Reactivity of the Inversely Polarized Phosphaalkenes RP=C(NMe$_2$)$_2$ (R = *t*Bu, Me$_3$Si, H) towards Arylcarbene Complexes [(CO)$_5$M=C(OEt)Ar] (Ar = Ph, M = Cr, W; Ar = 2-MeC$_6$H$_4$, 2-MeOC$_6$H$_4$, M = W)

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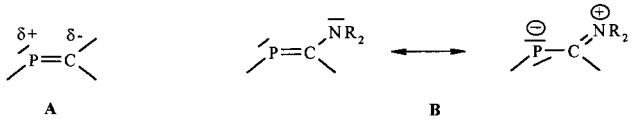
Dedicated to Professor Barry Trost on the occasion of his 60th birthday

Abstract: The reaction of the arylated Fischer carbene complexes [(CO)$_5$M=C(OEt)Ar] (Ar = Ph; M = Cr, W; 2-MeC$_6$H$_4$; 2-MeOC$_6$H$_4$; M = W) with the phosphaalkenes RP=C(NMe$_2$)$_2$ (R = *t*Bu, SiMe$_3$) afforded the novel phosphaalkene complexes [{RP=C(OEt)-Ar}M(CO)$_5$] in addition to the compounds [{RP=C(NMe$_2$)$_2$}M(CO)$_5$]. Only in the case of the R = SiMe$_3$ (*E*/*Z*) mixtures of the metathesis products were obtained. The bis(dimethylamino)-methylene unit of the phosphaalkene precursor was incorporated in olefins of the type (Me$_2$N)$_2$C=C(OEt)(Ar). Treatment of [(CO)$_5$W=C(OEt)-(2-MeOC$_6$H$_4$)] with HP=C(NMe$_2$)$_2$ gave rise to the formation of an *E*/*Z* mixture of [{(Me$_2$N)$_2$CH-P=C(OEt)-(2-MeOC$_6$H$_4$)}W(CO)$_5$] the organophosphorus ligand of which formally results from a combination of the carbene ligand and the phosphanediyl [P–CH(NMe$_2$)$_2$]. The reactions reported here strongly depend on an inverse distribution of π-electron density in the phosphaalkene precursors (P$^{\delta-}$C$^{\delta+}$), which renders these molecules powerful nucleophiles.

Keywords: carbene ligands · chromium · insertion · phosphaalkenes · tungsten

Introduction

The concepts of the diagonal relationship of phosphorus and carbon in the periodic table of elements and that of isoelectronic compounds have proven exceedingly useful in the synthetic design of organophosphorus compounds with low-coordinate P atoms.[1] However, confining organophosphorus chemistry merely to a "carbon copy"[2] would mean the reduction of its complexity to only one single aspect. In this context it is trivial to emphasize the role of the lone pair of electrons at the phosphorus atom in the coordination and redox chemistry of the phosphorus compounds. Despite the striking analogies between the cyclopentaphosphide ion P$_5^-$ and the ubiquitous cyclopentadienyl ligand and its complexes [Cp*(η^5-P$_5$) Fe][3] and ferrocene it should not be overlooked that according to quantum chemical calculations the species "FeP$_{10}$"[4] has nothing in common with the familiar class of ferrocenes or oligophosphaferrocenes. Recently it was pointed out by Zenneck et al. that the introduction of six phosphorus atoms into a manganocene skeleton affords a low-spin sandwich complex with an electronic structure different to that of decamethylmanganocene, and consistently the authors stated, that an analogy between P and C is no longer given, if formally analogous compounds differ significantly in their reactivities, spectra or molecular structures.[5] Accordingly, the olefin-like behavior of the phosphaalkenes crucially depends on the polarity (P$^{\delta+}$C$^{\delta-}$) of the P=C double bond as anticipated by Pauling's electronegativities. This π-electron distribution is easily reversed by the introduction of one or two amino groups to the carbon atom of the P=C unit (Scheme 1).



Scheme 1. Regular polarized P=C π-bond in phosphaalkenes (**A**) and inversely polarized P=C π-bond in C-aminophosphaalkenes (**B**).

In molecules of type **B** an olefin-like reactivity should be supressed in favor of a zwitterionic (ylide-like) behavior.[6] Recently, we reported on the reaction of ethoxy(methyl)carbene complexes I with the inversely polarized ferriophosphaalkene II, which yielded equal amounts of the novel phosphaalkene complexes III and the β-aminoalkenyl carbene complexes IV as a result of a sequence of addition and condensation processes (Scheme 2).[7] .

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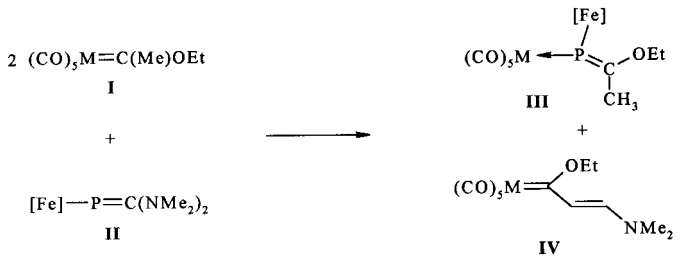


Scheme 2. Reaction of ferriophosphaalkene II with methylcarbene complexes I [Fe]=[(η^5-C_5Me_5)$(CO)_2$Fe]; M = Cr, W.

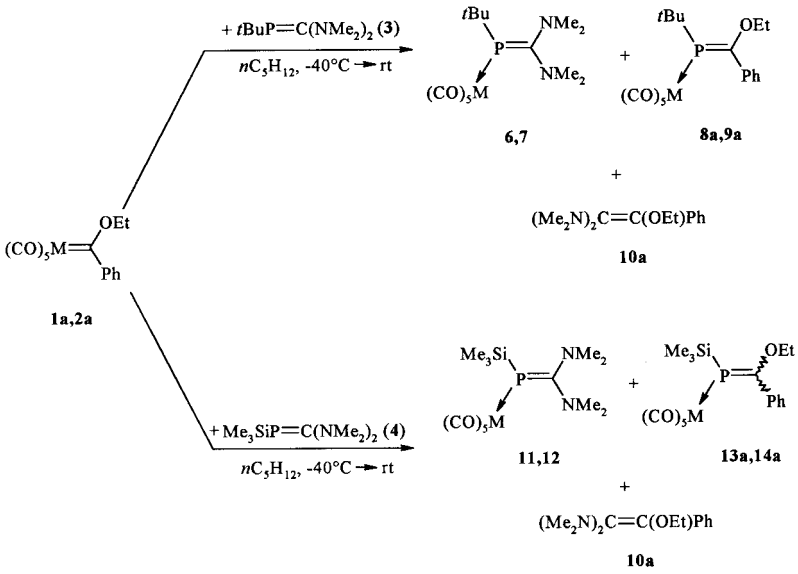
At this point reactions of II with phenylcarbene complexes became relevant, where such condensations cannot occur. First orientating experiments, however, were unsatisfactory. Treatment of II with [$(CO)_5$Cr=C(OEt)(Ph)] led to the formation of [$Cp^*_2(CO)_4Fe_2$] as the main product (70% yield). The only phosphorus containing product was the adduct [$Cp^*(CO)_2$FeP{$Cr(CO)_5$}=$C(NMe_2)_2$] (10% yield). In the tarry residue a ^{31}P NMR signal at $\delta = 210.0$ was tentatively assigned to [$Cp^*(CO)_2$FeP{$Cr(CO)_5$}=C(OEt)(Ph)].[8]

Obviously, Fe–P bond cleavage was the preferred process in this reaction. Employment of nonmetalled phosphaalkenes should circumvent this problem and provide a better insight into the reaction between arylcarbene complexes and inversely polarized phosphaalkenes.

Abstract in German: *Die Umsetzung von arylierten Fischer-Carbenkomplexen [$(CO)_5$M=C(OEt)Ar] (Ar = Ph; M = Cr, W; Ar = 2-MeC_6H_4; 2-$MeOC_6H_4$; M = W) mit den Phosphaalkenen RP=$C(NMe_2)_2$ (R = tBu, $SiMe_3$) führt zu Gemischen der neuartigen Phosphaalkenkomplexe [{RP=C(OEt)Ar}M-$(CO)_5$] und der Addukte [{RP=$C(NMe_2)_2$}M$(CO)_5$]. Nur im Falle für R = $SiMe_3$ treten die Metatheseprodukte als (E/Z)-Isomerengemische auf. Der Bis(dimethylamino)methylen-Baustein findet sich in Alkenen des Typs $(Me_2N)_2$C=C(OEt)-(Ar) wieder. Die Reaktion von [$(CO)_5$W=C(OEt)-(2-$MeOC_6H_4$)] mit HP=$C(NMe_2)_2$ liefert [{$(Me_2N)_2$CH-P=C(OEt)(2-$MeOC_6H_4$)}W$(CO)_5$] als (E/Z)-Gemisch. Der Organophosphorligand hierin ist das formale Kombinationsprodukt des Carbenliganden mit dem Phosphandiyl [P-$CH(NMe_2)_2$]. Die hier vorgestellten Reaktionen werden durch die inverse π-Elektronendichte in den Phosphaalkenen ($P^{\delta-}C^{\delta+}$) bedingt, wodurch letztere zu starken Nucleophilen werden.*

Results and Discussion

When the ethoxy(phenyl)carbene complexes **1a**, **2a**[8] were combined with the phosphaalkenes RP=$C(NMe_2)_2$ (**3**: R = *t*Bu, **4**: R = $SiMe_3$)[9] in *n*-pentane at −40 °C and stirred for 2 h at ambient temperature, the yellow η^1-phosphaalkene complexes **6**, **7** and **11**, **12** were isolated in 47–55% yield by fractioning crystallization. The yellow η^1-phosphaalkene complexes **8a**, **9a** and **13a**, **14a** were also formed (Scheme 3), but they cannot be separated from alkene $(Me_2N)_2$C=C(OEt)Ph (**10a**) without decomposition. Thus, the characterization of



Scheme 3. Reaction of **1a** and **2a** with RP=$C(NMe_2)_2$ [**3**: R = *t*Bu, **4**: R = Me_3Si]. M = Cr for compounds **1a**, **6**, **8a**, **11**, **13a**; M = W for compounds **2a**, **7**, **9a**, **12**, **14a**.

