Reactivity of the Metallophosphaalkene $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2]$ towards Alkyl-, Aryl-, Alkenyl-, and Alkynylcarbene Complexes $[(CO)_5M{=}C(OEt)R]$ ($M = Cr, W$; $R = CH_3, Ph, CH{=}CHPh, C{\equiv}CPh$)

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Dedicated to Professor Dr. Achim Müller on the occasion of his 60th birthday

Abstract: The reaction of Fischer carbene complexes with the ferriophosphaalkene $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2]$ depends on the substitution pattern of the carbene ligand. Treatment of the phosphaalkene with $[(CO)_5M{=}C(OEt)Me]$ ($M =$ Cr, W) affords the novel phosphaalkene complexes $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP\{M(CO)_5\}{=}C(OEt)Me]$ and the carbene complexes $[(CO)_5M{=}C(OEt){-}CH{=}CHNMe_2]$ as a result of formal metathesis and condensation processes. Alkenylcarbene complexes $[(CO)_5M{=}C(OEt)CH{=}CHPh]$ and the ferriophosphaalkene undergo a Michael-type addition, whereas the corresponding phenylethynylcarbene complexes are converted into a 1-ferriophosphacyclobutane by a series of Michael additions, cycloadditions, and cycloreversions. The reactions reported here underline the rich chemistry of phosphaalkenes and carbene complexes, and emphasize the concept of the diagonal relationship C/P in the periodic table of elements.

Keywords: carbene complexes · chromium · Michael additions · phosphaalkenes · tungsten

Introduction

The chemistry of low-coordination phosphorus compounds is a rapidly expanding field that highlights the remarkable ability of phosphorus to mimic the chemistry of carbon.[1] This is visible not only in the corresponding synthetic principles which lead to C–C or P–C multiple bonding (e.g., elimination, condensation) but also in the reactivity of such molecules (e.g., [2+*n*] cycloaddition, Cope rearrangements, η^2-coordination to transition metal atoms). Transition metal carbene complexes have also received considerable attention on account of their involvement in reactions such as olefin metathesis, olefin cyclopropanation, and Fischer–Tropsch synthesis.[2] Therefore, we decided to investigate the chemical behavior of phosphaalkenes towards a number of differently substituted Fischer carbene complexes. To the best of our knowledge, the only hitherto reported reactions of a phosphaalkene **I** with carbene complexes **II** or **IV** led to 2*H*-1-aza-2-phosphirene complexes **III**[3a] or 2-phosphabutadiene complexes **V**[3b] (Scheme 1).

Results and Discussion

Reactions of the ferriophosphaalkene with ethoxy(methyl)-carbene and ethoxy(phenyl)carbene chromium and tungsten complexes: When metallophosphaalkene **1**[4] was combined with two equivalents of the ethoxy(methyl)carbene complexes **2a**,**b**[5] in ether at $-70\,^\circ C$ orange precipitates were formed. However, the isolation of these compounds was thwarted by their decomposition. Upon warming to ambient temperature, the precipitates dissolved and the novel red crystalline ferriophosphaalkene pentacarbonylmetal adducts **3a**,**b** were generated in good yield. The yellow (*E*)-β-amino-alkenyl(ethoxy)carbene complexes **4a**,**b** were also formed in comparable yields and were separated by fractional crystallization (Scheme 2).

Compounds **4a**,**b** have previously been prepared, albeit in poorer yields, by the condensation of **2a**,**b** with Me_2NCHO in the presence of $POCl_3/Et_3N$.[6a] An alternative approach to **4a** made use of *N*,*N*-dimethylformamide dimethylacetal as a reactant for **2a**.[6b] The $^{31}P\{^1H\}$ NMR spectra of **3a**,**b** display singlets at $\delta = 190.6$ and 138.0, respectively. In the ^1H NMR spectra, the protons of the methyl substituents at the P–C bond were observed as doublets at $\delta = 2.31$ [$J(P,H) = 21.3$ Hz] (**3a**) and 2.28 [$J(P,H) = 21.8$ Hz] (**3b**). The size of the $^3J(P,H)$ coupling constant is consistent with a *cis* orientation between the CH_3 group and the $P \rightarrow M$ vector. Doublets in the $^{13}C\{^1H\}$

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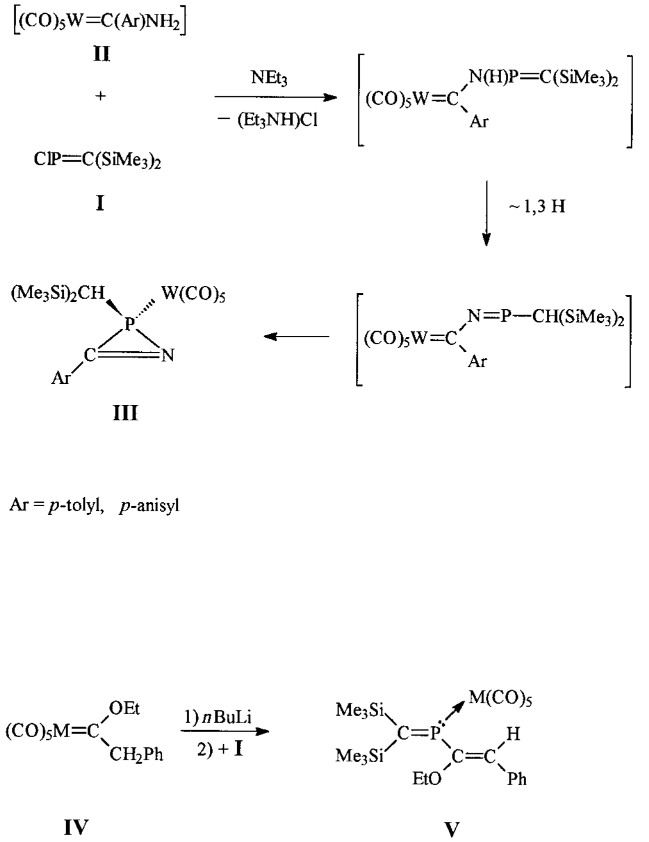
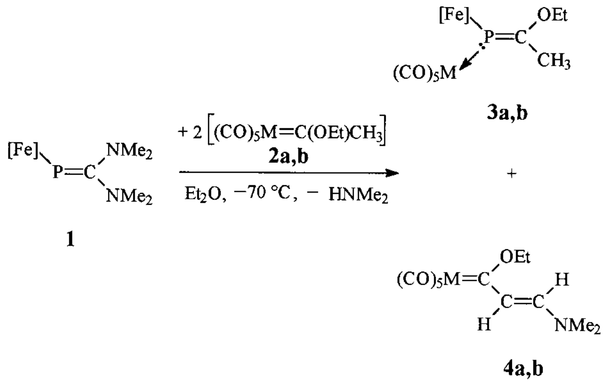


Scheme 1. Hitherto reported reactions of phosphaalkene **I** with carbene complexes **II** or **IV**. M = Cr, W.



