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Reactivity of the Inversely Polarized Phosphaalkene $HP{=}C(NMe_2)_2$ Toward Carbene Tungsten Complexes $[(CO)_5W{=}C(R^1)OR^2]$ (R^1 = *c*-C_3H_5, *c*-C_5H_9; R^2 = Me, Et, Me_3Si): A Novel Access to η^1-Phosphaalkene Complexes $[(CO)_5W{-}P(R^2){=}C(H)NMe_2]$

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Reaction of equimolar amounts of the phosphaalkene $HP{=}C(NMe_2)_2$ (**6c**) and carbene complex $[(CO)_5W{=}C(OSiMe_3)(c\text{-}C_3H_5)]$ (**11a**) in *n*-pentane afforded the novel phosphaalkene complex $[(CO)_5W\text{-}\kappa\text{-}P\{Me_3SiP{=}C(H)NMe_2\}]$ (**12**). Under comparable conditions carbene complexes $[(CO)_5W{=}C(OR)(c\text{-}C_3H_5)]$ (**11b**, R = Me; **11c**, R = Et) were converted by the phosphaalkene to dinuclear 1,3-diphosphetane complexes $[\{(CO)_5W\}_2\text{-}\kappa\text{-}P\{RP{-}C(H)(NMe_2){-}P(R){-}C(H)NMe_2\}]$ (**13b**,**c**). In contrast with this, treatment of $[(CO)_5W{=}C(OEt)(c\text{-}C_5H_9)]$ (**11d**) with $XP{=}C(NMe_2)_2$ (X = H, D) gave rise to the formation of a bis(pentacarbonyltungsten) complex of a PH-functionalized 1,3-diphosphetane $[\{(CO)_5W\}_2\text{-}\kappa\text{-}P\{HP{-}C(X)(NMe_2){-}P(H){-}C(X)NMe_2\}]$ (**14**). The novel products were characterized by elemental analyses and IR and ^1H, ^{13}C, and ^{31}P NMR spectra. Moreover, the molecular structures of **12**, **13c**, and **14** were elucidated by X-ray structural analyses.

Introduction

The vast majority of phosphaalkenes feature an electron distribution $P^{\delta+}C^{\delta-}$ about the PC double bond, as would be anticipated from the different electronegativities of carbon (2.5) and phosphorus (2.1). Recently we have become interested in phosphaalkenes with an inverse polarity about the PC double bond, which expresses that negative charge is accumulated at the phosphorus atom and a deficiency of charge is left on the carbon atom. This situation is realized when one or two amino substituents are linked to the carbon atom of the P=C unit, establishing a planar 4π-electron phospha-eneamine moiety.[1]

When ferriophosphaalkene **1** (R = Cp*(CO)$_2$Fe) was exposed to 2 molar equiv of the ethoxy(methyl) carbene complexes **2a**,**b**, the formation of novel ferriophosphaalkene complexes **3a**,**b** and β-aminoalkenyl carbene complexes **4a**,**b** was observed.[2] The combination of the corresponding phenylcarbene complexes with **1** did not give tractable metathesis products. Instead, complex $[Cp^*(CO)_2Fe]_2$ (70%) and the adduct $[(CO)_5M\text{-}\kappa\text{-}P\{[Fe]\text{-}P{=}C(NMe_2)_2\}]$ (10%) were isolated. Obviously, in this reaction rupture of the Fe−P bond of **1** was the dominant process.[2]

Treatment of the *o*-anisylcarbene tungsten complex **5** with the metal-free phosphaalkenes $RP{=}C(NMe_2)_2$ (**6a**, R = *t*Bu; **b**, SiMe$_3$) gave a mixture of the complexes **7a**,**b** (as a result of ligand displacement) in addition to the metathesis products **8a**,**b** and alkene **9**.[3] The reaction of equimolar amounts of **5** and $HP{=}C(NMe_2)_2$ (**6c**) proceeded in a quite different way and led to the formation of the novel phosphaalkene complex **10** as a *E*/*Z*-mixture (1:2) (80% yield).[3] Decomposition occurred during reaction of **6c** with complexes $(CO)_5W{=}C(OEt)$-Ar (Ar = Ph, *o*-Tol). In the following we focused our interest on the reactivity of inversely polarized phosphaalkenes with Fischer carbene complexes displaying secondary alkyl or cycloalkyl substituents at the carbene carbon atom, which are less electron-withdrawing then aryl groups, but cannot be involved in condensations, such as primary alkyl substituents at the carbene center.

Results and Discussions

Cyclopropylcarbene complex **11a** was treated with an equimolar amount of phosphaalkene $HP{=}C(NMe_2)_2$ (**6c**)[4] in *n*-pentane in the range of −40 °C to room temperature. Phosphaalkene complex **12** separated from the filtered reaction mixture at −16 °C as orange air- and moisture-sensitive crystals in 47% yield. If the reaction vessel was purged with argon and the emitting gas was blubbled through hydrochloric acid, dimethylammonium chloride was isolated and unambigiously

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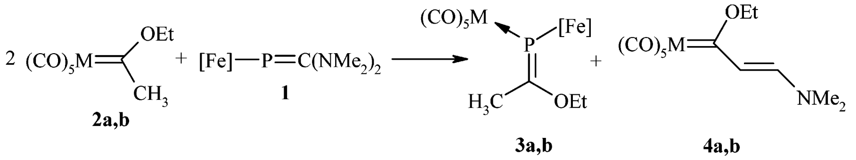
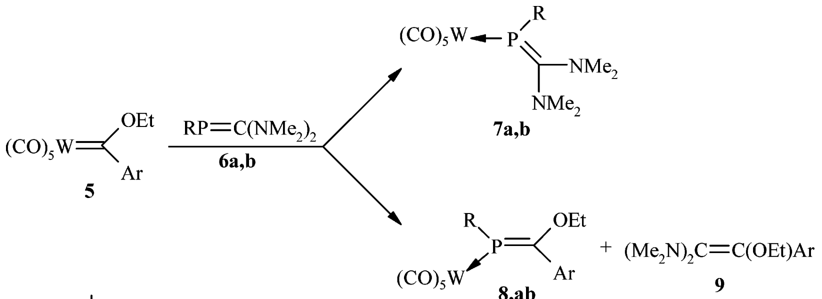
Publication on Web 10/31/2003