8a, **9a** and **13a**, **14a** was limited to spectra (IR, ^{1}H; ^{13}C, ^{31}P NMR) whereas alkene **10a** was distilled off in vacuo.

When compounds **1a**, **2a** were treated with equimolar amounts of HP=$C(NMe_2)_2$ (**5**)[10] in *n*-pentane at −40 °C, a yellow solid precipitated. Upon warming to ambient temperature the precipitates decomposed to brown oils.

It was assumed that an increase of the steric bulk at the aryl ring might provide additional stability to the novel phosphaalkene complexes, which contain the former carbene ligand as the methylene unit at the P atom. In keeping with this, the ethoxy(*o*-tolyl) carbene complex **2b** was subjected to reaction with equimolar amounts of the phosphaalkenes under comparable conditions. No reaction was observed between **2b** and *t*BuP=$C(NMe_2)_2$ (**3**), which may be explained by the steric bulky of the *tert*-butyl group. On the other hand combination of **2b** with HP=$C(NMe_2)_2$ (**5**) led to the formation of a yellow precipitate, which as in the case of **1a**, **2a** decomposed at 20 °C to a brown oil. The treatment of **2b** with Me_3SiP=$C(NMe_2)_2$ (**4**) afforded yellow **12** (38%) in addition to the novel orange crystalline η^1-phosphaalkene complex **14b** (14%) and alkene **10b** (Scheme 4).

The reaction of *o*-methoxyphenyl carbene complex **2c**[11] with **3** under comparable conditions yielded the yellow η^1-phosphaalkene complex **7** (29%) and the orange η^1-phosphaalkene complex **9c** (39%). Both compounds were sepa-

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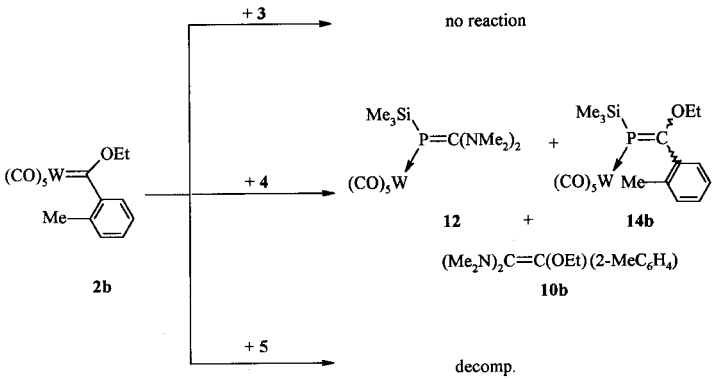
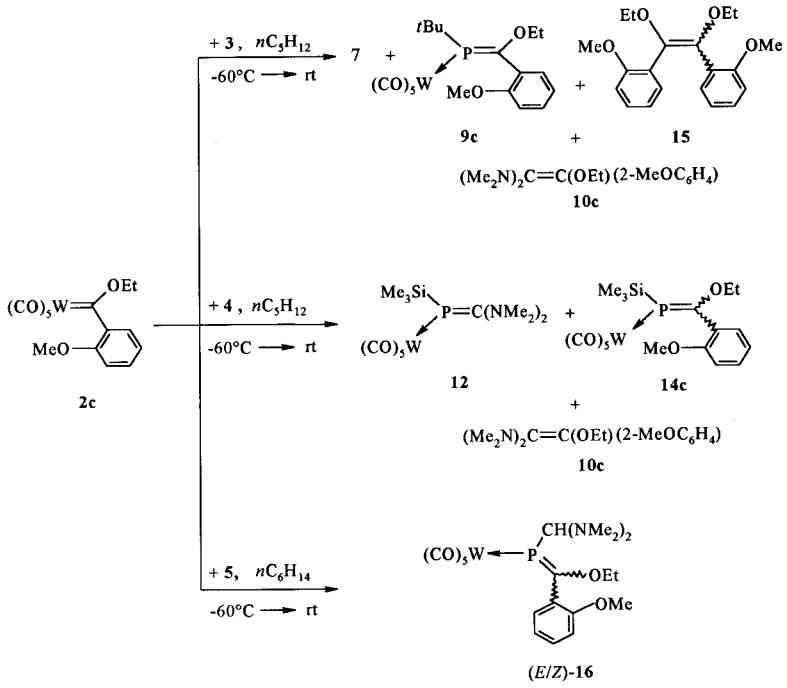


Scheme 4. Reaction of **2b** with phosphaalkenes $RP{=}C(NMe_2)_2$ (**3**: R = *t*Bu, **4**: R = Me_3Si, **5**: R = H).

rated by fractioning crystallization from *n*-pentane. After removal of compounds **7**, **9c** and solvent small amounts of an orange oil remained, which was purified by vacuum distillation. According to NMR spectroscopy the light yellow distillate was identified as a 1:1 mixture of the alkenes $[(E/Z)\text{-}2\text{-}MeOC_6H_4(EtO)C]_2$ (**15**) and $(Me_2N)_2C{=}C(OEt)\text{-}(2\text{-}MeOC_6H_4)$ (**10c**).

Combination of **2c** with $Me_3SiP{=}C(NMe_2)_2$ (**4**) under similar conditions gave rise to the formation of **12** (51%) and the metathesis product $[\{Me_3SiP{=}C(OEt)\text{-}(2\text{-}MeOC_6H_4)\}W(CO)_5]$ (**14c**), which was isolated as an orange solid in 21% yield. The reaction residue contained $(Me_2N)_2C{=}C(OEt)(2\text{-}MeOC_6H_5)$ (**10c**) as the only olefin. The course of the reaction of carbene complex **2c** with $HP{=}C(NMe_2)_2$ (**5**) was completely different. Here $[(CO)_5W]$ complexes of the two geometric isomers of the phosphaalkene $(Me_2N)_2CHP{=}C(OEt)(2\text{-}MeOC_6H_4)$ [(*E*/*Z*)-**16**] were obtained as orange crystals in 80% yield. An (*E*/*Z*) ratio of 1:2 was determined by ^1H and ^{31}P NMR spectroscopy (Scheme 5)



Scheme 5. Reaction of **2c** with the phosphaalkenes $RP{=}C(NMe_2)_2$ (**3**: R = *t*Bu, **4**: R = Me_3Si, **5**: R = H).