Scheme 2. Reaction of metallophosphaalkene **1** with the ethoxy(methyl)-carbene complexes **2a**,**b**. [Fe] = $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe]$; **2a**, **4a**: M = Cr; **2b**, **4b**: M = W.

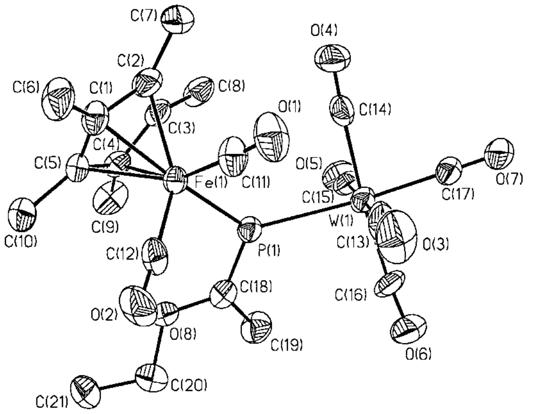


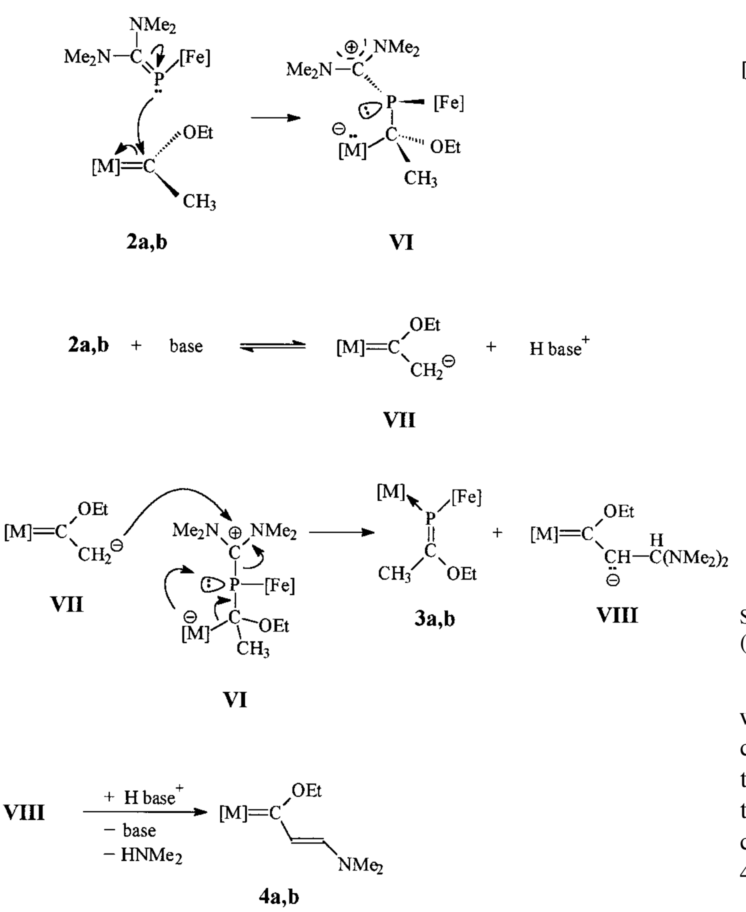
Figure 1. Molecular structure of **3b** in the crystal. Selected bond lengths [Å] and angles [°]: Fe1−P1 2.262(3), W1−P1 2.567(3), P1−C18 1.689(10), C18−O8 1.382(11), C20−O8 1.412(12), C18−C19 1.515(12); Fel-P1-W1 126.0(1), W1-P1-C18 120.7(3), Fel-P1-C18 112.8(3), P1-C18-O8 119.0(6), P1-C18-C19 124.9(7), O8-C18-C19 115.9(8); W1-P1-C18-O8 170.0, W1-P1-C18-C19 −15.7, Fel-P1-C18-O8 −1.9, Fel-P1-C18-C19 172.4.

NMR spectra of **3a**,**b** at $\delta = 206.1$ [J(P,C) = 4.9 Hz] and 204.9 [J(P,C) = 3.5 Hz], respectively, are attributed to the carbon atoms of the P=C bond.

In order to confirm the geometry of the phosphaalkenyl−iron fragment, a single-crystal X-ray structural analysis of **3b** was performed. The ORTEP drawing (Figure 1) reveals a Z-configured ferriophosphaalkene, which is η^1-ligated to a $[(CO)_5W]$ unit. The bond length W1−P1 [2.567(3) Å] is considerably longer than the W−P bond lengths in $[W(CO)_5\{\kappa\text{-}P\text{-}PhCH{=}CH{-}P{=}CH{-}CHMe_2\}]$ [2.472(2) Å][7] or in $[W(CO)_5\{\kappa\text{-}P\text{-}2\text{-}ClC_5H_4P\}]$ [2.457(2) Å],[8] but compares well with the corresponding W−P bond lenght in $[W(CO)_5\{\kappa\text{-}P\text{-}(\eta^5\text{-}t\text{Bu}_2C_2P_3)Fe(\eta^5\text{-}t\text{Bu}_3C_3P_2)\}]$ [2.561(2) Å].[9] The Fe−P single bond length of 2.262(3) Å is markedly shorter than that in $[(Z)\text{-}(\eta^5\text{-}C_5H_5)(CO)_2FeP{=}C(OSiMe_3)(t\text{Bu})]$ [2.298(1) Å][10] and resembles that in $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2]$ [2.256(2) Å].[11] The double bond distance P1−C18 [1.689(10) Å] is within 3 esd in all three ferriophosphaalkenes [1.701(4)[10] and 1.680(9) Å[11]] and falls within the range usually encountered in phosphaalkenes (1.66−1.71 Å).[12] The angle Fel-P1-C18 of 112.8(3)° corresponds to the situation in $[(Z)\text{-}(\eta^5\text{-}C_5H_5)(CO)_2FeP{=}C(OSiMe_3)(t\text{Bu})]$ [113.8(2)°].[10] The coordination geometry about P1 and C18 is trigonal planar (sum of angles 359.5° and 359.8°, respectively).