Scheme 1



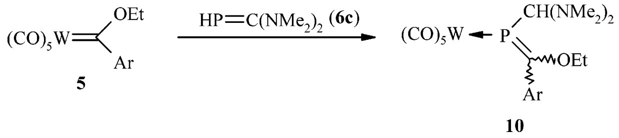
M = Cr, W; [Fe] = Cp*(CO)$_2$Fe

Scheme 2

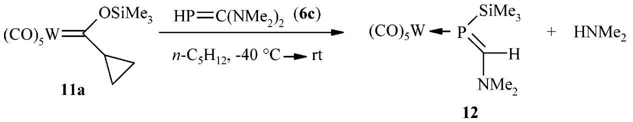


6 - 8	R	Ar
a	*t*Bu	2-MeOC$_6$H$_4$
b	Me$_3$Si	2-MeOC$_6$H$_4$

Scheme 3



Scheme 4



identified. Product **12** is a pentacarbonyltungsten complex of the yet unkown phosphaalkene Me$_3$SiP=C(H)-NMe$_2$. The ^{31}P{^{1}H} NMR spectrum of the complex displayed a singlet at δ −59.8 with ^{183}W satellites ($^1J_{WP}$ = 185.9 Hz). If one regards that the replacement of one dimethylamino group in *t*BuP=C(NMe$_2$)$_2$ (δ 91.9)[3,5] by a hydrogen atom leads to a deshielding $\Delta\delta^{31}$ of 27.1 in *t*BuP=C(H)NMe$_2$[6] and if one assumes that a similar deshielding occurs on going from Me$_3$-SiP=C(NMe$_2$)$_2$ (δ^{31}P −47.1)[7] to Me$_3$SiP=C(H)NMe$_2$, the phosphorus resonance of this ligand may roughly be estimated as δ −20. Consequently, upon ligation to the [W(CO)$_5$] fragment, the ^{31}P nucleus in **12** experiences a shift of ca. 40 ppm to high field. This shielding is much less pronounced than that of the ligand in [(CO)$_5$W-κ-*P*{Me$_3$SiP=C(NMe$_2$)$_2$}] (δ −141.3).[3]

In the ^{1}H NMR spectrum of **12** the proton at the P=C bond is observed as a singlet at δ 8.17. The corresponding resonances in R−P=C(H)NMe$_2$ (R = Mes, *t*Bu, Ph, Me) appear as doublets at δ 8.08−8.71 ($^2J_{PH}$ = 14.9−16.4 Hz).[6]

The absence of a PH coupling in **12** points to a mutual trans-orientation of the hydrogen atom and the W−P vector. The ^{13}C NMR signal of the tricoordinate carbon atom was encountered as a doublet at δ 184.3 ($^1J_{PC}$ = 6.9 Hz). For *t*Bu−P=C(H)NMe$_2$ the respective resonance was registered at δ 187.5 ($^1J_{PC}$ = 48.0 Hz).[6]

Comparison of the ^{13}C NMR signal of the axial carbonyl in **12** (δ 200.6 d, $^2J_{PC}$ = 21.8 Hz) with that in [(CO)$_5$W-κ-*P*{Me$_3$SiP=C(NMe$_2$)$_2$}] (δ 202.4 d, $^2J_{PC}$ = 16.1 Hz)[3] agrees with the lower donor capacity of Me$_3$SiP=C(H)NMe$_2$ with respect to Me$_3$SiP=C(NMe$_2$)$_2$. This fact is also reflected in the IR spectra of both compounds [**12**: ν(CO) 2063, 1913, 1889 cm^{-1}; [(CO)$_5$W-κ-*P*{Me$_3$-SiP=C(NMe$_2$)$_2$}]: ν(CO) 2056, 1904, 1864 cm^{-1}], where a hypsochromic shift of the carbonyl stretches was observed for **12**.

Orange crystals, obtained from a pentane solution of **12** at −16 °C, were subjected to an X-ray structure determination. The analysis of **12** (Figure 1) features an *E*-configurated phosphaalkene ligand which is η^1-coordinated to a [W(CO)$_5$] fragment. The bond length W(1)−P(1) [2.5740(12) Å] is considerably longer than that of [(CO)$_5$W-κ-*P*{Me$_3$SiP=C(OEt)(2-MeC$_6$H$_4$)}] [2.5139(8) Å][3] and compares well with the respective bond length in [(CO)$_5$W-κ-*P*{Cp*(CO)$_2$FeP=C(OEt)Me}] [2.567(3) Å][2]. The double-bond length P(1)−C(9) [1.731(5) Å] falls in the range 1.70−1.76 Å encountered in a series of *C*-amino-substituted phosphaalkenes where π-delocalization between the lone pair at nitrogen and the PC-π-bond is operating.[1,7] In line with this, the short distance N(1)−C(9) [1.314(6) Å] is due to multiple bonding. The coordination geometry about N(1) is trigonal-planar (sum of angles 359.9°), whereas the P atom is slightly pyramidalized (sum of angles 350.3°). This bonding situation is between that of classically polarized phosphaalkenes (where the PC bond lengths remain uneffected by metal coordination and the P atom is planarly configurated) and that of complexes with inversely polarized phosphaalkene ligands with a sig-