In line with an inverse polarity of π-electron density in **3** and **4** the ^{31}P NMR resonances of the complexes $[\{t\text{BuP}{=}C\text{-}(NMe_2)_2\}M(CO)_5]$ (**6**: M = Cr, s, $\delta = -1.2$; **7**: M = W, s, $\delta = -25.2$, $J(P,W) = 153.5$ Hz) and $[\{Me_3SiP{=}C(NMe_2)_2\}M(CO)_5]$ (**11**: M = Cr, s, $\delta = -117.7$; **12**: M = W, s, $\delta = -141.3$) are strongly shielded when compared with the free ligands **3** (s, $\delta = 90.1$) and **4** (s, $\delta = 47.1$). In contrast to this, the metathesis products $[\{t\text{BuP}{=}C(OEt)Ph\}M(CO)_5]$ (**8a**: M = Cr, s, $\delta = 180.1$; **9a**: M = W, s, $\delta = 143.2$, $J(P,W) = 253.9$ Hz) and $[(E,Z)\{Me_3SiP{=}C(OEt)Ph\}M(CO)_5]$ (**13a**: M = Cr, s, $\delta = 123.7$ and s, 131.0; **14a**: M = W, s, $\delta = 81.4$, $J(P,W) = 204.2$ Hz; s, 87.7, $J(P,W) = 197.3$ Hz) feature ^{31}P NMR resonances at much lower field. It is interesting that with **8a** and **9a** *Z* isomers were formed exclusively, where as with the sterically less demanding Me_3Si group at the phosphorus atom in **13a** and **14a** (*E*) and (*Z*) isomers occur. The increased coupling constants *J*(P,W) of **9a** and **14a** compared with **7** and **12** point to an increased s-orbital contribution in the W–P σ-bond and a planar configuration at the P atom. Thus in **7** and **12** a pyramidal geometry at the phosphorus center has to be assumed. Similar observations were made for (*Z*)-**9c** ($\delta = 131.3$; $J(P,W) = 237.1$ Hz), (*E*/*Z*)-**14a** (s, $\delta = 81.4$, $J(P,W) = 204.2$ Hz; s, 87.7, $J(P,W) = 197.3$ Hz), (*E*/*Z*)-**14b** (s, $\delta = 73.7$, $J(P,W) = 206.5$ Hz; s, 78.8, $J(P,W) = 195.0$ Hz) and (*E*/*Z*)-**14c** (s, $\delta = 63.9$, $J(P,W) = 206.5$ Hz; s, 74.7, $J(P,W) = 195.0$ Hz). The increased electron transfer in the adducts $[\{RP{=}C(NMe_2)_2\}M(CO)_5]$ in comparison to the metathesis products $[\{RP{=}C(OEt)(Ar)\}M(CO)_5]$ is also reflected in the region of the carbonyl stretching frequencies of the IR spectra (e.g. **7**: $\tilde{\nu}(CO) = 2054$ (m), 1909 (s), 1868 cm^{-1} (s) compared with **9a**: $\tilde{\nu}(CO) = 2071$ (m), 1982 (m), 1944 cm^{-1} (s) or **12**: $\tilde{\nu}(CO) = 2056$ (m), 1904 (s), 1864 cm^{-1} (s) compared with **14b**: $\tilde{\nu}(CO) = 2075$ (m), 1924 cm^{-1} (s)]. Two ^{31}P NMR signals for product **16** at $\delta = 102.1$ (s, $J(P,W) = 222.3$ Hz) and 114.1 (s, $J(P,W) = 236.3$ Hz) agree with the generation of (*E*/*Z*) isomers in the reaction of **2c** with **5**. According to these data and IR absorptions at $\tilde{\nu} = 2069$, 2044, 1934, 1918 and 1870 cm^{-1} the ligand in **16** has to be regarded as a classically polarized phosphaalkene. In the $^{13}C\{^1H\}$ NMR spectra of the products **8a**, **9a** and **9c** with a *tert*-butyl substituent at the phosphorus atom doublet resonances at $\delta = 199.5–204.5$ ($J(P,W) = 20.7–60.9$ Hz) were attributed to the carbon atoms of the P=C bond. In complexes **13a**, **14a**, **14b**, and **14c** featuring a $PSiMe_3$ function two doublets were observed for the methylene carbon atoms due to the presence of (*E*/*Z*) isomers. They range from $\delta = 210.3–215.3$ with coupling constants $J(P,C) = 11.5–40.5$ Hz.

In order to confirm the stereochemistry of the alkene fragment, single crystal X-ray structural analyses of **9c**, **14b** and the major isomer of **16** were performed. Single crystals of the compounds were grown from *n*-pentane at $-16\,^{\circ}C$. The ORTEP drawing (Figure 1) reveals **9c** as a *Z*-configured phosphaalkene, which is η^1-ligated to a $[(CO)_5W]$ unit. The bond length W1–P1 (2.529(1) Å) is considerably longer than the W–P lengths in $[W(CO)_5\{\kappa$-*P*-PhCH=CH-P=CH-$CHMe_2\}]$ (2.472(2) Å)[12] or in $[W(CO)_5\{\kappa$-*P*-2-$ClC_5H_4P\}]$ (2.457(2) Å)[13] but markedly shorter than the corresponding bond length in $[W(CO)_5$-κ-*P*-$\{Cp^*(CO)_2FeP{=}C(OEt)CH_3\}]$ (2.567(3) Å). The double bond length P1–C8 (1.694(2) Å) is well comparable to that in the latter complex (1.689(10) Å) and falls within the range usually observed in phosphaalkenes (1.66 – 1.71 Å). The angle at phosphorus C8-P1-C11 of 108.0(1)° is more acute than the angle Fe-P-C in $[W(CO)_5$-κ-*P*-$\{Cp^*(CO)_2FeP{=}C(OEt)CH_3\}]$ (112.8(3)°). The coordination geometry about C8 is trigonal planar (sum of angles 360.0°), whereas the P atom is slightly pyramidalized (sum of angles 356.9°). Atom P1 deviates from the plane defined by the atoms W1, C8 and C11 by 0.203 Å towards O4 and O6. The plane of the aryl ring and the plane defined by the atom C1, C8 and P1 enclose a dihedral angle $\psi = 65.3°$.

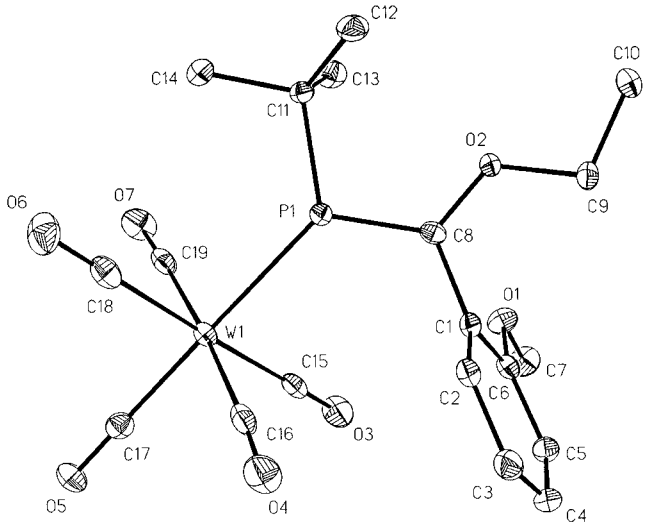


Figure 1. Molecular structure of **9c** in the crystal. Selected bond lengths [Å] and angles [°]: W1–P1 2.529(1), P1–C8 1.694(2), P1–C11 1.874(2), C8–O2 1.359(2), C9–O2 1.454(2), C8–C1 1.478(3); W1-P1-C11 125.13(7), W1-P1-C8 123.76(7), C8-P1-C11 108.0(1), P1-C8-O2 120.56(15), P1-C8-C1 120.31(15), O2-C8-C1 119.08(17), W1-P1-C8-O2 159.4, W1-P1-C8-C1 – 23.0, C11-P1-C8-O2 – 1.5, C11-P1-C8-C1 176.1.

As with complex **9c**, the X-ray structural analysis of **14b** (Figure 2) features a *Z*-configurated phosphaalkene ligand, which is η^1-coordinated to a $[W(CO)_5]$ fragment. The bond lengths W1–P1 (2.5139(8) Å) and P1–C9 (1.694(3) Å) compare well with **9c**. The bond length P1–Si1 of 2.2720(11) Å is longer than in $[(\eta^5$-$C_5Me_4Et)(CO)_2FeP$-$(SiMe_3)_2]$ (2.233(2) Å)[14] but compares well with the P–Si bond length in $(Me_3Si)_3C$-P=P-$SiPh_3$ (2.269(2) Å).[15] Si–P bond lengths usually range from 2.25 to 2.29 Å,[16] but may be as short as 2.209(9) Å when incorporated in small rings or spiro compounds such as $(t$BuP$)_2$Si(P*t*Bu$)_2$.[17] The angle

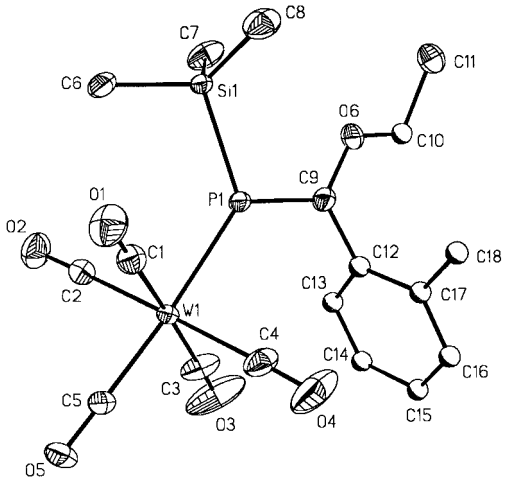


Figure 2. Molecular structure of **14b** in the crystal. Selected bond lengths [Å] and angles [°]: W1–P1 2.5139(8), P1–C9 1.694(3), P1–Si1 2.2720(11), O6–C9 1.347(4), O6–C10 1.447(8), C9–C12 1.517(6); W1-P1-Si1 126.84(4), W1-P1-C9 127.33(11), Si1-P1-C9 105.81(11), P1-C9-O6 119.0(2), P1-C9-C12 120.6(3), O6-C9-C12 119.5(3); O6-C9-P1-W1 – 177.0, C12-C9-P1-W1 14.0, O6-C9-P1-Si1 1.1, C12-C9-P1-Si1 – 167.8.

Si1-P1-C9 at the trigonal planar phosphorus atom (sum of angles 360°) amounts to 105.81(11)°. The carbon atom C10 of the ethoxy group is disordered on three positions (46:31:23) and the atoms C12–C18 of the *o*-tolyl substituent are disordered on two positions (58:42). In Figure 2 only the preferred geometry is shown. The carbon atom C9 is trigonal planar (sum of angles 359.1°). In the major conformer the plane of the aryl ring and the plane defined by the atoms P1, C9 and C12 enclose a dihedral angle of 68.2°, whereas in the minor conformer this angle was determined to 109.0°.