The formation of ferriophosphaalkenes **3a**,**b** is most likely initiated by nucleophilic attack of the electron-rich phosphorus atom of **1** at the carbene carbon atom of **2a**,**b** (Scheme 3). The formation of an adduct to give **VI** parallels the synthesis of an ylide complex starting from carbene complexes and

Abstract in German: *Der Reaktionsverlauf von Fischer-Carbenkomplexen mit dem Ferriophosphaalken* $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(NMe_2)_2]$ *hängt vom Substitutionsmuster am Carbenliganden ab. So liefert die Umsetzung dieses Phosphaalkens mit* $[(CO)_5M{=}C(OEt)Me]$ *(M = Cr, W) die neuartigen Phosphaalkenkomplexe* $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP\{M(CO)_5\}{=}C(OEt)Me]$ *und die Carbenkomplexe* $[(CO)_5M{=}C(OEt){-}CH{=}C(H)NMe_2]$*, die formal als Ergebnisse von Metathese- und Kondensationsprozessen aufzufassen sind. Alkenylcarbenkomplexe* $[(CO)_5M{=}C(OEt){-}CH{=}C(H)Ph]$ *reagieren mit dem Ferriophosphaalken im Sinne einer Michael-Addition, während die entsprechenden Phenylethinylcarbenkomplexe in 1-Ferriophosphacyclobutane überführt werden. Hierbei laufen Michael-Additionen, Cycloadditionen und Cycloreversionen ab. Die hier vorgestellten Reaktionen unterstreichen die reichhaltige Chemie von Phosphaalkenen und Carbenkomplexen und zeigen einmal mehr den Wert des Konzepts der Schrägbeziehung zwischen C und P im Periodensystem der Elemente.*

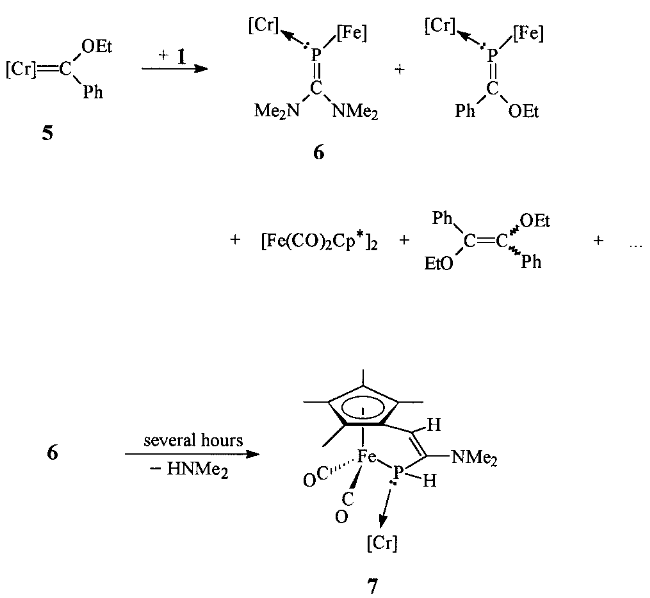


Scheme 3. Reaction of **2a**,**b** to ferriophosphaalkenes **3a**,**b** and the by-products **4a**,**b**. [Fe] = [(η^5-C_5Me_5)$(CO)_2$Fe]; [M] = [M$(CO)_5$], M = Cr, W.

phosphanes, as devised by Fischer et al.[13] The nucleophilic attack of carbene complex anion **VII** (which is readily formed from base and **2a**,**b**) at the carbenium center of **VI** leads to the carbene complex anions **VIII** and the novel ferriophosphaalkenes **3a**,**b**. Protonation of **VIII** and elimination of dimethylamine yield the observed by-roducts **4a**,**b**.

The reaction of phenylcarbene complex **5**[14] with **1** under similar conditions is complicated. Again, the combination of the reactants in *n*-pentane at $-70\,^{\circ}C$ gave an orange-yellow precipitate, which decomposed to a black tar as it warmed up. The ^{31}P NMR spectrum of this tar (C_6D_6 solution) displays a weak singlet at $\delta = 210.0$. By comparison with the stable complex [(η^5-C_5Me_5)$(CO)_2$FeP[Cr$(CO)_5$]=C($OSiMe_3$)Ph] ($\delta = 215.6$),[15] this singlet may be assigned to a ferriophosphaalkene complex analogous to **3a**. Isolation of this compound, however, was also thwarted by its decomposition. The major product was the dimeric complex [Cp*$(CO)_2$Fe$]_2$ obtained in 70% yield (Scheme 4). The only product containing phosphorus isolated from this reaction is the microcrystalline black-violet pentacarbonylchromium adduct **6** (10% yield). In the mass spectrum (CI/methane), the parent peak at $m/z = 269$ is attributed to the protonated stilbene as the formal dimer of the carbene ligand. The base peak at $m/z = 135$ is due to the ion [Ph(OEt)CH$]^+$.

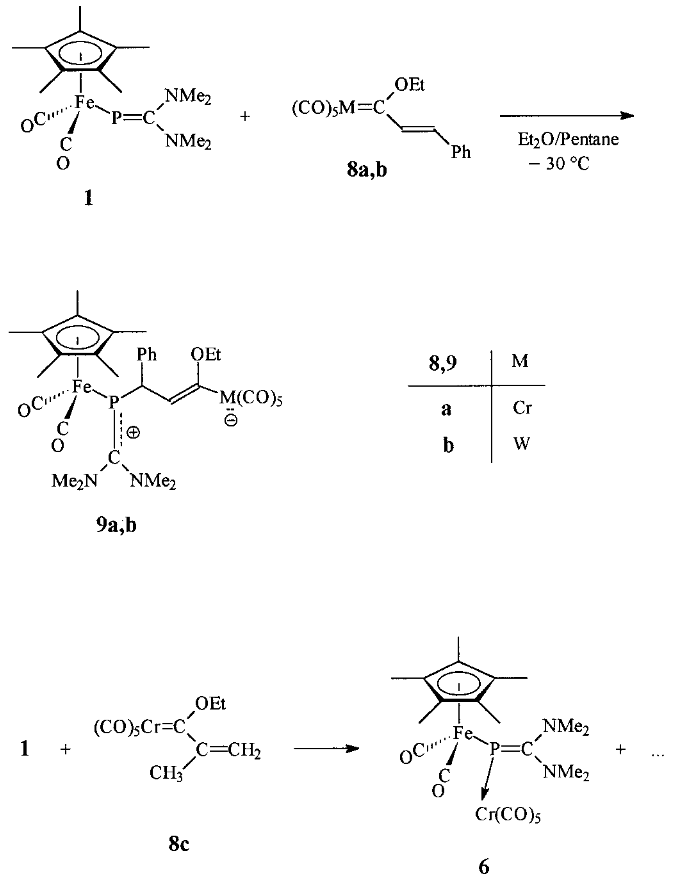
A more efficient route to microcrystalline black-violet **6** is based upon the treatment of [Cr$(CO)_5${(*Z*)-cyclooctene}][16] with an equimolar amount of **1** (59% yield). In solution, complex **6** slowly underwent an intramolecular condensation to give yellow **7**,[17] complicating the isolation of pure **6** from the carbene complex reaction. In the ^{31}P NMR spectrum, this conversion is evident from a slight shift from $\delta = -1.0$ (**6**) to 4.6 (**7**).