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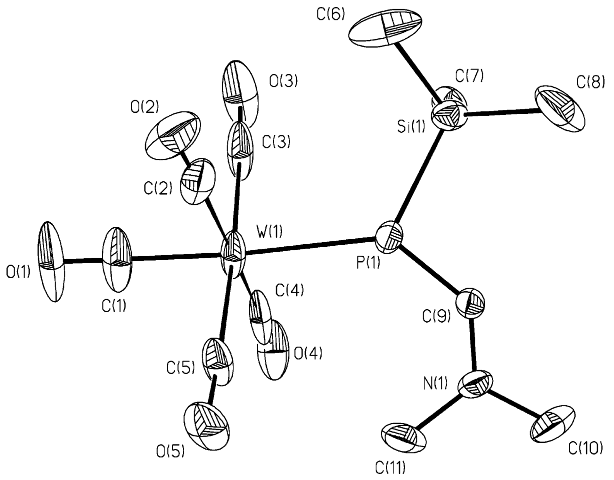
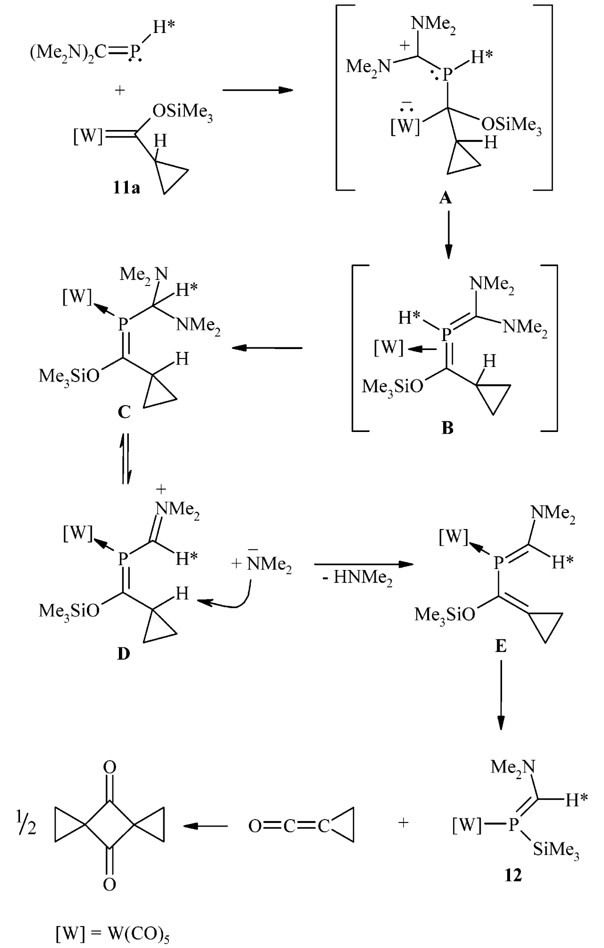


Figure 1. Molecular structure of **12** in the crystal. Selected bond lengths [Å] and angles [deg]: W(1)−P(1) 2.5740(12), P(1)−C(9) 1.731(5), P(1)−Si(1) 2.2463(18), N(1)−C(9) 1.314(6), N(1)−C(10) 1.449(7), N(1)−C(11) 1.450(7), W(1)−C(1) 1.978(6), W(1)−C(2−5) 2.024(7)−2.045(6); W(1)−P(1)−Si(1) 120.03(6), W(1)−P(1)−C(9) 130.65(17), Si(1)−P(1)−C(9) 99.58(16), P(1)−C(9)−N(1) 132.6(4), C(9)−N(1)−C(10) 121.6(5), C(9)−N(1)−C(11) 122.5(5), C(10)−N(1)−C(11) 115.8(5).

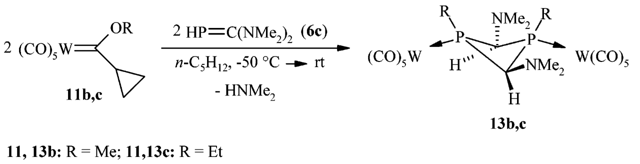
nificant PC bond elongation and trigonal pyramidal P atoms as well as short CN bonds [cf. $Cp^*(CO)_2FeP[Cr(CO)_5]{=}C(NMe_2)_2$; P−C = 1.793(5) Å, N−C = 1.355 (av) Å, sum of angles at P = 346.1°].[8] The bond length P(1)−Si(1) of 2.2463(18) Å is significantly shorter as in $[(CO)_5W\text{-}\kappa\text{-}P\{Me_3SiP{=}C(OEt)(2\text{-}MeC_6H_4)\}]$ [2.2720(11) Å][3]. The angle Si(1)−P(1)−C(9) [99.58(16)°] is more acute than in the previous compound [105.81(11)°].

It is conceivable that the formation of **12** was initiated by the nucleophilic attack of the electron-rich P atom of the phosphaalkene at the carbene carbon atom of **11a** to give zwitterion **A**. **A** underwent rearrangement to phosphaalkene complex **C** via intermediate bis(methylene)phosphorane **B**. Elimination of dimethylamine from **C** furnished 2-phosphabuta-1,4-diene **E**, which finally experienced a 1,3-(O → P) silyl migration and extrusion of cyclopropylidene ketene. The latter species most certainly dimerized to a cyclobutadiene-1,3-dione derivative. In the mass spectrum (CI/NH_3) of the reaction mixture a peak at 126 [M + NH_4] was tentatively assigned to 2,3-bis(ethane-1,2-diyl)cyclopropanone, which originated from the dimer by loss of CO (Scheme 5).

Scheme 5



Scheme 6



Our investigations were extended to cyclopropyl(methoxy)- and cyclopropyl(ethoxy)carbene complexes **11b**[9] and **11c**.[10] Reaction with equimolar amounts of $HP{=}C(NMe_2)_2$ in *n*-pentane at −50 °C to room temperature led to the formation of the bis(pentacarbonyl)-1,3-diphosphetane complexes **13b** and **13c**, which were obtained from pentane solutions at −16 °C as yellow to orange crystals in 60% and 72% yield, respectively. In many cases 1,3-diphosphetanes result from a [2+2] head-to-tail dimerization of sterically unsufficiently protected phosphaalkenes. Accordingly, it is most likely that phosphaalkene complexes analogous to **12** were initially generated and subsequently suffered from self-dimerization. The ^1H NMR spectrum of **13b** reveals a doublet at δ 2.09 ($^2J_{PC}$ = 3.8 Hz) for the PCH_3 protons and a triplet at δ 3.45 ($^2J_{PC}$ = 10.1 Hz) for the protons at the four-membered ring. In the uncomplexed ligand the corresponding resonances were located at δ 1.4 ($^2J_{PC}$ = 3.0 Hz) and 2.4 (^2J = 8.0 Hz).[6] The ^{31}P NMR signal of the free 1,3-diphosphetane (δ −22.7) is significantly shifted to low field upon complexation (δ 30.3, $^1J_{PW}$ = 218.1 Hz). The ring carbons of the free ligand were registered as a singlet at δ 64.1,[6] whereas in complex **13b** they were attributed to a triplet at δ 60.5 ($^1J_{PC}$ = 29.7 Hz). From the inspection of the IR spectra in the region of the CO-stretching vibrations (**13b**: ν 2074, 2067, 1916 cm^{-1}) it is obvious that the 1,3-diphosphetane transfers less electron density onto the $[W(CO)_5]$ fragment than the phosphaalkene ligand in **12**. Similar observations were made with **13c**.