The X-ray structural analysis of (*Z*)-**16** (Figure 3) features a (*Z*)-configurated phosphaalkene which is coordinated to the

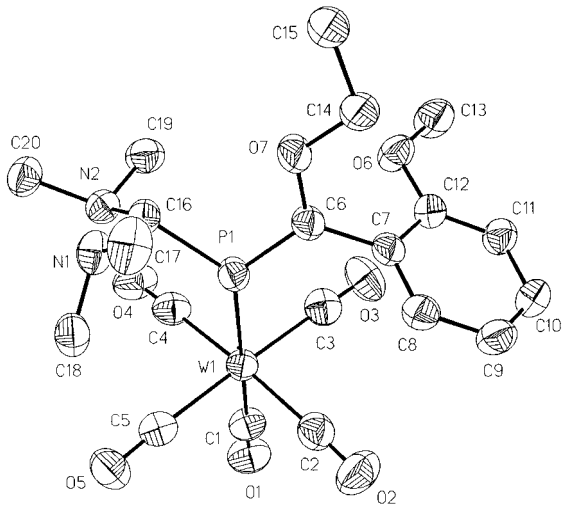


Figure 3. Molecular structure of $[\{(Z)$-κ-*P*-$(Me_2N)_2CH$-P=C(OEt)(2-$MeOC_6H_4)\}W(CO)_5]$. Selected bond lengths [Å] and angles [°]. W1–P1 2.536(2), P1–C6 1.686(6), P1–C16 1.908(6), N1–C16 1.453(8), N2–C16 1.452(8), C6–C7 1.490(8), C6–O7 1.352(7), O7–C14 1.443(8); W1-P1-C6 125.7(2), W1-P1-C16 127.2(2), C6-P1-C16 103.9(3), P1-C6-C7 120.9(4), P1-C6-O7 119.1(4), O7-C6-C7 120.0(5), P1-C16-N1 113.4(4), P1-C16-N2 107.6(4), N1-C16-N2 112.3(5); C16-P1-C6-O7 – 2.4, C16-P1-C6-C7 179.8, W1-P1-C6-O7 158.4, W1-P1-C6-C7 – 19.3.

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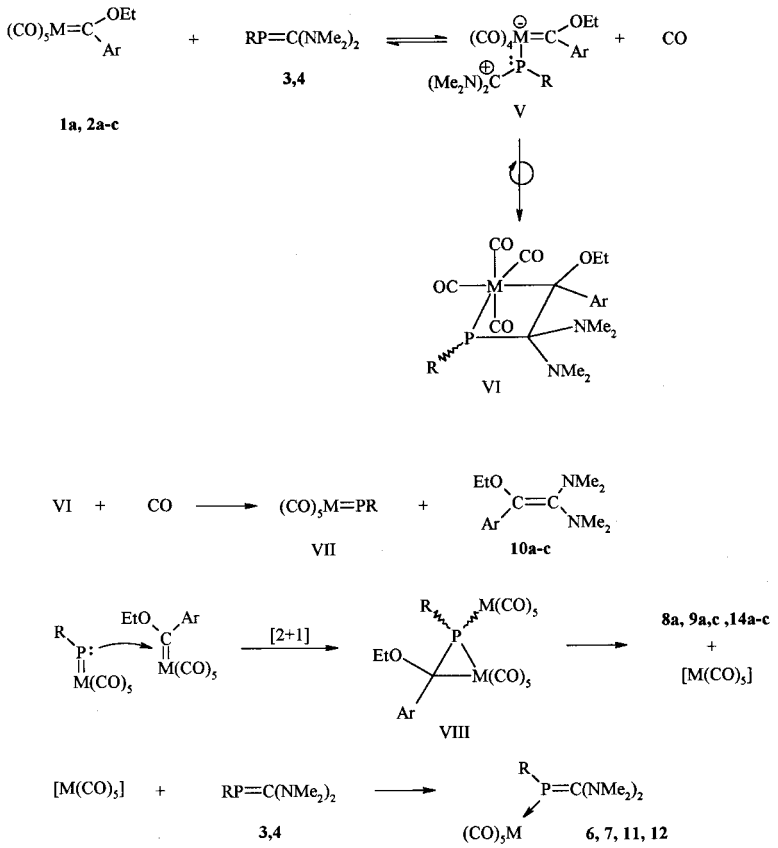
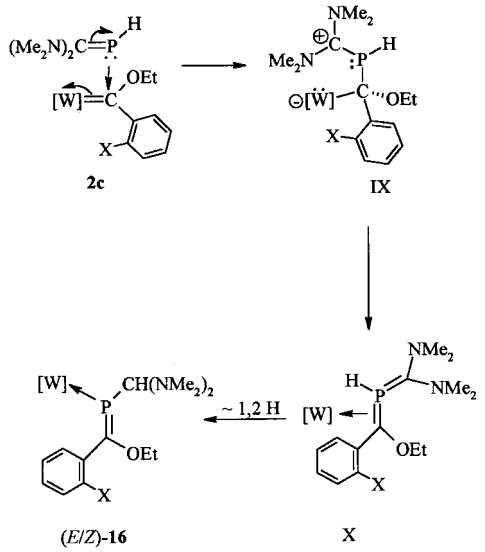
$[W(CO)_5]$ moiety through a W–P single bond of 2.536(2) Å. The length of the P–C double bond P1–C6 (1.686(6) Å) is similar to that in **9c**. The phosphorus atom is connected to a bis(dimethylamino)methyl substituent through a long P–C single bond (P1–C16 1.908 Å). The atoms C16, P1, C6, O7 and C7 are located in the same plane from which the tungsten atom deviates by 0.743 Å. As a consequence, the geometry at P1 is not completely planar (sum of angles 356.8°). The geometry at carbon atom C6 is perfectly trigonal planar (sum of angles 360°). The interplanar angle enclosed by the aryl ring and the plane defined by the atoms P1, C6 and C7 was determined to 106.4°.

To rationalize the formation of the organometallic metathesis products **8a**, **9a–c**, **13a**, **14a–c** and the alkenes **10a–c** we suggest the initial replacement of a carbonyl ligand by the nucleophilic phosphaalkenes to give V (Scheme 6). This would agree with the reaction behavior of Fischer carbene complexes towards tertiary phosphanes.[18] Ring closure to afford 1,2-metallophosphetane VI parallels a mechanistic key step in olefin metathesis.[19] Degradation of VI leads to the observed alkenes **10a–c** and a very reactive electrophilic phosphanediyl complex VII.[20] The [2+1] cycloaddition of VII to the starting materials **1a**, **2a–c** yields a dinuclear $\eta^1{:}\eta^2$-phosphaalkene complex VIII as an intermediate which eventually liberates the $[M(CO)_5]$ fragment to give the observed metathesis products **8a**, **9a**, **c** and **14a–c**. A similar argumentation was given by Mathey et al. to rationalize the formation of a 1,2-diphosphetane from a carbene complex and transient $[PhP{=}W(CO)_5]$.[21]

Combination of **3**, **4** with the pentacarbonylmetal unit would give one rationale for the generation of the complexes **6**, **7**, and **11**, **12**. The direct attack of **3**, **4** at VIII is also conceivable. The direct replacement of aryl(alkoxy)carbene ligands by Lewis bases is usually accompanied by the formation of stilbenes.[18] This pathway can only be considered for the reaction of **2c** with **3** where indeed stilbenes **15** were detected. The generation of complexes (*E*/*Z*)-**16** from **2c** and the sterically less demanding **5** is most likely initiated by the nucleophilic attack of the electron-rich phosphorus atom of **5** at the carbene carbon atom of **2c**. The formation of a zwitterionic adduct IX (Scheme 7) agrees with the synthesis of ylide complexes from carbene complexes and non-bulky phosphanes, as devised by Fischer et al.[18]



Scheme 6. Reaction of carbene complexes **1a**, **2a–c** with phosphaalkenes **3**, **4** to give metathesis products **8a**, **9a**, **c**, **10a–c** and **14a–c** as well as the complexes **6**, **7**, **11**, **12** (Ar = Ph, *o*-Me-C_6H_4, *o*-MeO-C_6H_4).



Scheme 7. Reaction of **2c** and **5** to the complexes (*E*/*Z*)-**16** ([W] = $W(CO)_5$, X = OMe).

A σ/π-rearrangement would give complex X featuring a λ^5,σ^3-phosphorane ligand. Stable λ^5,σ^3-phosphoranes have previously been studied by Appel et al.[22] A 1,2-hydrogen shift and a π/σ rearrangement would finally account for the formation of (*E*/*Z*)-**16**. We postulate that the major isomer has the (*Z*)-configuration with the most bulky substituents in a *trans*-arrangement.

Experimental Section

All operations are performed by Schlenk techniques under an atmosphere of dry nitrogen. The carbene complexes **1a**, **2a**,[8] **2c**,[11] the phosphaalkenes **4**,[9] and **5**;[10] $[(Me_2N)_2CSMe]I$[23] and $tBuP(SiMe_3)Li$[24] were prepared as described in the literature. IR spectra: Bruker FTIR IFS66. NMR spectra: in C_6D_6, 20 °C, Bruker AC 100; AC250; AM Avance DRX 500. Standards: $SiMe_4$(^1H, ^{13}C), external 85 % H_3PO_4 (^{31}P). Mass Spectra VG Autospec X (Micromass).