Scheme 4. Synthesis and further reaction of **6**. [Fe] = [(η^5-C_5Me_5)$(CO)_2$Fe]; [Cr] = [Cr$(CO)_5$].

Reactions of the ferriophosphaalkene with alkenyl(ethoxy)-carbene chromium and tungsten complexes: The combination of equimolar amounts of **1** and the alkenylcarbene complexes **8a**,**b**[18] in ether/pentane mixtures led to the precipitation of the orange zwitterionic Michael adducts **9a**,**b** in good yields (Scheme 5). The products were recrystallized from acetonitrile at $-30\,^{\circ}C$. In contrast to this, the reaction of alkenylcarbene complex **8c**[19] and **1** under comparable conditions afforded adduct **6** in 27% yield (Scheme 5). In the IR spectrum, **9a** displays seven intense bands in the region of the CO stretching vibrations. These range between $\tilde{\nu} = 2027$ to 1851 cm^{-1}, which indicates a considerable charge transfer from the metallophosphaalkene through the vinylogous carbene onto the [Cr$(CO)_5$] fragment. The poor solubility of **9a**,**b** in hydrocarbons and its propensity to decompose in polar solvents made it impossible to obtain useful ^{1}H and ^{13}C NMR spectra. In the solid state, the ^{31}P NMR spectra of the Michael adducts show singlets at $\delta = 15.7$ (**9a**) or 16.0 (**9b**).

The molecular structures of the adducts were elucidated by an X-ray crystal structure analysis with single crystals of **9b**, which were grown from acetonitrile at $-30\,^{\circ}C$. The ORTEP representation (Figure 2) shows that the ferriophosphaalkene is attached to the β-carbon atom C18 of the alkenylcarbene ligand of **9b** by a P–C single bond of 1.888(6) Å. As a consequence, the P=C double bond of **1** is elongated from 1.709(5) to 1.853(6) Å and must also be regarded as a single bond.[20] The trigonal pyramidal phosphorus atom P1 (sum of angles 324.1°) is thus part of a phosphanido ligand [Fe1–P1 = 2.326(2) Å] and constitutes one leg of a three-legged piano-stool complex. In contrast to the P atom of **1**, carbon atom C13



Scheme 5. Reactions of the ferriophosphaalkene **1** with alkenyl(ethoxy)-carbene chromium and tungsten complexes.

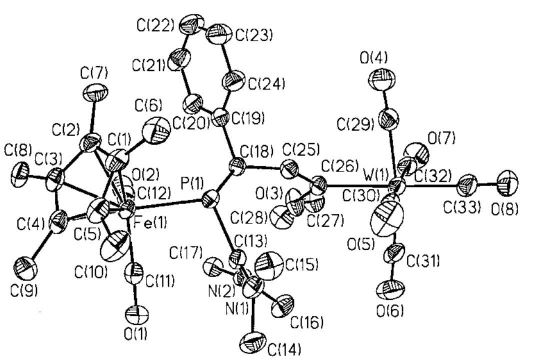
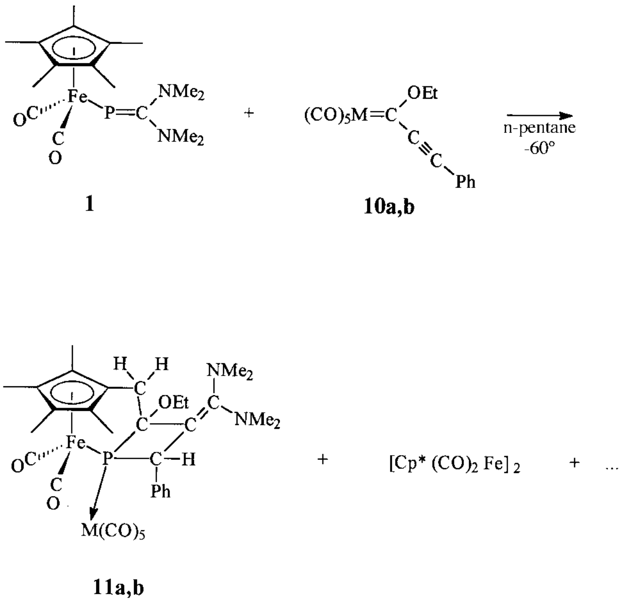


Figure 2. Molecular structure of **9b** in the crystal. Selected bond lengths [Å] and angles [°]: W1–C26 2.295(6), C25–C26 1.351(9), O3–C26 1.408(8), C18–C25 1.507(9), C18–C19 1.489(9), P1–C18 1.888(6), P1–C13 1.853(6), Fe1–P1 2.326(2), N1–C13 1.340(8), N2–C13 1.347(8); Fe1-P1-C18 118.4(2), Fe1-P1-C13 106.9(2), C13-P1-C18 98.8(3), P1-C18-C19 110.6(4), P1-C18-C25 106.2(4), C19-C18-C25 112.7(5), C18-C25-C26 126.9(6), W1-C26-C25 122.7(5), W1-C26-O3 125.3(4), O3-C26-C25 112.0(6), N1-C13-N2 117.1(6), N1-C13-P1 117.0(5), N2-C13-P1 125.8(5).

maintains its planarity (sum of angles 359.9°) and reflects the features of a bisamino carbenium ion (cf. the short bonds C13–N1 [1.340(8) Å] and C13–N2 [1.347(8) Å]). The bond length W1–C26 of 2.295(6) Å is similar to the W–C single bond in the ylide complex $[W(CH_2PMe_3)(CO)_2Cl(PMe2_3)_3][CF_3SO_3]$ [2.307(7) Å].[21] In general, tungsten–methyl bonds in hexacoordinated complexes vary from 2.131(10) to 2.313(17) Å.[22] The former carbene carbon atom C26 is still planar (sum of angles 360°) and now part of an *E*-configured C–C double bond [C25–C26 = 1.351(9) Å] in a metalated enol ether.

