## **Complexes with a Monohapto Bound Phosphorus Tetrahedron and Phosphaalkyne<sup>1</sup>**

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Received August 7, 1998

Summary: The reaction of white phosphorus with the coordinatively unsaturated  $[M(CO)_3(PR_3)_2]$  complexes (M = Mo, W; R = Cy,  $Pr^{i}$ ) yields the compounds  $[M(CO)_{3}$ - $(PR_3)_2(\eta^1 - P_4)$  in which the P<sub>4</sub>-tetrahedron is end-on bonded to the metal. In the same manner reacts  $Ar'C \equiv P$  $(Ar' = C_6 H_2 Bu^t_3 - 2, 4, 6)$  with this complex to give  $[W(CO)_3 - 2, 4, 6]$  $(PCy_3)_2(\eta^1 - P \equiv CAr')]$ . The X-ray structures of the products are discussed, and for the  $P_4$ -unit in  $[W(CO)_3(PCy_3)_2(\eta^1 P_4$ )] the librational analysis was performed to correct their translational and rotational motions.

Interest has been focused on unsubstituted group 15 ligands bonded to transition metal complexes for several years.<sup>3</sup> Most of the  $P_x$  ligand complexes are formed by reaction of white phosphorus with the appropriate transition metal complexes. However, only one type of compounds with a monohapto bound P<sub>4</sub>-tetrahedron is known, the  $[(\eta^1 - P_4)M(np_3)]$  (1) (M = Ni (a), Pd (b); np<sub>3</sub>  $= N(CH_2CH_2PPh_2)_3$ ) complexes reported by Sacconi and co-workers.<sup>4</sup> Moreover, Ginsberg and Lindsell suggested the occurrence of a side-on coordinated P<sub>4</sub>-unit in compounds of the type  $[(R_3P)_2MCl(\eta^2-P_4)]$  (2) (M = Rh (a), Ir (b)).<sup>5</sup> The nature of bonding to  $P_4$  in the latter complexes was established to be a side-on coordination of a P-P edge of the intact  $P_4$  tetrahedron. The long P–P bond of 2.4616(22) Å, however, rather gives evidence for an open edge, where a tetraphosphabicyclobutane coordinates to a metal(III) center. Other reactions of transition metal complexes with white phosphorus lead to transformation of the tetrahedral P<sub>4</sub>unit.<sup>3,6</sup> In a similar manner, the number of mononuclear coordination complexes formed with untransformed phosphaalkyne remains small.<sup>7</sup> Among them only the complexes *trans*- $[Mo(\eta^1-P=CAd)_2(depe)_2]$  **3a**<sup>8</sup> and *trans*-

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 $[FeH(\eta^1-P \equiv CBu^t)(dppe)_2][BPh_4]$  **3b**<sup>9</sup> with a  $\eta^1$ -ligated phosphaalkyne are structurally characterized. Recently, Bedford et al. reported the synthesis of the complex  $[Ru(\eta^1-P=CAr')(CO)_2(PPh_3)_2]$  suggesting an  $\eta^1$ -coordination of the phosphaalkyne  $P \equiv CAr'$  ( $Ar' = C_6H_2Bu^t_3$ -2,4,6) to the central ruthenium atom, which was confirmed by spectroscopic data.<sup>10</sup>



We found that in both respects—forming  $\eta^1$ -complexes of P<sub>4</sub> as well as of phosphaalkynes—the electronically and coordinatively unsaturated compounds [M(CO)<sub>3</sub>- $(PCy_3)_2$ ] (M = Mo, W), serve as the ideal starting material. These complexes are known to coordinate numerous small molecules such as H<sub>2</sub> and N<sub>2</sub>.<sup>11</sup>

The reaction of  $[M(CO)_3(PR_3)_2]$  with 1 equiv of P<sub>4</sub> in toluene at -78 °C leads to the capture of one phosphorus lone pair yielding the  $\eta^1$ -bonded P<sub>4</sub> complexes [M(CO)<sub>3</sub>- $(PR_3)_2(\eta^1 - P_4)$ ] (4a-c) (4a: M = W, R = Cy; 4b: M = W,  $R = Pr^{i}$ ; **4c**: M = Mo, R = Cy). These complexes are stable in solution (hexane, toluene) up to 0 °C, and then they decompose to the 18 VE compounds [M(CO)<sub>4</sub>- $(PR_3)_2]^{12}$  (**5a,b**) (M = W, Mo) and P<sub>4</sub>. However at low temperatures 4a-c crystallize as orange-yellow compounds. The air-sensitive solids are stable at ambient temperatures under argon. They are soluble in common organic solvents.