$[(CO)_5W{=}C(OEt)(2\text{-}MeC_6H_4)]$ (2b): A 1.5 M solution of *n*-butyllithium (10 mL, 15.0 mmol) was added at 0 °C to a solution of *o*-bromotoluene (2.60 g, 15.0 mmol) in diethyl ether (40 mL). The resulting mixture was stirred for 1 h, then added dropwise to a chilled (−30 °C) slurry of $[W(CO)_6]$ (5.30 g, 15.0 mmol) in diethyl ether (150 mL). The solution was warmed to ambient temperature and stirring was continued for 2 h. Solvent and volatile components were removed in vacuo and the yellow residue was dissolved in deoxygenated water (60 mL). The aqueous solution was layered with *n*-pentane (100 mL). Then a sample of $(Et_3O)BF_4$ (2.80 g, 15.0 mmol) was added, and stirring was continued until an acidic reaction of the aqueous phase occured. The two phases were separated and the aqueous layer was extracted with *n*-pentane (5 × 50 mL). The combined organic extracts were dried with Na_2SO_4. The solution was filtered, the filtrate was concentrated to half its volume and stored at −28 °C for 24 h. Dark red solid **2b** (6.16 g, 87 %) was collected by filtration. IR (KBr): $\tilde{\nu}$ = 2070 (m), 1930 cm^{-1} (vs) (C≡O); ^1H NMR: δ = 0.92 (br, 3H; OCH_2CH_3), 1.93 (s, 3H; aryl CH_3), 4.53 (br, 2H; OCH_2CH_3), 6.79 – 6.93 (m, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR: δ = 14.3 (s, OCH_2CH_3), 18.8 (s, aryl CH_3), 80.5 (br, OCH_2CH_3), 122.8 – 132.6 (s, *C*-aryl), 156.8 (br, i-*C*-aryl), 197.3 (s, $(CO)_{eq}$), 204.2 (br, $(CO)_{ax}$), 330.4 (s, W=*C*); elemental analysis calcd (%) for $C_{15}H_{12}O_6W$ (472.11): C 38.16, H 2.56; found C 38.13, H 2.55.

***t*BuP=C(NMe$_2$)$_2$ (3)**: A solution of $LiP(tBu)SiMe_3$ (prepared from $HP(tBu)SiMe_3$ (3.84 g, 28.6 mmol) and *n*BuLi (1.6 M, 17.9 mL) in 1,2-dimethoxyethane (DME, 30 mL) was added dropwise to a slurry of $[(Me_2N)_2CSMe]I$ (7.85 g, 28.6 mmol) in DME (40 mL). The resulting mixture was stirred overnight and then evaporated to dryness. The residue was combined with *n*-pentane (30 mL), stirred for 10 min and then filtered. The filter-cake was washed with *n*-pentane until the organic phases were colorless. The yellow filtrate and the combined organic phases were reduced in vacuo to afford an orange oil which was purified by distillation. Compound **3** was obtained as a yellow oil (3.92 g, 71 %). B.p. 0.03 mbar, 39 – 42 °C (lit.: 40.1 mbar, 62 – 64 °C); $^{31}P\{^1H\}$ NMR δ = 90.1 (s) (lit.: 91.9, (s)).

Reaction of [(CO)$_5$Cr=C(OEt)Ph] (1a) with *t*BuP=C(NMe$_2$)$_2$ (3): A solution of **3** (0.21 g, 1.13 mmol) in *n*-pentane (10 mL) was added dropwise to a cold (−40 °C) solution of **1a** (0.37 g, 1.13 mmol) in *n*-pentane (15 mL). The mixture was allowed to warm up, and stirring was continued at 20 °C for 2 h. Upon storage at −28 °C $[\{tBuP{=}C(NMe_2)_2\}Cr(CO)_5]$ (**6**, 0.24 g, 55 %) separated from the solution as an orange powder. The supernatant solution was decanted and the solvent was evaporated subsequently to afford an oily mixture of $[\{tBuP{=}C(OEt)Ph\}Cr(CO)_5]$ (**8a**) and $(Me_2N)_2C{=}C(OEt)Ph$ (**10a**). Analytically pure **8a** could not be isolated due to decomposition. A few drops of the alkene **10a** were distilled off in vacuo (10^{-3} Torr) by means of a heat gun (200 → 240 °C air temperature).

Compound 6: IR (KBr): $\tilde{\nu}$ = 2043 (m), 1911 (vs), 1874 cm^{-1} (st) (C≡O). ^1H NMR: δ = 1.16 (d, J(P,H) = 13.8 Hz, 9H; $C(CH_3)_3$), 2.45 (br, 12H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR: δ = 31.4 (d, J(P,C) = 11.5 Hz, $C(CH_3)_3$), 33.8 (d, J(P,C) = 23.0 Hz, $C(CH_3)_3$), 42.6 (br, $N(CH_3)_2$), 204.5 (d, J(P,C) = 52.9 Hz, P=*C*), 219.9 (d, J(P,C) = 4.6 Hz, $(CO)_{eq}$), 225.3 (J(P,C) = 3.5 Hz, $(CO)_{ax}$); $^{31}P\{^1H\}$ NMR: δ = −1.2 (s); elemental analysis calcd (%) for $C_{14}H_{21}CrN_2O_5P$ (380.30): C 44.22, H 5.57, N 7.37; found C 43.93, H 5.53, N 7.25.

Compound 8a: IR (KBr): $\tilde{\nu}$ = 2063 (w), 1917 cm^{-1} (vs) (C≡O); ^1H NMR: δ = 0.86 (t, J(H,H) = 6.9 Hz, 3H; OCH_2CH_3), 1.43 (d, J(P,H) = 13.9 Hz, 9H; $C(CH_3)_3$), 3.27 (q, J(H,H) = 6.9 Hz, 2H; OCH_2CH_3), 7.08 – 7.23 (m, 5H; *H*-phenyl); $^{13}C\{^1H\}$ NMR: δ = 14.6 (s, OCH_2CH_3), 30.3 (s, $C(CH_3)_3$), 34.4 (s, $C(CH_3)_3$), 68.3 (s, OCH_2CH_3), 128.8 (s), 130.1 (d, J(P,C) = 13.8 Hz, *o*-*C*-phenyl), 130.3 (s, *C*-phenyl), 135.8 (d, J(P,C) = 19.5 Hz, *i*-*C*-phenyl), 204.4 (d, J(P,C) = 20.7 Hz, P=*C*), 216.3 (d, J(P,C) = 14.9 Hz, $(CO)_{eq}$), 222.2 (d, J(P,C) = 4.6 Hz, $(CO)_{ax}$); $^{31}P\{^1H\}$ NMR: δ = 180.1 (s).

Compound 10a: ^1H NMR: δ = 1.26 (t, J(H,H) = 7.1 Hz, 3H; OCH_2CH_3), 2.33 (s, 6H; $N(CH_3)_2$), 2.60 (s, 6H; $N(CH_3)_2$), 3.51 (q, J(H,H) = 7.1 Hz, 2H; OCH_2CH_3), 7.30 – 7.00 (m, 5H; *H*-phenyl); $^{13}C\{^1H\}$ NMR: δ = 15.7 (s, OCH_2CH_3), 39.4 (s, NCH_3), 40.3 (s, NCH_3), 67.8 (s, OCH_2CH_3), 123.7 (s), 125.1 (s), 125.7 (s, *C*-phenyl), 140.0 (s, *C*(OEt)Ph), 146.6 (s, $C(NMe_2)_2$); MS/CI: *m*/*z*: 235 $[M+H]^+$; elemental analysis calcd (%) for $C_{14}H_{22}N_2O$ (234.34): C 71.76, H 9.46, N 11.95; found C 71.37, H 9.41, N 11.10.

Reaction of [(CO)$_5$W=C(OEt)Ph] (2a) with *t*BuP=C(NMe$_2$)$_2$ (3): Analogously, a solution of **3** (0.12 g, 1.10 mmol) in *n*-pentane (20 mL) was combined with a cold solution (−40 °C) of **2a** (0.51 g, 1.10 mmol) in *n*-pentane (25 mL). After 2 h of stirring at 20 °C, the solution was filtered, and the filtrate was stored at −28 °C to afford $[\{tBuP{=}C(NMe_2)_2\}W(CO)_5]$ (**7**) as a yellow solid (0.26 g, 47 %). The solvent was evaporated from the mother liquor. The oily residue was a mixture of $[\{tBuP{=}C(OEt)Ph\}W(CO)_5]$ (**9a**) and $(Me_2N)_2C{=}C(OEt)Ph$ (**10**). Compound **9a** decomposed during work-up, whereas a few drops of **10a** were isolated by vacuum distillation.

Compound 7: IR (KBr): $\tilde{\nu}$ = 2054 (m), 1909 (s), 1868 cm^{-1} (s) (C≡O); ^1H NMR: δ = 1.16 (d, J(P,H) = 14.2 Hz, 9H; $C(CH_3)_3$), 2.33 (br, 12H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR: δ = 31.2 (d, J(P,C) = 23.9 Hz, $C(CH_3)_3$), 33.3 (d, J(P,C) = 31.9 Hz, $C(CH_3)_3$), 42.6 (br, $N(CH_3)_2$), 191.1 (s, $(CO)_{eq}$), 199.6 (s, $(CO)_{ax}$), 202.4 (d, J(P,C) = 32.5 Hz, P=*C*); $^{31}P\{^1H\}$ NMR: δ = −25.1 (s, J(P,W) = 153.5 Hz); elemental analysis calcd for $C_{14}H_{21}N_2O_5PW$ (512.20): C 32.83, H 4.13, N 5.47; found C 32.67, H 3.91, N 5.34.