Reaction of the ferriophosphaalkene with ethoxy(phenylethynyl)carbene chromium and tungsten complexes: The course of the reaction of metallophosphaalkene **1** with phenylethynylcarbene complexes **10a,b**[23] in *n*-pentane was completely different. Here $[(CO)_5M]$ adducts **11a,b** of a 1-metallophosphetane were isolated in low yields (19 and 21%). Dimeric $[C_p^*(CO)_2Fe]_2$ was the only by-product which could be unambigiously identified. Elemental analyses and mass spectra indicated that **11a,b** are 1:1 adducts of the reactants (Scheme 6). However, they were characterized by a single-crystal X-ray diffraction analysis of **11a** (Figure 3).



Scheme 6. Reaction of the ferriophosphaalkene **1** with ethoxy(phenylethynyl)carbene chromium and tungsten complexes. **10a**, **11a**: M = Cr; **10b**, **11b**: M = W.

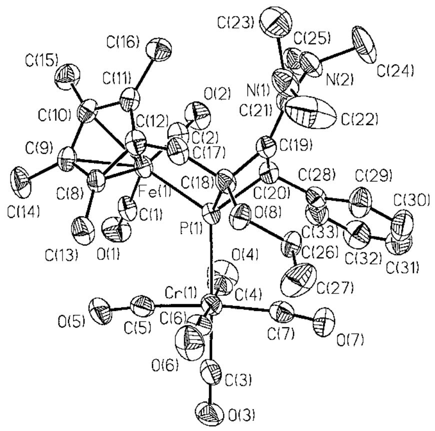


Figure 3. Molecular structure of **11a** in the crystal. Selected bond lengths [Å] and angles [°]: Cr1–P1 2.455(2), Fe1–P1 2.326(2), P1–C18 1.933(4), P1–C20 1.921(4), C18–C19 1.528(6), C19–C20 1.533(6), C19–C21 1.350(6), N1–C21 1.409(5), N2–C21 1.394(5), O8–C18 1.474(6), C17–C18 1.526(6); C18-P1-C20 76.7(2), C18-C19-C20 102.8(3), P1-C20-C19 89.7(3), P1-C18-C19 89.4(3), C18-C19-C21 127.2(4), C20-C19-C21 129.3(4), C19-C21-N1 120.6(4), C19-C21-N2 126.1(4), N1-C21-N2 113.2(4), Fe1-P1-Cr1 118.94(6).

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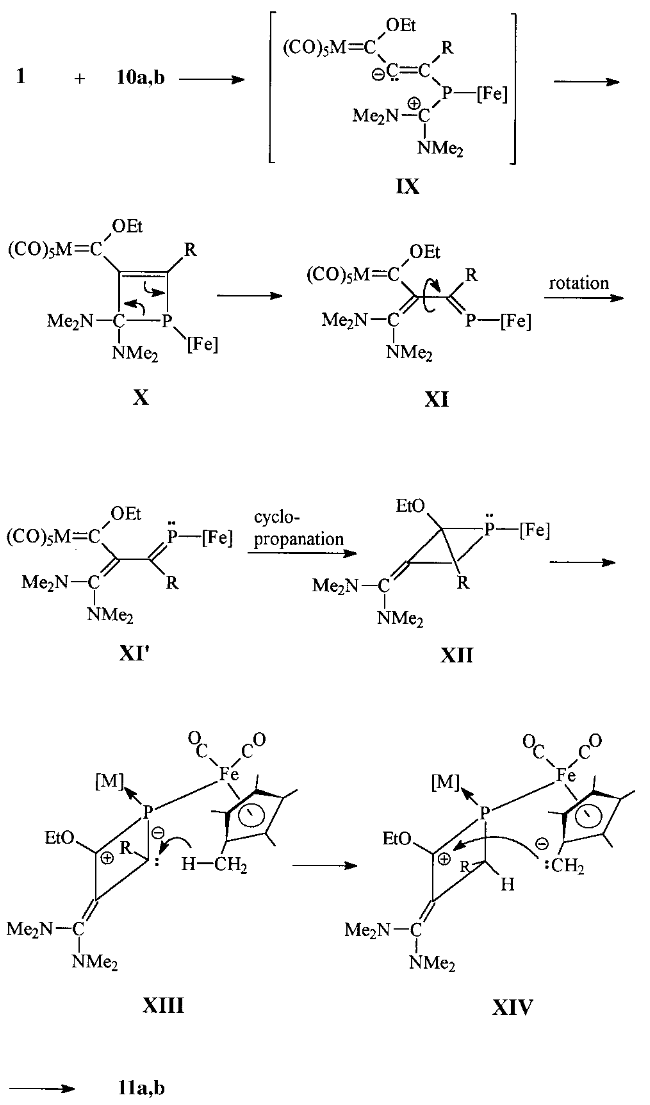
The skeleton of the organophosphorus ligand in **11a** is best described as a 2-tetramethylcyclopentadienylmethylphosphetan-1-yl group, which chelates the iron atom in an η^1-P-η^5-Cp-fashion. The four-membered ring is slightly folded along the axis P1–C19, with an interplanar angle of 167.4°. The Fe–P bond distance of 2.326(2) Å is elongated compared to the ferriophosphetene Cp*(CO)$_2$Fe–PC(NMe$_2$)=C(CO$_2$Me)CH(CO$_2$Me) [2.2983(10) Å].[4] The [Cr(CO)$_5$] unit is attached to the lone pair of the P atom [Cr1–P1 = 2.455(2) Å] in a *cis*-orientation to the phenyl ring. Both P–C bond distances in **11a** [1.921(4) and 1.933(4) Å] markedly exceed the standard value for a P–C single bond (1.85 Å)[20]. The bis(dimethylamino)methylene group of precursor **1** is linked to the planar ring carbon atom C19 by a carbon–carbon double bond [C19–C21 = 1.350(6) Å].

To rationalize the formation of products **11a,b**, we suggest an attack of the nucleophilic phosphorus atom of **1** at the β-carbon atom of the C–C triple bond to give adduct **IX**. Formation of a transient 1,2-dihydrophosphete **X** and subsequent cycloreversion affords phosphabutadiene **XI**. Rotation about the C–C single bond and intramolecular cyclopropanation leads to bicyclophosphabutane **XII**, which could open to the highly reactive zwitterion **XIII**. Proton transfer from a ring methyl group onto C20 and combination of the carbocationic and anionic centers eventually gives **11a,b** (Scheme 7).



Scheme 7. Proposed reaction mechanism for the formation of **11a,b**. [Fe] = [(η^5-C$_5$Me$_5$)(CO)$_2$Fe]; [Cr] = [Cr(CO)$_5$], [W(CO)$_5$]; R = phenyl.

