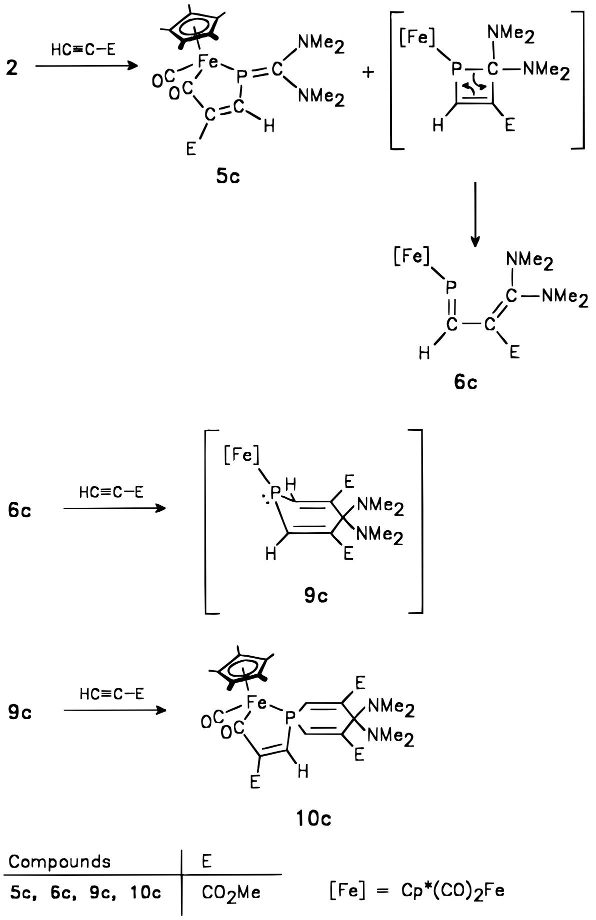


I

The surprising formation of **8c** and **8d** may be rationalized by the addition of two molecules of the alkyne to the phosphaalkene to yield intermediate **A**. Rapid transprotonation led to zwitterion **B**, which by C−C and P−O bond formation collapsed to the final product. Intermediates, however, could not be detected by ^{31}P NMR spectroscopy. Reactions involving one methyl group of a η^5-C_5Me_5 ligand are not without precedent in the chemistry of metallophosphaalkenes containing the $[(C_5Me_5)(CO)_2Fe]$ fragment.[13,14]

A completely different behavior was encountered in the reaction of metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2$-FeP═C$(NMe_2)_2$ (**2**) with the propiolates (Scheme 3). When complex **2** was treated with 3 molar equiv of methyl propiolate in *n*-pentane at 20 °C, a red-brown solid precipitated from a dark red solution. According to ^{31}P NMR evidence, the precipitate was a mixture of the five-membered cycloadduct **5c** (δ 70.5) and the 1:3 adduct **10c** (δ 49.0). A $^{31}P\{^1H\}$ NMR spectrum of the supernatant solution only exhibited the singlet at δ 49.0. Repeated extraction of the precipitate with a total of 50 mL of *n*-pentane led to the isolation of pure **10c** as red crystals in moderate yield. Analogously, **10d** resulted from reaction of **2** and 3 molar equiv of ethyl propiolate (72% yield). Two singlets for a total of two dimethylamino groups (δ 2.40, 2.57), three singlets at

Scheme 3



Compounds	E
5c, 6c, 9c, 10c	CO_2Me

[Fe] = $Cp^*(CO)_2Fe$

δ 3.20, 3.31, and 3.40 for three different methyl ester functions as well as two doublets of doublets in the olefinic region [δ 6.13 ($^2J_{PH} = 24.1$, $^4J_{HH} = 3.4$ Hz); 6.63 (dd, $^2J_{PH} = 19.0$, $^4J_{HH} = 3.4$ Hz)] and a doublet of equal intensity at δ 6.99 ($^2J_{PH} = 7.9$ Hz) in the ^{1}H NMR spectrum of **10c** are in accordance with a 1:3 adduct of **2** and the alkyne ester. The IR spectrum of **10a** displays one intense stretch from the terminal CO ligand at ν 1921 cm^{-1} and a band of medium intensity at ν 1596 cm^{-1} for the acylic CO group of the five-membered metalloheterocycle.

The formation of compounds **10c** and **10d** from **2** and 3 equiv of the propiolates is explained by a sequence of three different types of cycloaddition. The process was initiated by a [2 + 2] cycloaddition to give a transient *P*-metallo-1,2-dihydrophosphete, which underwent a rapid [2 + 2] cycloreversion to the *P*-metallophosphabutadienes **6c** and **6d**, respectively. In contrast to **6a** and **6b**, **6c** and **6d** underwent a [2 + 4] cycloaddition with a second molecule of alkyne to give the 1,4-dihydrophosphinines **9c** and **9d**. An ensuing dipolar [3 + 2] cycloaddition of the third equivalent of propiolate to the [OC–Fe–P] unit of **9c** (or **9d**, respectively) led to the final products.

This proposal is supported by the reaction of **2** with 1 equiv of methyl propiolate in *n*-pentane. Here a 1:1 mixture of metalloheterocycle **5c** and phosphabutadiene **6c** was obtained as a red-brown precipitate. Because of their very similar solubilities, **5c** and **6c** could not be separated on a preparative scale. Repeated and tedious fractional crystallization furnished only small amounts of the pure compounds, just enough for elemental analyses and spectroscopy. The ^{31}P NMR resonance of **5c** is close to the respective absorption observed for **5a** (δ 72.4 s).[7] In the ^{1}H NMR spectrum of **5c**, the methyne proton of the heterocycle is observed as a doublet at δ 8.05 ($^2J_{PH} = 12.8$ Hz).

The ^{31}P{^{1}H} NMR resonance of **6c** compares well with the singlet in the spectrum of **6b** (δ 388.7 s).[7] The proton at the P=C bond was assigned to a doublet at δ 9.67 ($^2J_{PH} = 12.6$ Hz). The relatively small P–H coupling is consistent with a trans disposition of this proton and the lone pair of electrons of the phosphorus atom. The ^{13}C{^{1}H} NMR spectrum of **6c** exhibited a doublet at δ 186.8 ($^1J_{PC} = 64.4$ Hz). The ^{31}P NMR spectrum of the supernatant pentane solution showed a singlet at δ −37.9, which was tentatively assigned to intermediate **9c**. The isolation of pure **9c** by fractional crystallization or by chromatography failed due to its lability. Reactions between **2** and 2 equiv of propiolate or, alternatively, between the 1:1 mixture of **5c** and **6c** with 1 equiv of alkyne, led to an increase in the proportion of **9c** in addition to considerable amounts of **10c** according to ^{31}P NMR evidence. The isolation of pure **9c** from these experiments was unsuccessful.

Acknowledgment. The present work was generously supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, Frankfurt, and the BASF AG, Ludwigshafen, Germany, whose funding is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and ORTEPs for **8c** (8 pages). Ordering information is on any current masthead page.

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