Compound 9a: IR (KBr): $\tilde{\nu}$ = 2071 (m), 1982 (m), 1944 cm^{-1} (s) (C≡O); ^1H NMR: δ = 0.81 (t, J(H,H) = 7.0 Hz, 3H; OCH_2CH_3), 1.40 (d, J(P,H) = 14.2 Hz, 9H; $C(CH_3)_3$), 3.24 (q, J(H,H) = 7.0 Hz, 2H; OCH_2CH_3), 7.14 – 7.00 (m, 5H; *H*-phenyl); $^{13}C\{^1H\}$ NMR: δ = 14.7 (s, OCH_2CH_3), 30.3 (s, $C(CH_3)_3$), 38.5 (s, $C(CH_3)_3$), 68.5 (s, OCH_2CH_3), 128.3 (s), 128.8 (s), 130.1 (d, J(P,C) = 13.7 Hz, o-*C*-phenyl), 130.3 (s, *C*-phenyl), 135.8 (d, J(P,C) = 18.4 Hz, *i*-*C*-phenyl), 196.4 (d, J(P,C) = 9.2 Hz, $(CO)_{eq}$), 199.0 (d, J(P,C) = 28.7 Hz, $(CO)_{ax}$), 202.1 (d, J(P,C) = 32.2 Hz, P=*C*); $^{31}P\{^1H\}$ NMR: δ=143.2 (s, J(P,W)=253.9 Hz).

Reaction of [(CO)$_5$Cr=C(OEt)Ph] (1a) with Me$_3$SiP=C(NMe$_2$)$_2$ (4): The combination of *n*-pentane solutions of **4** (0.55 g, 2.70 mmol, 15 mL) and **1a** (0.88 g, 2.70 mmol, 30 mL) at −40 °C and stirring at 20 °C for 2 h afforded yellow solid (0.52 g, 52 %) $[\{Me_3SiP{=}C(NMe_2)_2\}Cr(CO)_5]$ (**11**) which precipitated from the reaction mixture at −28 °C. The solvent was evaporated to dryness to afford a mixture of (*E*/*Z*)-$[\{Me_3SiP{=}C(OEt)Ph\}Cr(CO)_5]$ (**13a**) and $(Me_2N)_2C{=}C(OEt)Ph$ (**10a**). Compound **13a** decomposed during work up, whereas **10a** was distilled off in vacuo.

Compound 11: IR (KBr): $\tilde{\nu}$ = 2044 (s), 1907 (s) (C≡O), 1260 (w) (δ ($SiMe_3$)), 840 cm^{-1} (w) (ρ($SiMe_3$)); ^1H NMR: δ = 0.30 (d, J(P,H) = 6.3 Hz, 9H; $Si(CH_3)_3$), 2.48 (br, 12H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR: δ = 1.8 (d, J(P,C) = 14.9 Hz, $Si(CH_3)_3$), 43.1 (s, $N(CH_3)_3$), 203.6 (d, J(P,C) = 45.8 Hz, P=*C*), 219.9 (d, J(P,C)=5.7 Hz, $(CO)_{eq}$), 225.6 (s, $(CO)_{ax}$); $^{31}P\{^1H\}$ NMR: δ = −117.7 (s); elemental analysis calcd for $C_{13}H_{21}CrN_2O_5PSi$ (369.36): C 39.39, H 5.34, N 7.07; found C 39.60, H 5.53, N 6.78.

Compound 13a: IR (KBr): $\tilde{\nu}$ = 2062 (m), 1922 cm^{-1} (vs) (C≡O); ^1H NMR: δ = −0.06 (d, J(P,H) = 6.3 Hz) and 0.44 (d, J(H,H) = 5.7 Hz, 9H; $Si(CH_3)_3$), 0.84/1.08 (2t, 2 × J(H,H) = 6.9 Hz, 3H; OCH_2CH_3), 3.32/3.38 (2q, 2 × J(H,H) = 6.9 Hz, 2H; OCH_2CH_3), 7.00 – 7.13 (m, 5H; *H*-phenyl); $^{13}C\{^1H\}$ NMR: δ = 1.07/1.31 (2d, 2 × J(P,C) = 9.2 Hz, $Si(CH_3)_3$), 14.7/15.7 (2s, OCH_2CH_3), 68.0/68.7 (2s, OCH_2CH_3), 128.8 (s), 128.9 (s), 129.0 (s), 129.1 (s), 130.1 (s), 130.4 (s, *C*-phenyl), 137.2 (d, J(P,C) = 13.8 Hz, *i*-*C*-phenyl), 138.9 (s, *i*-*C*-phenyl), 214.6 (d, J(P,C) = 31.0 Hz) and 215.3 (d, J(P,C) = 11.5 Hz, P=*C*), 216.6 (d, J(P,C) = 13.8 Hz, $(CO)_{eq}$) and 217.6 (d, J(P,C) = 14.9 Hz, $(CO)_{eq}$), 222.7/223.9 (2d, 2 × J(P,C) = 5.7 Hz, (CO_{ax})); $^{31}P\{^1H\}$ NMR: δ = 131.0 (s), 123.7 (s).

Reaction of [(CO)$_5$W=C(OEt)Ph] (2a) with Me$_3$SiP=C(NMe$_2$)$_2$ (4): Analogously, reaction of **2a** (0.66 g, 1.44 mmol) and **4** (0.29 g, 1.44 mmol) in cold (−40 °C) *n*-pentane (50 mL) afforded $[\{Me_3SiP{=}C(NMe_2)_2\}W(CO)_5]$ (**12**) (0.40 g, 53 %) which separated from the reaction mixture at −28 °C as an orange solid. The mother liquor contained a mixture of $[\{Me_3SiP{=}C(OEt)Ph\}W(CO)_5]$ (**14a**) and $(Me_2N)_2C{=}C(OEt)Ph$ (**10a**). Compound **14a** could not be isolated due to decomposition, whereas **10a** was distilled off in vacuo.

Compound 12: IR (KBr): $\tilde{\nu}$ = 2056 (m), 1904 (s), 1864 (s) (C≡O), 1259 (w) (δ($SiMe_3$)), 843 cm^{-1} (w) (ρ($SiMe_3$)); ^1H NMR: δ = 0.27 (d, J(P,H) = 6.3 Hz, 9H; $Si(CH_3)_3$), 2.44 (br, 12H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR: δ = 1.6

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(d, J(P,C) = 14.9 Hz, Si(CH_3)$_3$), 43.2 (s, N(CH_3)$_2$), 199.7 (s, (CO)$_{eq}$), 201.6 (d, J(P,C) = 37.9 Hz, P=C), 202.4 (d, J(P,C) = 16.1 Hz, (CO)$_{ax}$); ^{31}P{^{1}H} NMR: $\delta = -141.3$ (s, J(P,W) = 143.7 Hz); elemental analysis calcd for $C_{13}H_{21}N_2O_5$SiPW (528.24): C 29.56, H 4.02, N 5.30; found C 29.13, H 4.12, N 5.32.

Compound 14a: IR (KBr): $\tilde{\nu} = 2059$ (w), 1920 cm^{-1} (s) (C≡O)x; ^{1}H NMR: $\delta = -0.09/0.41$ (2d, 2 × J(P,H) = 5.7 Hz, 9H; Si(CH_3)$_3$)), 0.79/1.05 (2d, 2 × J(H,H) = 7.6 Hz, 3H; OCH$_2$$CH_3$), 3.29/3.36 (2q, 2 × J(H,H) = 6.9 Hz, 2H; OCH_2CH$_3$), 7.00–7.13 (m, 5H; H-phenyl); ^{13}C{^{1}H} NMR: $\delta = 0.89$ (d, J(P,C) = 8.0 Hz) and 1.09 (d, J(P,C) = 10.4 Hz, Si(CH_3)$_3$), 14.7 (s, OCH$_2$$CH_3$), 68.8/69.3 (2s, OCH$_2CH_3$), 128.8 (s), 128.9 (s), 129.0 (s), 130.1 (s), 130.4 (s, C-phenyl), 137.4 (d, J(P,C) = 14.9 Hz, i-C-phenyl), 138.7 (s, i-C-phenyl), 192.2 (d, J(P,C) = 8.0 Hz) and 196.6 (d, J(P,C) = 6.9 Hz, (CO)$_{eq}$), 199.7 (d, J(P,C) = 10.4 Hz).and 201.1 (d, J(P,C) = 21.8 Hz, (CO)$_{ax}$), 212.4 (d, J(P,C) = 36.8 Hz) and 213.0 (d, J(P,C) = 21.8 Hz, P=C); ^{31}P{^{1}H} NMR: δ = 81.4 (s, J(P,W) = 204.2 Hz), 87.7 (s, J(P,W) = 197.3 Hz).

Reaction of [(CO)$_5$Cr=C(OEt)Ph] (1a) with HP=C(NMe$_2$)$_2$ (5): A solution of **5** (0.08 g, 0.61 mmol) in n-pentane (15 mL) was added dropwise to a cold (−40 °C) solution of **1a** (0.28 g, 0.61 mmol) in n-pentane (20 mL). A yellow precipitate separated, which upon warming decomposed to a brown oil.

Reaction of [(CO)$_5$W=C(OEt)Ph] (2a) with HP=C(NMe$_2$)$_2$ (5): Analogously, combination of equimolar amounts of **2a** and **5** (0.61 mmol) in n-pentane at −40 °C led to a yellow precipitate which decomposed to a brown oil upon warming to room temperature.