The structure of 4a reveals the 18-valence-electron complex  $[W(CO)_3(PCy_3)_2(\eta^1-P_4)]$  with a  $\eta^1$ -bonded  $P_4$ tetrahedron (Figure 1). The distance of the coordinated

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phosphorus to the central tungsten atom is of 2.463(2) Å, which is shorter than the P–W bond lengths of the two tricyclohexylphosphine phosphorus atoms which increase from 2.463(1) and 2.494(1) Å in the starting complex to 2.520(2) and 2.525(2) Å upon coordination of P<sub>4</sub>.

There are substantial differences in the bond distances within the P4-tetrahedron compared to those in **1a** reported by Sacconi and co-workers.<sup>4a</sup> The basal P-P bonds [P(4)-P(5), P(5)-P(6), P(6)-P(4)] in **4a** vary between 2.183(3) Å and 2.195(5) Å and hence tend to be longer than the apical P-P distances [P(3)-P(4)], P(3)-P(5), P(3)-P(6), which are in the range of 2.162(3) Å to 2.181(3) Å. Whereas in 1a was found the basal P-P distances at 2.09(3) Å to be shorter than the apical P-Pbond lengths at 2.20(3) Å (due to symmetry reasons, all basal as well as apical distances are equal). The structure of 1a was established at ambient temperature without a librational analysis. For the X-ray structure of 4a at 200 K, the rigid-body model was applied for the P<sub>4</sub> unit to correct the shortened bond length due to translational and rotational motions of the P atoms.<sup>13</sup> By using a "dummy atom" as described for  $\beta$ -P<sub>4</sub><sup>14</sup> the iterations converged to R = 0.020 with a lengthening of the P-P bond distance between 1.8 and 4.3 pm (Figure 1). The analysis shows the same relation of the P-P bonds, longer basal and shorter apical bonds. These experimental features are furthermore supported by recent MP2/6-31G(d,p) calculations, revealing at the "end-on" H<sup>+</sup> attached P<sub>4</sub> tetrahedron longer basal P-P bonds of 2.269 Å and shorter apical ones of 2.122 Å.15

<sup>31</sup>P NMR data of the isostructural complexes **4a**–**c** reveals three different groups of signals as an A<sub>2</sub>MX<sub>3</sub> spin system [A = P(1), P(2); M = P(3); X = P(4), P(5), P(6)], two of which, a doublet and a quartet, are assignable to the  $\eta^1$ -bound P<sub>4</sub>-tetrahedron. No WP-coupling can be observed in the quartet resonance of the coordinated P<sub>M</sub>-atom, probably due to the similarity between PP- and WP-coupling constants, which causes the set of satellites to be obscured by the main signals. The <sup>1</sup>J<sub>P(M),P(X)</sub> values, ranging from 206 (**4b**) to 185 (**4c**)



**Figure 1.** Molecular structure of **4a** (ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (deg) [by librational analysis corrected distances]: W–P(1) 2.520(2), W–P(2) 2.525(2), W–P(3) 2.463(2), P(3)–P(4) 2.162(3) [2.187], P(3)–P(5) 2.181(3) [2.199], P(3)–P(6) 2.172(3) [2.199], P(4)–P(5) 2.191(3) [2.225], P(4)–P(6) 2.195(5) [2.238], P(5)–P(6) 2.183(3) [2.214], P(1)–W–P(2) 179.29(5), C(2)–W–P(3) 174.5(2), C(1)–W–C(3) 171.9(3).