Conclusion

The reactions described here provide an insight into the versatile reactivity of the metallophosphaalkene towards differently substituted Fischer carbene complexes to give products of carbene ligand displacements, Michael additions, metathesis, condensation reactions, cycloadditions, and cycloreversions. These transformations underline the rich chemistry of phosphaalkenes, and emphasize the concept of the diagonal relationship C/P in the periodic table of elements.

Experimental Section

All reactions were performed by Schlenk techniques under an atmosphere of dry nitrogen. The metallophosphaalkene **1**[4] and the carbene complexes **2a,b**,[5] **5**,[14] **8a,b**,[18] **8c**,[19] and **10a,b**[23] were prepared as described in the literature. IR spectra: Bruker FTIR IFS66. NMR spectra: in C$_6$D$_6$, 20 °C, Bruker AC100; AC250; AMAdvance DRX500. Standards: SiMe$_4$ (^{1}H, ^{13}C), external 85% H$_3$PO$_4$ (^{31}P) "quint" means apparent quintet. Mass spectra: VG Autospec (Micromass).

[Cp*(CO)$_2$FeP{W(CO)$_5$}=C(OEt)Me] (3b) and **[(CO)$_5$W{=C(OEt)-(CH=CHNMe$_2$)}] (4b)**: A solution of **1** (0.35 g, 0.93 mmol) in ether (15 mL) was added dropwise to a chilled solution (−70 °C) of **2b** (0.74 g, 1.86 mmol) in ether (25 mL). The reaction mixture was warmed to RT, stirred for 2 h, and then filtered. The filtrate was stored overnight at −30 °C to give yellow crystalline **4b**[6] (0.29 g, 69% yield). The red mother liquor was evaporated and the red-brown oily residue dissolved in acetonitrile (10 mL). Crystallization at −30 °C afforded 0.38 g (61% yield) of red crystalline **3b**.

3b: IR (KBr): $\tilde{\nu}$ = 2064 m, 2014 s, 1985 s, 1961 s, 1930 vs, 1903 vs, 1885 vs (C≡O) cm^{-1}; ^{1}H NMR: δ = 0.98 [t, J(H,H) = 7.0 Hz, 3H, OCH$_2$CH_3], 1.39 [d, J(P,H) = 0.8 Hz, 15H, C$_5$(CH$_3$)$_5$], 2.28 [d, J(P,H) = 21.8 Hz, 3H, P=C-CH$_3$], 3.40 [dq, J(H,H) = 7.0 Hz, J(P,H) = 2.0 Hz, 2H, OCH_2CH$_3$]; ^{13}C{^{1}H} NMR: δ = 9.3 [s, C$_5$(CH$_3$)$_5$], 15.2 [s, OCH$_2$CH$_3$], 25.5 [d, J(P,C) = 14.5 Hz, P=C-CH$_3$], 65.7 (s, OCH$_2$CH$_3$), 97.1 (s, C_5(CH$_3$)$_5$), 199.8 [d, J(P,C) = 7.2 Hz, W(CO)$_{eq}$], 201.7 [d, J(P,C) = 20.5 Hz, W(CO)$_{ax}$], 204.9 [d, J(P,C) = 3.5 Hz, P=C], 215.4 [d, J(P,C) = 13.5 Hz, FeCO]; ^{31}P{^{1}H} NMR: δ = 138.0 s; MS/EI (70 eV): m/z = 674 [M^+], 646 [M^+ − CO], 618 [M^+ − 2CO], 562 [M^+ − 4CO], 534 [M^+ − 5CO], 506 [M^+ − 6CO], 350 [M^+ − W(CO)$_5$]; C$_{21}$H$_{23}$FeO$_8$PW (674.06): calcd C 37.42, H 3.44; found C 37.07, H 3.35.

The analytical and spectroscopic data of **4b** were identical to those reported in ref. [6].

[Cp*(CO)$_2$FeP{Cr(CO)$_5$}=C(OEt)Me] (3a) and **[(CO)$_5$Cr=C(OEt)-(CH=CHNMe$_2$)] (4a)**: In an analogous manner, **1** (0.35 g, 0.93 mmol) and **2a** (0.49 g, 1.86 mmol) were reacted to afford 0.29 g (57% yield) of red crystalline **3a** and 0.21 g (71% yield) of yellow crystalline **4a**.[6]

3a: IR (KBr): $\tilde{\nu}$ = 2052 s, 2014 s, 1988 s, 1966 s, 1927 vs, 1896 vs (C≡O) cm^{-1}; ^{1}H NMR: δ = 1.02 [t, J(H,H) = 7.1 Hz, OCH$_2$CH_3], 1.43 [s, 15H, C$_5$(CH$_3$)$_5$], 2.31 [d, J(P,H) = 21.3 Hz, P=C–CH$_3$], 3.43 [dq, J(H,H) = 7.1 Hz, J(P,H) = 1.7 Hz, OCH_2CH$_3$]; ^{13}C{^{1}H} NMR: δ = 9.3 [s, C$_5$(CH$_3$)$_5$], 15.2 (s, OCH$_2$$CH_3$), 24.9 [d, J(P,C) = 12.8 Hz, P=C–CH$_3$], 65.5 (s, OCH$_2$CH$_3$), 97.3 [s, C_5(CH$_3$)$_5$], 206.1 [d, J(P,C) = 4.9 Hz, P=C], 215.2 [d, J(P,C) = 12.6 Hz, FeCO], 219.1 [d, J(P,C) = 13.6 Hz, Cr(CO)$_{eq}$], 224.6 [d, J(P,C) = 5.9 Hz, Cr(CO)$_{ax}$]; ^{31}P{^{1}H} NMR: δ = 190.6 s; MS/EI (70 eV): m/z = 542 [M^+], 514 [M^+ − CO], 486 [M^+ − 2CO], 430 [M^+ − 4CO], 402

$[M^+ - 5\,CO]$, 374 $[M^+ - 6\,CO]$, 346 $[M^+ - 7\,CO]$; $C_{21}H_{23}CrFeO_8P$ (542.21): calcd C 46.52, H 4.28; found C 45.05, H 4.03.

The analytical and spectroscopic data of **4a** were identical to those reported in ref. [6].