Reaction of [(CO)$_5$W=C(OEt)(2-MeC$_6$H$_4$)] (2b) with Me$_3$SiP=C(NMe$_2$)$_2$ (4): A solution of **4** (0.35 g, 1.72 mmol) in n-pentane (20 mL) was added dropwise to a cold solution (−40 °C) of **2b** (0.81 g, 1.72 mmol) in n-pentane (30 mL). The solution was warmed to ambient temperature, stirred for 2 h and filtered. Storing the filtrate at −28 °C afforded **12** (0.35 g, 39 %) as a yellow precipitate. The mother liquor was concentrated to ≈30 mL and stored at −28 °C to yield (E/Z)-[{Me$_3$SiP=C(OEt)(2-MeC$_6$H$_4$)}W(CO)$_5$] (**14b**) (0.14 g, 14 %) as orange crystals. The supernatant solution was decanted and subsequently freed from solvent to afford an orange oil which contained (Me$_2$N)$_2$C=C(OEt)(2-MeC$_6$H$_4$) (**10b**). A few drops of the alkene **10b** were distilled off in vacuo (10^{-3} Torr) by means of a heat gun (200–240 °C air temperature).

Compound 14b: IR (KBr): $\tilde{\nu} = 2075$ (m), 1924 (s) (C≡O), 1256 (w) (δ(SiMe$_3$)), 844 cm^{-1} (w) (ρ(SiMe$_3$)); ^{1}H NMR: $\delta = -0.11$ (d, J(P,H) = 6.3 Hz) and 0.41 (d, J(P,H) = 5.7 Hz, 9H; Si(CH_3)$_3$), 0.72/1.00 (2t, 2 × J(H,H) = 7.0 Hz, 3H; OCH$_2$$CH_3$), 1.94/2.07 (2s, 3H; C$H_3$), 3.15–3.30 (m, 2H; OC$H_2CH_3$), 6.65–7.05 (m, 4H; C$_6H_4$); ^{13}C{^{1}H} NMR: $\delta = 0.8$ (d, J(P,C) = 10.4 Hz) and 1.4 (s, Si(CH_3)$_3$), 14.6/14.7 (2s, OCH$_2$$CH_3$), 19.1/19.2 (2s, aryl-$CH_3$), 67.9 (d, J(P,C) = 4.6 Hz) and 68.3 (s, OCH$_2$CH$_3$), 130.2 (s), 130.3 (s), 130.4 (s), 130.7 (s), 131.0 (s), 131.1 (s, C-aryl), 135.4 (d, J(P,C) = 10.3 Hz, Me-C-aryl), 135.5 (d, J(P,C) = 10.5 Hz, Me-C-aryl), 136.7 (d, J(P,C) = 12.6 Hz, i-C-aryl), 138.1 (s, i-C-phenyl), 196.4/197.2 (2d, 2 × J(P,C) = 8.0 Hz, (CO)$_{eq}$), 199.7/201.1 (2d, 2 × J(P,C) = 23.0 Hz, (CO)$_{ax}$), 212.3 (d, J(P,C) = 37.9 Hz) and 212.6 (d, J(P,C) = 25.3 Hz, P=C); ^{31}P{^{1}H} NMR: $\delta = 73.7$ (s, J(P,W) = 206.5 Hz), 79.9 (s, J(P,W) = 195.0 Hz); elemental analysis calcd for $C_{18}H_{21}O_6$SiPW (576.27): C 37.52, H 3.67; found C 37.24, H 3.84.

Compound 10b: ^{1}H NMR: $\delta = 1.14$ (t, J(H,H) = 6.9 Hz, 3H; OCH$_2$CH_3), 2.24 (s, 6H; NCH_3), 2.69 (s, 6H; NCH_3), 2.32 (s, 3H; aryl-CH_3), 3.31 (q, J(H,H) = 6.9 Hz, 4H; OCH_2CH$_3$), 7.04–7.18 (m, 4H; H-aryl); ^{13}C{^{1}H} NMR: $\delta = 16.2$ (s, OCH$_2$$CH_3$), 20.6 (s, C$H_3$), 40.3 (s, NC$H_3$), 40.4 (s, NC$H_3$), 64.9 (s, OCH$_2CH_3$), 125.6 (s), 126.1 (s), 126.3 (s), 130.5 (s), 130.7 (s, C-aryl), 137.0 (s, Me-C-aryl), 138.3 (s, C(OEt)(aryl)), 145.2 (s, C(NMe$_2$)$_2$); MS/CI: m/z: 249 [M+H]$^+$.

Reaction of [(CO)$_5$W=C(OEt)(2-MeOC$_6$H$_4$)] (2c) with tBuP=C(NMe$_2$)$_2$ (3): A solution of **3** (0.19 g, 0.78 mmol) in n-pentane (10 mL) was added dropwise to a cold (−60 °C) solution of **2c** (0.38 g, 0.78 mmol) in n-pentane (15 mL). The solution was warmed to 20 °C, stirred for 3 h and filtered. The filtrate was stored at −16 °C to afforded **7** (0.12 g, 29 %) as a yellow powder. The mother liquor was concentrated to ca half its volume and crystallizing at −16 °C led to the separation of [{tBuP=C(OEt)(2-MeOC$_6$H$_4$)}W(CO)$_5$] (**9c**) (0.18 g, 39 %) as orange crystals. The mother liquor was concentrated, and the remaining orange oil was distilled in vacuo (0.03 Torr, 200–240 °C) with heat gun to give a few drops of a mixture of (E,Z)-[(EtO)(2-MeOC$_6$H$_4$)C]$_2$ (**15**) and (Me$_2$N)$_2$C=C(OEt)(2-MeOC$_6$H$_4$) (**10c**) as a yellow oil.

Compound 9c: IR (KBr): $\tilde{\nu} = 2071$ (s), 1983 (s), 1941 (vs), 1930 (vs), 1897 cm^{-1} (vs) (C≡O); ^{1}H NMR: $\delta = 0.86$ (t, J(H,H) = 7.2 Hz, 3H; OCH$_2$$CH_3$), 1.45 (d, J(P,H) = 14.5 Hz, 9H; C(CH_3)$_3$), 3.20 (s, 3H; OCH_3), 3.28–3.54 (m, 2H; OCH_2CH$_3$), 6.37–7.31 (m, 4H; C$_6H_4$); ^{13}C{^{1}H} NMR: $\delta = 14.8$ (s, OCH$_2$$CH_3$), 30.3 (s, C(C$H_3$)$_3$), 38.0 (s, C(CH$_3$)$_3$), 54.8 (s, OCH$_3$), 67.7 (s, OCH$_2CH_3$), 111.0 (s), 120.8 (s), 124.1 (d, J(P,C) = 18.4 Hz, o-C-aryl), 132.2 (s, C-aryl), 134.1 (d, J(P,C) = 16.1 Hz, i-C-aryl), 157.3 (d, J(P,C) = 11.5 Hz, o-C-aryl), 196.4 (d, J(P,C) = 9.2 Hz, (CO)$_{eq}$), 199.5 (s, (CO)$_{ax}$), 199.5 (d, J(P,C) = 60.9 Hz, P=C); ^{31}P{^{1}H} NMR: $\delta = 131.3$ (s, J(P,W) = 237.1 Hz); elemental analysis calcd for $C_{19}H_{21}O_7$PW (576.20): C 39.61, H 3.67; found C 39.61, H 3.72.

Compound 10c: ^{1}H NMR: $\delta = 1.26$ (t, J(H,H) = 7.2 Hz, 3H; OCH$_2$CH_3), 2.33 (s, 6H; NCH_3), 2.75 (s, 6H; NCH_3), 3.35 (s, 3H; OCH_3), 3.59 (q, J(H,H) = 7.1 Hz, 4H; OCH_2CH$_3$), 6.62–7.30 (m, 4H; H-aryl); ^{13}C{^{1}H} NMR: $\delta = 16.1$ (s, OCH$_2$$CH_3$), 40.0 (s, NC$H_3$), 40.1 (s, NC$H_3$), 55.0 (s, OC$H_3$), 66.4 (s, OCH$_2CH_3$), 111.0 (s), 120.5 (s), 122.4 (s), 126.4 (s, C-aryl), 129.2 (s, i-C-aryl), 130.4 (s, =C(OEt)(aryl)), 146.3 (s,=C(NMe$_2$)$_2$), 157.3 (s, o-C-aryl); MS/CI: m/z: 264 [M]$^+$; elemental analysis calcd for $C_{15}H_{24}N_2O_4$ (264.37): C 68.15, H 9.15, N 10.60; found C 66.45, H 8.76, N 10.28.

Compound 15: ^{1}H NMR: $\delta = 1.05$ (t, J(H,H) = 6.9 Hz, 6H; OCH$_2$CH_3), 3.28 (s, 6H; OCH_3), 4.18 (q, J(H,H) = 7.1 Hz, 4H; OCH_2CH$_3$), 6.44–7.30 (m, 8H; C$_6H_4$); ^{13}C{^{1}H} NMR: $\delta = 16.1$ (s, OCH$_2$$CH_3$), 55.0 (s, OC$H_3$), 66.4 (s, OCH$_2CH_3$), 112.3–159.3 (s, C-aryl), 169.7 (s, C=O); MS/CI: m/z: 327 [M − H]$^+$.