**Figure 2.** Molecular structure of **5a** (ellipsoids drawn at 30% probability level). Selected bond distances (Å) and angles (deg): W-P(2) 2.506(3), W-P(1) 2.525(3), W-C(1) 2.129(13), W-C(2) 2.064(13), W-C(3) 2.018(14), W-C(4) 1.99(2), P(2)-W-P(1) 170.93(8), C(4)-W-C(2) 170.0(4), C(3)-W-C(1) 177.9(5), C(2)-W-C(1) 96.6(4).

Hz, reflect a relatively high s-character in the P-P bonds of the  $P_4$  tetrahedron. The third group of signals ( $P_A$ ) can be assigned to the phosphine phosphorus atoms and bears a set of satellites due to a WP-coupling. The spectra of **4a,b** reveal a doublet with a very small  ${}^2J_{P(A)P(M)}$  of 11 and 20 Hz, respectively.

The molecular structure of the complex **5a** is shown in Figure 2. For the isostructural Mo complex **5b**, the X-ray structural analysis was also carried out.<sup>16</sup> The cyclohexyl substituents are eclipsed with a slightly bent P-M-P axis. In contrast to this, the Cy groups in the P<sub>4</sub>-complex **4a** are staggered with an almost linear P(2)-W-P(1) arrangement.

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	Table 1.	Crystallograu	phic Data fo	or 4a and 5a	<b>.b</b>
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	<b>4a</b> •0.5C <sub>7</sub> H <sub>8</sub>	<b>5a</b> •0.5C <sub>7</sub> H <sub>8</sub>	<b>5b</b> •0.5C <sub>6</sub> H <sub>6</sub>		
formula	C <sub>42.5</sub> H <sub>70</sub> O <sub>3</sub> P <sub>6</sub> W	$C_{43.5}H_{70}O_4P_2W$	C <sub>43</sub> H <sub>69</sub> O <sub>4</sub> P <sub>2</sub> Mo		
formula weight	998.15	902.79	807.86		
cryst size, mm	0.15 imes 0.15 imes 0.08	0.15 imes 0.04 imes 0.02	0.12 imes 0.08 imes 0.02		
T, K	200(1)	203(2)	200(1)		
space group	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)		
crystal system	triclinic	triclinic	triclinic		
a, Å	9.518(2)	10.996(2)	10.913(2)		
b, Å	10.096(2)	14.247(3)	14.150(3)		
<i>c</i> , Å	24.217(5)	14.799(4)	14.807(4)		
α, deg	92.54(3)	66.02(2)	65.63(2)		
$\beta$ , deg	100.13(3)	82.91(2)	83.34(2)		
$\gamma$ , deg	96.20(3)	82.92(2)	83.03(2)		
<i>V</i> , Å <sup>3</sup>	2272.6(8)	2089.5(7)	2061.9(7)		
Ζ	2	2	2		
$d_{\rm c}$ , g/cm <sup>3</sup>	1.459	1.435	1.301		
$\mu_{\rm c},{\rm cm}^{-1}$	27.89	28.80	4.35		
radiation (λ, Å)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)		
diffractometer	STOE IPDS	STOE IPDS	STOE IPDS		
$2\theta$ range, deg	$4.40 \leq 2\Theta \leq 52.26$	$4.62 \le 2\Theta \le 52$	$3.74 \le 2\Theta \le 52$		
<i>hkl</i> range	$-11 \le h \le 11, -12 \le k \le 9,$	$-11 \le h \le 13, -17 \le k \le 13,$	$-13 \le h \le 13, -17 \le k \le$		
	$-29 \le l \le 28$	$-18 \le l \le 15$	$17-18 \leq l \leq 18$		
data/restraints/parameters	6855/0/480	5873/14/446	7481/0/458		
independent reflections with $I > 2\sigma(I)$	5866 ( $R_{\rm int} = 0.0234$ )	4207 ( $R_{\rm int} = 0.0611$ )	$6042 \ (R_{\rm int} = 0.0363)$		
goodness-of-fit on F <sup>2</sup>	1.067	0.938	1.007		
$R_1,^a W R_2^b (I > 2\sigma(I))$	0.0418, 0.1037	0.0525, 0.1168	0.0313, 0.0734		
$R_1$ , <sup><i>a</i></sup> $wR_2^b$ (all data)	0.0519, 0.1097	0.0815, 0.1266	0.0454, 0.0776		
largest diff peak, hole, e/ų	1.250, -1.238	0.895, -1.488	0.603, -0.339		
${}^{a}R = \sum  F_{0}  -  F_{c}   / \sum  F_{0} . \ {}^{b}WR_{2} = [\sum \omega (F_{0}^{2} - F_{c}^{2})^{2}] / [\sum (F_{0}^{2})^{2}]^{1/2}; \ \omega^{-1} = \sigma^{2}(F_{0}^{2}) + \mathbf{a}(P)^{2} + \mathbf{b}P, \ P = [F_{0}^{2} + 2F_{c}^{2}]/3.$					