Orange crystals grown from an *n*-pentane solution of **13c** were subjected to an X-ray structure determination (Figure 2). The analysis displays the picture of a puckered 1,3-diphosphetane. The planes defined by atoms P(1), C(11), C(12) and P(2), C(11), C(12) enclose

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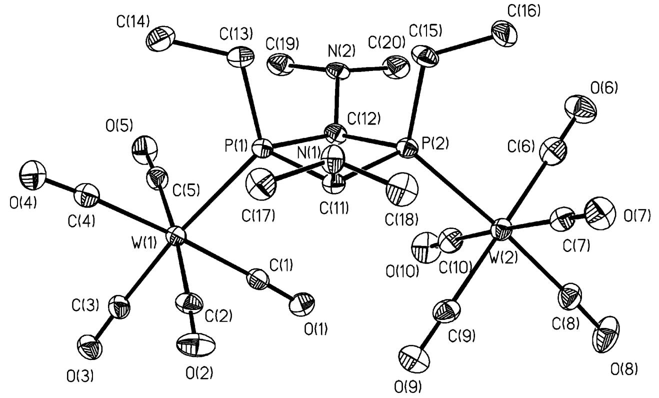


Figure 2. Molecular structure of **13c** in the crystal. Selected bond lengths [Å] and angles [deg]: W(1)−P(1) 2.5221(12), W(2)−P(2) 2.5135(2), P(1)−C(11) 1.886(5), P(1)−C(12) 1.885(5), P(1)−C(13) 1.850(5), P(2)−C(11) 1.882(5), P(2)−C(12) 1.892(5), P(2)−C(15) 1.851(5), C(11)−N(1) 1.451(6), N(1)−C(17) 1.469(6), N(1)−C(18) 1.462(6), C(12)−N(2) 1.452(6), N(2)−C(19) 1.473(6), N(2)−C(20) 1.462(7); W(1)−P(1)−C(11) 115.33(15), W(1)−P(1)−C(12) 115.40(15), W(1)−P(1)−C(13) 125.24(16), W(2)−P(2)-C(11) 118.09(15), W(2)−P(2)−C(12) 117.51(15), W(2)−P(2)−C(15) 123.02(17), C(11)−P(1)−C(12) 85.0(2), P(1)−C(12)−P(2) 93.7(2), C(11)−P(2)−C(12) 84.9(2), P(1)−C(11)−P(2) 94.0(2), C(11)−N(1)−C(17) 112.2(4), C(11)−N(1)−C(18) 110.2(4), C(17)−N(1)−C(18) 109.7(4), C(12)−N(2)−C(19) 111.1(4), C(12)−N(2)−C(20) 111.1(4), C(19)−N(2)−C(20) 109.9(4); C(12)−P(1)−C(11)−P(2) 11.9, C(12)−P(2)−C(11)−P(1) −11.9, C(11)−P(1)−C(12)−P(2) −11.8, C(11)−P(2)−C(12)−P(1) 11.9.

a dihedral angle $\psi = 163.8°$. Two [W(CO)$_5$] units are ligated to the phosphorus atoms via W−P single bonds of 2.5221(12) and 2.5135(12) Å. The endocyclic P−C bonds [1.882(5)−1.892(5) Å] are well comparable with those in the related 1,3-diphosphetane [PhPC(H)NMe$_2$]$_2$ (1.89 Å$_{av}$)[11] and thus elongated relative to the standard value of PC single bonds (1.85 Å).[12]

The endocyclic angles at P(1) [85.0(4)°] and P(2) [84.9(2)°] are more acute than those at the carbon atoms C(11) [94.0(2)°] and C(12) [93.7(2)°]. The ethyl groups at the P atoms are located in axial positions and the dimethylamino groups occupy equatorial positions at the four-membered heterocycle. Thus, all four substituents are in mutual cis-orientations. This geometry contrasts with the structure of [PhPC(H)NMe$_2$]$_2$, where the phenyl groups and the amino substituents are trans-orientated like in the monomeric precursor.[11] The bulky [W(CO)$_5$] units are placed in equatorial positions at the P atoms.

Cyclopentyl(ethoxy) carbene complex **11d** was reacted with XP═C(NMe$_2$)$_2$ (X = H, D) in order to obtain further information on the mechanism of this novel reaction as well as on the fate of the cycloalkyl carbene ligand. Reaction of **11d** and **6c** in *n*-pentane in the range from −40 °C to room temperature did not give the expected complex **13c**. Instead the PH-functionalized 1,3-diphosphetane complex **14** was obtained from *n*-pentane at −16 °C as colorless crystals (42% yield) (Scheme 7).

With DP═C(NMe$_2$)$_2$, product **14-*d*$_2$** was obtained, where the ring carbon atoms are deuterated. Thus the phosphaalkene cannot be the source of the hydrogen atom at phosphorus in the 1,3-diphosphetane. The origin of this hydrogen is yet unclear. As the yield of **14** is only 40%, the proton may be abstracted from the remaining 60% of starting material. It is also conceivable that the hydrogen was transferred intramolecularly from the ethyl group. Moreover, even the N-Me group cannot be excluded completely as the origin of the hydrogen. The ^{1}H NMR spectrum of **14** displayed a triplet at δ 3.41 ($^2J_{PH}$ = 10.1 Hz) and a doublet of multiplets at δ 6.13 ($^1J_{PH}$ = 312.5 Hz) for the ring hydrogens at carbon and phosphorus, respectively. The phosphorus nuclei give rise to a singlet in the ^{31}P NMR spectrum at δ 8.9.