[Cp*(CO)$_2$FeP{Cr(CO)$_5$}=C(NMe$_2$)$_2$] (6): A solution of [(η^2-cyclooctene)Cr(CO)$_5$] (1.18 g, 3.90 mmol) in *n*-pentane (20 mL) was added dropwise to a chilled solution (−30 °C) of **1** (1.48 g, 3.90 mmol) in *n*-pentane (50 mL). Stirring was continued for 30 min at −30 °C and 2 h at ambient temperature to give a dark violet precipitate. The mixture was filtered and the solid dried at 10^{-3} Torr to give microcrystalline **6**. Yield: 1.32 g (59 %). Single crystals of **6** were grown from CH_3CN at −30 °C; IR (KBr): $\tilde{\nu} = 2033$ s, 1980 s, 1941 s, 1915 vs, 1897 vs, 1860 vs (C≡O) cm^{-1}; ^{1}H NMR: $\delta = 1.48$ [s, 15 H, $C_5(CH_3)_5$], 2.69 (s, 6 H, NCH_3), 2.71 (s, 6 H, NCH_3); ^{31}P{^{1}H} NMR: $\delta = -1.0$ s; MS/LSIMS (*p*-nitrobenzyl alcohol matrix): $m/z = 571$ $[M^+{+}H]$, 431 $[M^+{+}H - 5\,CO]$, 379 $[M^+{+}H - Cr(CO)_5]$, 351 $[M^+{+}H - Cr(CO)_6]$; $C_{22}H_{27}CrFeN_2O_7$ (570.29): calcd C 46.33, H 4.77, N 4.91; found C 46.32, H 4.85, N 5.18.

[Cp*(CO)$_2$FeP{C(NMe$_2$)$_2$}C(H)Ph−CH=C(OEt){Cr(CO)$_5$}] (9a): A solution of carbene complex **8a** (0.40 g, 1.14 mmol) in ether (10 mL) was added dropwise to a chilled solution (−30 °C) of **1** (0.43 g, 1.14 mmol) in 20 mL of *n*-pentane. An orange precipitate separated immediately. After stirring for 30 min at 20 °C, the precipitate was collected, washed with 10 mL of *n*-pentane, and dried at 10^{-3} Torr to afford **9a**. Yield: 0.59 g (71 %). The compound was crystallized from acetonitrile at −30 °C. Owing to the poor solubility in polar solvents and the pronounced tendency to decompose in solution at 20 °C, no satisfactory NMR spectra were obtained. IR (KBr): $\tilde{\nu} = 2027$ m, 1998 s, 1956 s, 1948 s, 1892 vs, 1882 vs, 1851 s (C≡O) cm^{-1}; ^{31}P{^{1}H} NMR (solid state): $\delta = 15.7$ s; MS/LSIMS (*p*-nitrobenzyl alcohol matrix): $m/z = 731$ $[M^+{+}H]$, 703 $[M^+{+}H - CO]$, 539 $[M^+{+}H - Cr(CO)_5]$; $C_{33}H_{39}CrFeN_2O_8P$ (730.47): calcd C 54.26, H 5.38, N 3.84; found C 53.96, H 5.48, N 3.72.

[Cp*(CO)$_2$FeP{C(NMe$_2$)$_2$}C(H)Ph−CH=C(OEt){W(CO)$_5$}] (9b): In an analogous manner, **1** (0.43 g, 1.14 mmol) and **8b** (0.55 g, 1.14 mmol) were combined in an *n*-pentane/ether mixture at −30 °C to afford orange **9b**. Yield: 0.71 g (73 %). The poor solubility and instability of the complex in polar solvents prevented the recording of NMR spectra. IR (KBr): $\tilde{\nu} = 2041$ m, 1996 s, 1950 s, 1882 vs, 1847 s (C≡O) cm^{-1}; ^{31}P{^{1}H} NMR (solid state): $\delta = 16.0$ s; MS/LSIMS (*p*-nitrobenzyl alcohol matrix): $m/z = 863$ $[M^+{+}H]$, 835 $[M^+{+}H - CO]$, 539 $[M^+{+}H - W(CO)_5]$; $C_{33}H_{39}FeN_2O_8PW$ (862.06): calcd C 45.96, H 4.52, N 3.25; found C 45.08, H 4.27, N 3.32.

Reaction of [(CO)$_5$Cr{=C(OEt)C(CH$_3$)=CH$_2$}] (8c) with 1: A sample of **1** (0.42 g, 1.10 mmol) and **8c** (0.32 g, 1.10 mmol) were combined in *n*-pentane (40 mL) at −30 °C. The mixture was stirred for 1 h at 20 °C to afford a precipitate of black-violet **6**. Crystallization of the crude product from acetonitrile at −30 °C gave 0.17 g (27 %) of black crystals.

[Cr(CO)$_5${κ-*P*-η^5-Me$_4$C$_5$CH$_2$C(OEt)P[Fe(CO)$_2$]CHPhC=C(NMe$_2$)$_2$}] (11a): A sample of **10a** (0.46 g, 1.32 mmol) was added to a cold solution (−60 °C) of **1** (0.50 g, 1.32 mmol) in *n*-pentane (50 mL). The mixture was stirred for 30 min at −60 °C and 12 h at 20 °C. The dark brown precipitate was filtered off and dried at 10^{-3} Torr. The filtercake was taken up in acetonitrile (20 mL) and stored at −30 °C for 4 d to afford orange-yellow crystals of **11a**. Yield: 0.18 g (19 %). IR (KBr): $\tilde{\nu} = 2048$ vs, 1995 s, 1942 vs, 1916 vs, 1890 vs (C≡O) cm^{-1}; ^{1}H NMR: $\delta = 1.26$ (s, 3 H, C_5CH_3), 1.38 (s, 3 H, C_5CH_3), 1.40 [t, J(H,H) = 7.1 Hz, 3 H, OCH_2CH_3], 1.64 (s, 3 H, C_5CH_3), 1.77 (s, 3 H, C_5CH_3), 2.21 (s, 6 H, NCH_3), 2.67 (s, br, 6 H, NCH_3), 2.76–2.86 (m, 2 H, C_5CH_2), 3.80 ["quint", J(H,H) = 7.1 Hz, 1 H, OCH_2CH_3], 4.13 ["quint", J(H,H) = 7.1 Hz, 1 H, OCH_2CH_3], 4.89 [d, J(P,H) = 7.3 Hz, 1 H, CHPh], 7.28 (m, 3 H, H-phenyl), 7.61 (m, 2 H, H-phenyl); ^{13}C{^{1}H} NMR: $\delta = 9.1$ (s, C_5CH_3), 9.4 (s, C_5CH_3), 9.6 (s, C_5CH_3), 15.6 (s, OCH_2CH_3), 27.3 [d, J(P,C) = 7.5 Hz, C_5CH_2], 39.3 (s, NCH_3), 42.4 (s, NCH_3), 53.6 [d, J(P,C) = 14.0 Hz, CHPh], 61.1 (s, OCH_2CH_3), 91.5 (s, C_5Me_4), 93.6 (s, C_5Me_4), 95.6 (s, C_5Me_4), 100.2 (s, C_5Me_4), 105.2 (s, C_5Me_4), 110.9 [d, J(P,C) = 26.4 Hz, PC(OEt)], 124.8 [s, C=C(NMe$_2$)$_2$], 127.1–129.8 (*o*-, *m*-, *p*-C-phenyl), 146.9 (s, *i*-C-phenyl), 152.4 [d, J(P,C) = 13.5 Hz, C=C(NMe$_2$)$_2$], 214.6 (s, FeCO), 217.0 (s, FeCO), 218.7 [d, J(P,C) = 10.2 Hz, Cr(CO)$_{eq}$], 224.3 [s, Cr(CO)$_{ax}$]; ^{31}P{^{1}H} NMR: $\delta = 165.3$ s; MS/LSIMS (*m*-nitrobenzyl alcohol matrix): $m/z = 729$ $[M^+{+}H]$, 701 $[M^+{+}H - CO]$, 645 $[M^+{+}H - 3\,CO]$, 617 $[M^+{+}H - 4\,CO]$, 589 $[M^+{+}H - 5\,CO]$, 509 $[M^+{+}H - Cr(CO)_6]$; $C_{33}H_{37}CrFeN_2O_8P$ (728.49): calcd C 54.40, H 5.12 N 3.85; found C 53.66, H 5.20, N 3.84.