Reaction of [(CO)$_5$W=C(OEt)(2-MeOC$_6$H$_4$)) (2c) with Me$_3$SiP=C-(NMe$_2$)$_2$ (4): Compound **2c** (0.60 g, 1.23 mmol) and **4** (0.25 g, 1.23 mmol) were added to a cold solution of n-pentane (50 mL, −50 °C). The reaction mixture was subsequently warmed and stirred for 2 h at room temperature and afforded a yellow solution. Storing at −28 °C overnight led to the precipitation of **12** (0.33 g, 51 %). The mother liquor was concentrated to about 30 mL; crystallization at −28 °C gave a mixture of (E/Z)-[{Me$_3$-SiP=C(OEt)(2-MeOC$_6$H$_4$)}W(CO)$_5$] (**14c**) as an orange solid (0.15 g, 21 %). The mother liquor was concentrated and the dark-orange oily residue was distilled in vacuo (10^{-3} Torr) with a heat gun (200–240 °C) to give (Me$_2$N)$_2$C=C(OEt)(2-MeOC$_6$H$_4$) (**10c**) as a light yellow oil.

Compound 14c: IR (KBr): $\tilde{\nu} = 2069$ (m), 1936 (s), 1884 (s) (C≡O), 1245 (w) (δ(SiMe$_3$)), 842 cm^{-1} (w) (ρ(SiMe$_3$)); ^{1}H NMR: $\delta = -0.03$ (d, J(P,H) = 6.9 Hz) and 0.44 (d, J(P,H) = 5.7 Hz, 9H; Si(CH_3)$_3$), 0.85/1.09 (2t, 2 × J(H,H) = 6.9 Hz, 3H; OCH$_2$$CH_3$), 3.10/3.21 (2s, 3H; OC$H_3$), 3.38–3.44/3.58–3.63 (2m, 2H; OCH_2CH$_3$), 6.27–7.18 (m, 4H; C$_6H_4$); ^{13}C{^{1}H} NMR: $\delta = 0.9$ (s) and 0.9 (d, J(P,C) = 18.3 Hz, Si(CH_3)$_3$), 14.7/14.8 (2s, OCH$_2$$CH_3$), 54.9/55.0 (2s, OCH$_3$), 67.9/68.5 (2s, OCH$_2CH_3$), 110.7 (s), 111.1 (s), 120.3 (s), 120.8 (s), 125.8 (s), 125.9 (s), 132.0 (s), 132.1 (s, C-aryl), 132.3 (d, J(P,C) = 11.5 Hz, i-C-aryl), 132.8 (d, J(P,C) = 12.7 Hz), 155.8 (d, J(P,C) = 9.2 Hz, o-C-aryl), 156.3 (d, J(P,C) = 9.2 Hz, i-C-aryl), 196.6 (d, J(P,C) = 6.9 Hz) and 197.4 (d, J(P,C) = 8.0 Hz, (CO)$_{eq}$), 201.1 (d, J(P,C) = 24.1 Hz) and 201.5 (d, J(P,C) = 21.8 Hz, (CO)$_{ax}$), 210.3 (d, J(P,C) = 40.2 Hz) and 211.1 (d, J(P,C) = 24.1 Hz, P=C); ^{31}P{^{1}H} NMR: $\delta = 63.9$ (s, J(P,W) = 206.5 Hz), 74.7 (s, J(P,W) = 195.0 Hz); elemental analysis calcd for $C_{18}H_{21}O_7$SiPW (592.27): C 36.50, H 3.57; found C 36.06, H 3.54.

[{(E)-(Me$_2$N)$_2$CH-P=C(OEt)(2-MeOC$_6$H$_4$)}W(CO)$_5$] [(E)-16] and **[{(Z)-(Me$_2$N)$_2$CH-P=C(OEt)(2-MeOC$_6$H$_4$)}W(CO)$_5$] [(Z)-16]**: Treatment of **2c** (0.81 g, 1.70 mmol) with HP=C(NMe$_2$)$_2$ (**5**) (0.22 g, 1.70 mmol) in cold (−60 °C) n-hexane (35 mL), and stirring for 2 h at room temperature afforded an orange-red solution. The solution was filtered off and the filtrate was stored at −16 °C. A mixture of compounds (E)-(**16**) and (Z)-(**16**) (0.84 g, 80 %) separated as orange crystals. IR (KBr): $\tilde{\nu} = 2069$ (m), 2044 (m), 1934 (vs), 1918 (vs), 1870 cm^{-1} (s) (C≡O); (Z)-(**16**): ^{1}H NMR: $\delta = 0.79$ (s, 3H; OCH$_2$$CH_3$), 2.38 (s, 12H; N(C$H_3$)$_2$), 3.06 (s, 3H; OC$H_3$), 3.52 (br s, 1H; C(NMe$_2$)$_2$$H$), 4.39 (br s, 2H; OC$H_2CH_3$), 6.27–7.10 (m, 4H; C$_6H_4$); ^{13}C{^{1}H} NMR: $\delta = 14.8$ (s, OCH$_2$$CH_3$), 41.3 (s, N($CH_3$)$_2$), 55.2 (s, OCH$_3$), 67.4 (s, OCH$_2CH_3$), 111.4 (s), 121.0 (s), 132.2 (s, C-aryl), 133.2 (d, J(P,C) = 14.9 Hz, i-C-aryl), 196.7 (d, J(P,C) = 8.0 Hz, P=C), 199.8 (d, J(P,C) = 28.7 Hz, (CO)$_{eq}$), 201.7 (d, J(P,C) = 34.5 Hz, (CO)$_{ax}$); ^{31}P{^{1}H} NMR: $\delta = 102.1$ (s, J(P,W) = 222.3 Hz); (E)-(**16**): ^{1}H NMR: $\delta = 1.09$ (s, 3H; OCH$_2$$CH_3$), 2.38 (s, 12H; N(C$H_3$)$_2$), 3.25 (s, 3H; OC$H_3$), 3.52 (br s, 1H; C(NMe$_2$)$_2$$H$), 4.39 (br s, 2H; OC$H_2CH_3$), 6.27–7.10 (m, 4H; C$_6H_4$); ^{13}C{^{1}H} NMR: $\delta = 14.8$ (s, OCH$_2$$CH_3$), 41.8 (s, N($CH_3$)$_2$), 54.7 (s, OCH$_3$), 67.1 (s, OCH$_2CH_3$), 110.8 (s), 120.3 (s), 131.6 (s, C-aryl), 132.0 (d, J(P,C) = 12.7 Hz, i-C-aryl), 197.2 (d, J(P,C) = 13.0 Hz, P=C), 199.8 (d, J(P,C) = 28.7 Hz,

Table 1. Crystallographic data for **9c**, **14b**, and (*Z*)-**16**.

	9c	**14b**	(*Z*)-**16**
formula	$C_{19}H_{21}O_7PW$	$C_{18}H_{21}O_6PSiW$	$C_{20}H_{25}N_2O_7PW$
color	light yellow	yellow	orange
size [mm^3]	$0.21 \times 0.17 \times 0.07$	$0.30 \times 0.24 \times 0.22$	$0.6 \times 0.2 \times 0.2$
M_r	576.18	576.26	620.24
diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Siemens $P2_1$
system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	9.9690(1)	10.0170(1)	9.611(2)
b [Å]	21.6190(2)	19.9560(2)	13.038(4)
c [Å]	10.8240(1)	11.2680(1)	19.150(4)
β [°]	114.5330(3)	90.3570(4)	90.84(2)
V [Å^3]	2122.19(3)	2252.42(4)	2399.4(10)
ρ_{calcd} [g cm^{-1}]	1.803	1.699	1.717
Z	4	4	4
F(000)	1120	1120	1216
μ [mm^{-1}]	5.554	5.281	4.922
absorption corr.	multiscan from equivalents	multiscan from equivalents	semiempirical from Ψ scans
2θ range [°]	$4 < 2\theta < 50$	$6 < 2\theta < 55$	$4 < 2\theta < 60$
T [K]	100	100	173
refl. measured	50024	48316	7383
unique refl.	3731	5140	7005
refl. used	3731	5140	7005
refl $(I) > 2\sigma(I)$	3476	4852	5162
parameters	259	247	286
residual density [e Å^{-3}]	0.905	0.694	2.189
$R1$ $(I > 2(I))$	0.014	0.022	0.050
w$R2$(all data)	0.033	0.047	0.1280
remarks		disorder of C10 on three positions (46:31:23) disorder of C12 – C18 on two positions (58:42)	max. diff. peaks [> 1 e Å^{-3}] nearby $W1$ [0.77 – 0.79 Å]

$(CO)_{eq}$), 201.7 (d, J(P,C) = 34.5 Hz, $(CO)_{ax}$); $^{31}P\{^1H\}$ NMR: $\delta = 114.1$ (s, J(P,W) = 236.3 Hz); elemental analysis calcd for $C_{20}H_{25}N_2O_7PW$ (620.24): C 38.73, H 4.06, N 4.52; found C 38.45, H 4.18, N 4.41.

X-ray structural determinations: Table 1 summarizes the important parameters. All data were collected using $Mo_{K\alpha}$ radiation (0.71073 Å). Semiempirical absorption corrections applied. Programs used were DENZO and SCALEPACK, Siemens SHELXTL PLUS and SHELXL 97. The structures were solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms.[25]

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[25] 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-159897 (**9c**), -159898 (**14b**), -159899 ([*Z*]-**16**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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