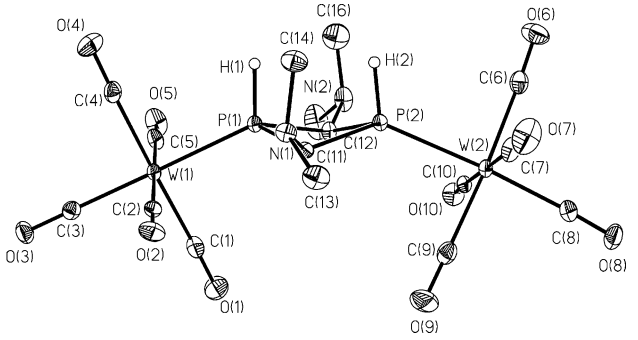
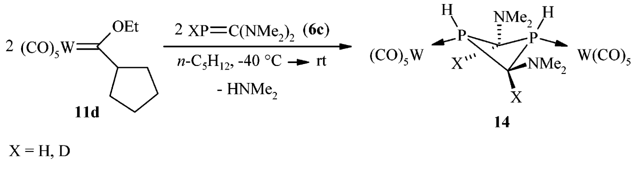


Figure 3. Molecular structure of **14** in the crystal. Selected bond lengths [Å] and angles [deg]: W(1)−P(1) 2.4732(6), W(2)−P(2) 2.4620(5), P(1)−C(11) 1.8694(18), P(1)−C(12) 1.9025(18), P(2)−C(11) 1.9055(18), P(2)−C(12) 1.8562(18), P(1)−H(1) 1.32(2), P(2)−H(2) 1.30(2), N(1)−C(11) 1.433(2), N(1)−C(14) 1.457(2), N(1)−C(13) 1.462(2), N(2)−C(12) 1.428(2), N(2)−C(15) 1.450(3), N(2)−C(16) 1.458(3); W(1)−P(1)−C(11) 120.20(6), W(1)−P(1)−C(12) 130.69(6), W(1)−P(1)−H(1) 116.6(9), W(2)−P(2)-C(11) 129.81(6), W(2)−P(2)−C(12) 118.61(6) W(2)−P(2)−H(2) 119.2(10), P(1)−C(12)−P(2) 93.27(8), C(11)−P(2)−C(12) 82.53(8), P(2)−C(11)−P(1) 92.76(8), C(11)−P(1)−C(12) 82.26(8), C(11)−N(1)−C(13) 112.97(15), C(11)−N(1)−C(14) 115.19(15), C(13)−N(1)−C(14) 111.67(15), C(12)−N(2)−C(15) 112.47(17), C(12)−N(2)−C(16) 115.06(16), C(15)−N(2)−C(16) 111.69; C(12)−P(1)−C(11)−P(2) 22.3, C(12)−P(2)−C(11)−P(1) −22.9, C(11)−P(1)−C(12)−P(2) −23.0, C(11)−P(2)−C(12)−P(1) 22.5.

Scheme 7



The exact geometry of the product was elucidated by an X-ray diffraction study on single crystals grown from *n*-pentane at −16 °C. The analysis (Figure 3) revealed **14** as a dinuclear complex, where a 1,3-diphosphetane ligand is bridging two [W(CO)$_5$] units via its P atoms.

The dihedral angle enclosed by the planes P(1), C(11), C(12) and P(2), C(11), C(12) (149.2°) is markedly compressed as compared with the one in **13c**. The axial positions at the phosphorus atoms are occupied by hydrogen atoms, whereas the sterically demanding [W(CO)$_5$] units are located equatorially. The geometries of the bridging 1,3-diphosphetane ligands in compounds **13c** and **14** differ significantly. The pyramidal dimethylamino groups in the equatorial positions at C(11) and

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C(12) are twisted out of the average ring plane into a nearly perpendicular situation, which brings the lone pairs of atoms N(1) and N(2) into an anti-periplanar orientation to the bonds P(2)−C(11) and P(1)−C(12). These bonds [1.9055(18) and 1.9025(18) Å] are markedly elongated with respect to P(1)−C(11) [1.8694(18) Å] and P(2)−C(12) [1.8562(18) Å]. While in complex **13c** the exocyclic bond angles W(1)−P(1)−C(11) [115.33(15)°] and W(1)−P(1)−C(12) [115.40(15)°] are identical, they differ in **14** by ca. 10° [120.20(6)° and 130.69(6)°]. Similar observations were made for the exocyclic angles W(2)−P(2)−C(11) and W(2)−P(2)−C(12) in both complexes. The contacts between the P and W atoms in **14** are more intense than in **13c**, as evidenced by relatively short distances of 2.4732(6) and 2.4620(5) Å. Reactions of carbene complexes **11** and RP═C(NMe$_2$)$_2$ (R = *t*Bu, Me$_3$Si) led to uncharacteristic decomposition.

Conclusions

The course of the reaction between Fischer carbene complexes [(CO)$_5$M═C(OR^1)R^2] and the nucleophilic inversely polarized phosphaalkenes R^{3}P═C(NMe$_2$)$_2$ strongly depends on the substitution pattern at both reactants. Thus, the methyl carbene complexes [(CO)$_5$M═C(OEt)CH$_3$] (M = Cr, W) react with [Cp*(CO)$_2$FeP═C(NMe$_2$)$_2$] to form equal amounts of the novel phosphaalkene complexes [(CO)$_5$M-κ-*P*{Cp*(CO)$_2$FeP═C-(OEt)CH$_3$}] and the β-aminoalkenyl carbene complexes [(CO)$_5$M═C(OEt)−CH═C(H)NMe$_2$]. Clearly, the presence of activated hydrogens at the carbon atom in α-position to the carbene center is a prerequisite for this type of condensation process. With phosphaalkenes R^{3}P═C(NMe$_2$)$_2$ (R^3 = H, *t*Bu, Me$_3$Si) a similar reaction occurred, leading to the β-aminoalkenyl carbene complexes in 50−70% yield, although no tractable phosphorus-containing products could be obtained. With carbene complexes bearing a secondary alkyl group at the carbene ligand such a pathway should be obstructed. Treatment of complex [(CO)$_5$W═C(OSiMe$_3$)(*c*-C$_3$H$_5$)] with HP═C(NMe$_2$)$_2$ did not afford the anticipated metathesis products [(CO)$_5$W-κ-*P*{HP═C(OSiMe$_3$)(*c*-C$_3$H$_5$)}] or [(CO)$_5$W-κ-*P*{(Me$_2$N)$_2$CH−P═C(OSiMe$_3$)(*c*-C$_3$H$_5$)}], as was previously encountered in the reaction with aryl carbene complexes. Instead phosphaalkene complex [(CO)$_5$W-κ-*P*{Me$_3$SiP═C(H)NMe$_2$}] was obtained in addition to dimethylamine. The hydrogen atom at the P═C backbone originated from the PH function of the phosphaalkene precursor. When the steric bulk of the oxygen substituent was decreased from trimethylsilyl to ethyl or methyl, the resulting phosphaalkene ligands are no longer sufficently shielded and dimerize to the observed 1,3-diphosphetane ligands. The fate of the cyclopropyl group remains unclear, but it seems likely that its activated hydrogen atom is the source of the hydrogen in the byproduct HNMe$_2$. Thus, the presence of at least one acidic hydrogen in the α-position of the carbene atom is a prerequisite for this result. The change from the cyclopropyl- to a cyclopentyl-carbene complex yet opens a further pathway. Instead of the transfer of an ethyl group from the ethoxy function onto the phosphorus atom P-protonation occurs to give a PH-functionalized 1,3-diphosphetane complex. Until now all attempts to synthesize carbene precursors with isopropyl, *sec*-butyl, and other acyclic substituents failed. The reaction of $[(CO)_5Cr{=}\overline{COCH_2CH_2C}(H)Me]$ with HP═C-(NMe$_2$)$_2$ gave no tractable products.