[W(CO)$_5${κ-*P*-η^5-Me$_4$C$_5$CH$_2$C$_5$CH$_2$C(OEt)P[Fe(CO)$_2$]CHPhC=C(NMe$_2$)$_2$}] (11b): In an analogous manner, **1** (0.53 g, 1.40 mmol) and **10b** (0.68 g, 1.40 mmol) gave orange-yellow **11b**. Yield: 0.25 g (21 %). Purification was achieved by recrystallization from acetonitrile; IR (KBr): $\tilde{\nu} = 2058$ s, 1996 s, 1942 vs, 1913 vs, 1884 vs (C≡O) cm^{-1}; ^{1}H NMR: $\delta = 1.25$ (s, 3 H, C_5CH_3), 1.37 (s, 3 H, C_5CH_3), 1.39 [t, J(H,H) = 7.1 Hz, 3 H, OCH_2CH_3], 1.64 (s, 3 H, C_5CH_3), 1.75 (s, 3 H, C_5CH_3), 2.22 (s, 6 H, NCH_3), 2.66 (s, br, 6 H, NCH_3), 2.72–2.85 (m, 2 H, C_5CH_2), 3.82 ["quint", J(H,H) = 7.1 Hz, 1 H, OCH_2CH_3], 4.15 ["quint", J(H,H) = 7.1 Hz, 1 H, OCH_2CH_3], 4.88 [d, J(P,H) = 8.1 Hz, 1 H, CHPh], 7.27 (m, 3 H, *p*-, *m*-H-phenyl), 7.56 (m, 2 H, *o*-H-phenyl); ^{13}C{^{1}H} NMR: $\delta = 9.4$ (s, C_5CH_3), 9.6 (s, C_5CH_3), 15.7 (s, OCH_2CH_3), 27.3 [d, J(P,C) = 7.7 Hz, C_5CH_2], 39.4 (s, NCH_3), 42.5 (s, NCH_3), 53.0 [d, J(PC) = 17.1 Hz, CHPh], 61.0 (s, OCH_2CH_3), 91.5 [s, C_5Me_4], 93.7 [s, C_5Me_4], 95.6 [s, C_5Me_4], 100.2 [s, C_5Me_4], 104.5 [s, C_5Me_4], 110.7 [d, J(P,C) = 19.7 Hz, PC(OEt)], 124.8 (s, C=C(NMe$_2$)$_2$), 127.0–129.6 (*o*-, *m*-, *p*-C-phenyl), 147.3 (s, *i*-C-phenyl), 152.7 [d, J(P,C) = 14.3 Hz, C=C(NMe$_2$)$_2$], 199.9 [d, J(P,C) = 5.0 Hz, W(CO)$_{eq}$], 201.5 [d, J(P,C) = 20.4 Hz, W(CO)$_{ax}$], 215.5 (s, FeCO), 216.9 (s, FeCO); ^{31}P{^{1}H} NMR: $\delta = 107.2$ s; MS/EI (70 eV): $m/z = 860$ $[M^+]$, 832 $[M^+ - CO]$, 804 $[M^+ - 2\,CO]$, 748 $[M^+ - 4\,CO]$, 720 $[M^+ - 5\,CO]$; $C_{33}H_{37}FeN_2O_8PW$ (860.34): calcd C 46.07, H 4.34, N 3.26; found C 46.10, H 4.36, N 3.32.

X-ray structural determinations: Table 1 summarizes the important parameters. All data were collected with a Siemens $P2_1$ diffractometer using Mo$_{K\alpha}$ radiation (0.71073 Å) at 173 K. Semiempirical absorption corrections by psi-scans were applied. Programs used were Siemens SHELXTL PLUS and SHELXL 93. The structures were solved by using direct methods and were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 128. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1. Crystallographic data for **3b**, **9b**, and **11a**.

	3b	**9b**	**11a**
formula	$C_{21}H_{23}FeO_8PW$	$C_{33}H_{39}FeN_2O_8PW$	$C_{33}H_{37}CrFeN_2O_8P$
color	orange	orange	yellow
size (mm^3)	0.50 × 0.30 × 0.20	0.70 × 0.35 × 0.25	0.40 × 0.30 × 0.20
M_r	674.06	862.33	728.47
system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	C_c	$P\bar{1}$
a (Å)	10.625(6)	16.988(3)	10.518(3)
b (Å)	15.474(5)	14.016(2)	11.690(5)
c (Å)	15.179(6)	16.764(3)	15.956(5)
α (°)	90	90	71.54(3)
β (°)	100.78(4)	115.61(1)	78.48(2)
γ (°)	90	90	66.85(3)
V (Å)^3	2452(2)	3599.4 (10)	1704.7(10)
ρ_{calcd} (g cm^{-3})	1.826	1.591	1.419
Z	4	4	2
F (000)	1312	1720	756
μ (mm^{-1})	5.387	3.690	0.843
2θ range (°)	$4 < 2\theta < 55$	$4 < 2\theta < 55$	$4 < 2\theta < 55$
T (K)	173	173	173
refl. measured	5893	4271	8083
unique refl.	5606	4271	7674
refl. used	5584	4243	7629
refl. $(I) > 2\sigma(I)$	4056	3996	4491
parameters	296	425	429
resid. dens., e Å^{-3}	1.8	1.4	0.7
R[a]	0.052	0.030	0.073
R_w[a]	0.123	0.080	0.105

[a] $R = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$, $R_w = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma[w(F_0^2)^2]\}^{0.5}$

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