Experimental Section

All operations were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard techniques and freshly distilled under nitrogen prior to use. Infrared spectra were recorded with a Bruker FT-IR VECTOR22 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 22 °C using Bruker AC 100 (^{1}H, 100.13 MHz, ^{31}P, 40.53 MHz) and Bruker AM Avance DRX 500 (^{1}H, 500.13 MHz, ^{13}C, 125.76 MHz, ^{31}P, 200.46 MHz). References: SiMe$_4$ (^{1}H, ^{13}C), 85% H$_3$PO$_4$ (^{31}P). Elemental analyses were performed at the microanalytical laboratory of the University of Bielefeld and at Mikroanalytisches Laboratorium H. Kolbe, Mülheim, Ruhr, Germany. Compounds *t*BuP═C(NMe$_2$)$_2$ (**6a**),[3] Me$_3$SiP═C(NMe$_2$)$_2$ (**6b**),[13] HP═C(NMe$_2$)$_2$ (**6c**),[4] [(CO)$_5$W═C(OMe)(*c*-C$_3$H$_5$)] (**11b**),[9] and [(CO)$_5$W═(OEt)-(*c*-C$_3$H$_5$)][10] (**11c**) were synthesized according to literature procedures.

Preparation of Compounds: [(CO)$_5$W═C(OSiMe$_3$)(*c*-C$_3$H$_5$)] (11a). At 0 °C a solution of 1.70 g (35.0 mmol) of cyclopropyllithium in 60 mL of diethyl ether was added dropwise to a slurry of [W(CO)$_6$] (12.3 g, 35.0 mmol) in diethyl ether (200 mL). After 90 min of stirring at ambient temperature solvent was removed. The brown-yellow residue was dissolved in 100 mL of dichloromethane, and the mixture was cooled to −20 °C. Then a sample of chlorotrimethylsilane (5.70 g, 52.5 mmol) was added dropwise to the solution. Stirring was continued for 30 min at 0 °C. After removal of solvent and volatiles in vacuo the residue was extracted with *n*-pentane (3 × 20 mL). The combined extracts were freed from solvent to afford complex **11a** as a brown-yellow powder (13.9 g, 85% yield). IR (KBr, cm^{-1}) ν: 2070 (m, CO) 1920 (vs, CO). ^{1}H NMR (C$_6$D$_6$): δ 0.50 [s, 9H, OSi(CH$_3$)$_3$], 1.21 (br, 2H, CH$_2$), 1.37 (br, 2H, CH$_2$), 3.45 (br, 1H, CH). ^{13}C{^{1}H} (C$_6$D$_6$): δ 1.07 [s, OSi-(CH$_3$)$_3$], 18.5 [s, CH(*C*H$_2$)$_2$], 49.4 [s, *C*H(CH$_2$)$_2$], 199.0 (s, CO$_{eq}$), 204.7 (s, CO$_{ax}$), 326.0 (s, W═C). ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ 26.8. Due to the pronounced sensitivity to oxidation and hydrolysis, no reliable elemental analyses of **11a** were obtained.

[(CO)$_5$W═C(OEt)(*c*-C$_5$H$_9$)] (11d). A solution of cyclopentyllithium (2.66 g, 35.0 mmol) in *n*-pentane (70 mL) was added at 0 °C to a slurry of [W(CO)$_6$] (12.3 g, 35.0 mmol) in 250 mL of diethyl ether. The mixture was stirred at 0 °C for 30 min, warmed to room temperature, and stirred for another 2 h. After removal of solvent the yellow residue was dissolved in 70 mL of CH$_2$Cl$_2$. A solution of (Et$_3$O)(BF$_4$) (8.50 h, 45.0 mmol) in 25 mL of CH$_2$Cl$_2$ was added to this mixture. Solvent was removed, and the resulting residue was then extracted with *n*-pentane (3 × 100 mL). It was filtered, and the filtrate of the combined pentane extracts was stored at −16 °C. After 48 h a brown-yellow precipitate was isolated and recrystallized from diethyl ether to give **11d** as a yellow microcrystalline solid (11.2 g, 71% yield). IR (KBr, cm^{-1}): ν 2067 (m, CO), 1927 (vs, CO). ^{1}H NMR (C$_6$D$_6$): δ 0.85 (t, $^3J_{HH}$ = 7.55 Hz, 3H, OCH$_2$C*H*$_3$), 1.43 (m, 8H, *c*-C$_5$*H*$_9$), 4.25 (m, 1H, CH), 4.36 (q, $^3J_{HH}$ = 7.55 Hz, 2H, OC*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 14.0 (s, OCH$_2$*C*H$_3$), 26.7 (s, 3,4-CH$_2$), 31.3 (s, 2,5-CH$_2$), 73.4 (s, *C*H), 80.6 (s, O*C*H$_2$-CH$_3$), 197.9 (s, CO$_{eq}$), 203.7 (s, CO$_{ax}$), 337.0 (s, W═C). Anal. Calcd for C$_{13}$H$_{14}$O$_6$W (450.10): C, 34.69; H, 3.14. Found: C, 34.72; H, 3.07.

[CO)$_5$W-κ-*P*{Me$_3$SiP═C(H)NMe$_2$}] (12). A solution of HP═C(NMe$_2$)$_2$ (**6c**) (0.30 g, 2.27 mmol) in *n*-pentane (20 mL) was added dropwise to a cooled solution (−40 °C) of **11a** (1.06 g, 227 mol) in 30 mL of *n*-pentane. The reaction mixture was warmed to 20 °C and stirred for another 2 h. It was filtered, and the filtrate was stored at −16 °C. After 48 h orange crystalline **12** was isolated (0.52 g, 47% yield). IR (KBr, cm^{-1}): ν 2063 (w, CO), 1913 (s, br, CO), 1889 (sh, CO) 1248 [w, δ(SiMe$_3$)], 844 [w, ρ(SiMe$_3$)]. ^{1}H NMR (C$_6$D$_6$): δ 0.31 (s, 9H, SiCH$_3$), 2.31 [br, 6H, N(CH$_3$)$_2$], 8.17 (s, 1H, CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 1.8 (d, $^2J_{\mathrm{PC}} = 11.5$ Hz, Si*C*H$_3$), 43.5 [s, br, N(*C*H$_3$)$_2$], 184.3 (d, $^1J_{\mathrm{PC}} = 6.9$ Hz, P═*C*), 198.2 (d, $^2J_{\mathrm{PC}} = 5.7$ Hz, CO$_{\mathrm{eq}}$), 200.6 (d, $^2J_{\mathrm{PC}} = 21.8$ Hz, CO$_{\mathrm{ax}}$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −59.8 (s, $^1J_{\mathrm{PW}} = 185.9$ Hz). Anal. Calcd for C$_{11}$H$_{16}$NO$_5$PSiW (485.00): C, 27.22; H, 3.32; N, 2.89. Found: C, 27.38; H, 3.17; N, 2.99.

[{(CO)$_5$W}$_2$-κ-*P*{MeP−C(H)NMe$_2$}$_2$] (13b). An *n*-pentane solution (10 mL) of **6c** (0.13 g, 0.97 mmol) was combined with a cold solution (−50 °C) of [(CO)$_5$W═C(OMe)(*c*-C$_3$H$_5$)] (**11b**) in 20 mL of *n*-pentane. The resulting cloudy mixture was warmed to 20 °C and stirred for 2 h. It was filtered, and the filtrate was stirred 24 h at −16 °C to afford 0.25 g (60%) of light yellow crystalline **13b**. IR (KBr, cm^{-1}): ν 2074 (s, CO), 2067 (s, CO), 1916 (s, br,CO). ^{1}H NMR (C$_6$D$_6$): δ 2.09 (t, $^2J_{\mathrm{PH}} = 3.8$ Hz, 6H, PCH$_3$), 2.40 [s, 12H, N(CH$_3$)$_2$], 3.45 (t, $^2J_{\mathrm{PH}} = 10.1$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 8.8 (m, P*C*H$_3$), 45.1 [t, $^3J_{\mathrm{PC}} = 6.9$ Hz, N(*C*H$_3$)$_2$], 60.5 [t, $^1J_{\mathrm{PC}} = 29.7$ Hz, *C*HN(CH$_3$)$_2$], 197.2 (m, CO$_{\mathrm{eq}}$), 199.4 (m, CO$_{\mathrm{ax}}$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 30.3 (s, $^1J_{\mathrm{PW}} = 218.1$ Hz). Anal. Calcd for C$_{18}$H$_{20}$N$_2$O$_{10}$W$_2$ (853.99): C, 25.32; H, 2.36; N, 3.28. Found: C, 25.37; H, 2.43; N, 3.11.

[{(CO)$_5$W}$_2$-κ-*P*{EtP−C(H)NMe$_2$}$_2$] (13c). Analogously, reaction of **6c** (0.55 g, 4.15 mmol) with 1.75 g (4.15 mmol) of [(CO)$_5$W═C(OEt)(*c*-C$_3$H$_5$)] (**11c**) afforded 1.31 g (72% yield) of orange-yellow crystalline **13c**. IR (KBr, cm^{-1}): ν 2074 (w, CO), 2067 (w, CO), 1948 (vs, CO), 1933 (s, CO). ^{1}H NMR (C$_6$D$_6$): δ 1.07 (dt, $^3J_{\mathrm{PH}} = 20.7$ Hz, $^3J_{\mathrm{HH}} = 7.6$ Hz, 6H, CH$_2$C*H*$_3$), 1.93 (m, 4H, C*H*$_2$CH$_3$), 1.95 [s, 12H, N(CH$_3$)$_2$], 3.65 (t, $^2J_{\mathrm{PH}} = 9.2$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 12.25 (m, *C*H$_2$CH$_3$), 13.1 (br, CH$_2$*C*H$_3$), 44.0 [t, $^3J_{\mathrm{PC}} = 6.9$ Hz, N(CH$_3$)$_2$], 62.7 (t, $^1J_{\mathrm{PC}} = 28.7$ Hz, CH), 197.0 (m, CO$_{\mathrm{eq}}$), 198.3 (m, CO$_{\mathrm{ax}}$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 51.1 (s, $^1J_{\mathrm{PW}} = 218.0$ Hz). Anal. Calcd for C$_{20}$H$_{24}$N$_2$O$_{10}$P$_2$W$_2$ (882.07): C, 27.23; H, 2.74; N, 3.18. Found: C, 27.33; H, 2.88; N, 3.39.

[{(CO)$_5$W}$_2$-κ-*P*{HP−C(H)NMe$_2$}$_2$] (14). Analogously, reaction of **6a** (0.14 g, 1.02 mmol) with [(CO)$_5$W═C(OEt)(*c*-C$_5$H$_9$)] (**11d**) in *n*-pentane afforded 0.17 g of colorless crystalline **14** (42%). IR (KBr, cm^{-1}): ν 2068 (s, CO), 1915 (s, br, CO). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.59 [s, 12H, N(CH$_3$)$_2$], 3.41 (t, $^2J_{\mathrm{PH}} = 10.1$ Hz, 2H, C*H*(NCH$_3$)$_2$], 6.13 (dm, $^1J_{\mathrm{PH}} = 312.5$ Hz, 2H, PH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 44.0 [t, $^3J_{\mathrm{PC}} = 4.6$ Hz, N(CH$_3$)$_2$], 59.7 (t, $^1J_{\mathrm{PC}} = 19.5$ Hz, *C*HN), 195.8 (s, CO$_{\mathrm{eq}}$), 198.8 (m, CO$_{\mathrm{ax}}$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 8.9 (s, $^1J_{\mathrm{PW}} = 188.2$ Hz). Anal. Calcd for C$_{16}$H$_{16}$N$_2$O$_{10}$P$_2$W (825.93): C, 23.27; H, 1.95; N, 3.39. Found: C, 22.92; H, 1.92; N, 3.32.

[{(CO)$_5$W}$_2$-κ-*P*{HP−C(D)NMe$_2$}$_2$] (14-*d*$_2$). Similarly, reaction of 0.88 g (1.96 mmol) of **11d** with DP═C(NMe$_2$)$_2$ (0.26 g, 1.96 mmol), **6c-*d*$_1$**, in cold *n*-pentane (−40 °C) gave 0.32 g (40%) of product **14-*d*$_2$** as a light yellow powder. IR (KBr, cm^{-1}): ν 2065 (s, CO), 1913 (s, br, CO). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.59 [s, 12H, N(CH$_3$)$_2$], 6.11 (dm, $^1J_{\mathrm{PH}} = 320.9$ Hz, 2H, PH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 44.0 [s, N(CH$_3$)$_2$], 59.5 (m, CD), 195.8 (s, CO$_{\mathrm{eq}}$), 198.9 (m, CO$_{\mathrm{ax}}$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 8.1 (s, $^1J_{\mathrm{PW}} = 174.4$ Hz).

X-ray Structural Analysis of 12. Single crystals of **12** were grown from *n*-pentane at −16 °C. An orange crystal of approximate dimensions 0.26 × 0.25 × 0.22 mm was measured on a Nonius Kappa CCD system with Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Crystal data and refinement details: space group $P\bar{1}$, all dimensions $a = 9.3103(4)$ Å, $b = 9.9153(4)$ Å, $c = 10.4837(4)$ Å, $\alpha = 86.344(3)°$, $\beta = 78.774(3)°$, $\gamma = 63.757(3)°$, $V = 851.16(6)$ Å^3 (refined from 97 reflections), $Z = 2$, $d_{\mathrm{calcd}} = 1.893$ g cm^{-3}, $\mu = 6.964$ mm^{-1}, absorption correction multiscan, max/min transmission 0.13616/0.07779. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-97, 26 064 intensities collected, 2980 unique ($R_{\mathrm{int}} = 0.0425$) and 2891 with $I > 2\sigma(I)$, 191 parameters, hydrogen atoms treated as riding groups, *R*-indices for reflections with $I > 2\sigma(I)$; $R_{\mathrm{F}} = 0.0267$; $wR_{\mathrm{F}^2} = 0.0638$, GooF($F^2$) = 1.132, maximum/minimum residual electron densities 0.996 and −3.261 e Å^{-3}.

X-ray Structural Analysis of 13c. Single crystals of **13c** were grown from *n*-pentane at −16 °C. An orange-yellow crystal of approximate dimensions 0.11 × 0.11 × 0.10 mm was measured on a Nonius Kappa CCD system with Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Crystal data and refinement details: space group $P2_12_12$, all dimensions $a = 15.7840(1)$ Å, $b = 19.8160(1)$ Å, $c = 8.8120(2)$ Å, $V = 2756.18(7)$ Å^3 (refined from 4528 reflections), $Z = 4$, $d_{\mathrm{calcd}} = 2.126$ g cm^{-3}, $\mu = 8.95$ mm^{-1}, absorption correction multiscan, max/min transmission 0.4833/0.4546. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-97, 47 511 intensities collected, 8035 unique ($R_{\mathrm{int}} = 0.186$) and 7572 with $I > 2\sigma(I)$, 332 parameters, hydrogen atoms treated as riding groups, *R*-indices for reflections with $I > 2\sigma(I)$; $R_{\mathrm{F}} = 0.0280$; $wR_{\mathrm{F}^2} = 0.0625$, GooF($F^2$) = 1.132, maximum/minimum residual electron densities 0.937 and −1.139 e Å^{-3}.

X-ray Structural Analysis of 14. Single crystals of **14** were grown from *n*-pentane at −16 °C. A colorless crystal of approximate dimensions 0.21 × 0.21 × 0.18 mm was measured on a Nonius Kappa CCD system with Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Crystal data and refinement details: space group $C2/c$, all dimensions $a = 21.241(3)$ Å, $b = 12.9850(7)$ Å, $c = 18.324(3)$ Å, $\beta = 108.142(8)°$, $V = 4802.8(9)$ Å^3 (refined from 7316 reflections), $Z = 8$, $d_{\mathrm{calcd}} = 2.285$ g cm^{-3}, $\mu = 9.757$ mm^{-1}, absorption correction multiscan max/min transmission 0.2726/0.2338. Structure solution and refinement on F^2 with SHELXS-97 and SHELXL-97, 59 851 intensities collected, 6998 unique ($R_{\mathrm{int}} = 0.0298$) and 6222 with $I > 2\sigma(I)$, 301 parameters, hydrogen atoms treated as riding groups except H1/H2, which were refined isotropically, *R*-indices for reflections with $I > 2\sigma(I)$; $R_{\mathrm{F}} = 0.0137$; $wR_{\mathrm{F}^2} = 0.0265$, GooF($F^2$) = 1.057, maximum/minimum residual electron densities 0.800 and −0.872 e Å^{-3}.

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, complete bond lengths and angles, and thermal ellipsoid plots for compounds **12**, **13c**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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