Addition of the phosphaalkyne  $P \equiv CAr'$  ( $Ar' = C_6H_2$ - $Bu_{3}^{t}-2,4,6$ ) to  $[M(CO)_{3}(PCy_{3})_{2}]$  (M = W, Mo) in hexane produces an orange precipitate of  $[M(CO)_3(PCy_3)_2(\eta^1 - \eta^2)]$ P≡CAr')] (6a,b),<sup>17</sup> which is insoluble in nonpolar solvents, but slightly soluble in toluene, CH<sub>2</sub>Cl<sub>2</sub>, and THF. The mass spectrum of 6b reveals the molecular ion, while 6a shows significant fragmentation assignable to the free phosphaalkyne and the complex fragment  $[W(CO)_3(PCy_3)_2]^+$ . <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **6** reveal a doublet at  $\delta$  29.6 and 54.1 ppm, respectively, assigned to the two equivalent phosphine phosphorus atoms and a triplet at  $\delta$  24.4 and 57.0 ppm, respectively, due to the phosphorus atom of the  $\eta^1$ -coordinated P=CAr', the two showing mutual PP-coupling of 25 and 31 Hz, respectively. In the X-ray structure analysis the poor quality of the very small crystals of **6a** led to significant residual electron density at the phosphine phosphorus atoms of the PCy<sub>3</sub> groups and hence did not allow the complete refinement of its structure. However, the position of all desired atoms could be determined and clearly reveals the monohapto coordination of P=CAr' to the tungsten atom (d(W-PC) = 2.390(5) Å, d(P=C)= 1.54(2) Å, Figure 3). To the best of our knowledge **6a** is one of the very rare examples for the coordination chemistry of the "supermesityl" phosphaalkyne  $P=CAr'^{10,18}$  and for a structurally characterized  $\eta^{1-1}$ ligated phosphaalkyne.<sup>3</sup>

In conclusion, the reactivity of  $[M(CO)_3(PR_3)_2]$  toward Lewis-base, diminished by the steric influence of its bulky phosphine ligands, allows the smooth formation of complexes with unusual  $\eta^1\text{-}\mathrm{coordination.}$ 



Figure 3. Molecular structure of 6a (ellipsoids drawn at 30% probability level). Selected bond distances (Å) and angles (deg): W-P(1) 2.390(5), W-P(2) 2.523(5), W-P(3) 2.510(5), P(1)-C(4) 1.54(2), P(1)-W-P(3) 92.4(2), P(1)-W-P(3) 92.4(2), P(1)-W-P(3)W-P(2) 91.5(2), P(3)-W-P(2) 175.1(2), C(4)-P(1)-W 179.3(7), C(5)-C(4)-P(1) 178(2)

## **Experimental Section**

General Comments. All reactions were performed under an Ar atmosphere using standard Schlenk techniques. Solvents were dried prior to use: toluene over Na/benzophenone, hexane over LiAlH<sub>4</sub>. Phosphaalkynes P=CAr', <sup>19</sup> P=CBu<sup>t 20</sup> as well as the complexes  $[M(CO)_3(PR_3)_2]$  (M = W, Mo; R = Cy, Pr<sup>i</sup>)<sup>11</sup> were prepared according to modified literature methods.

<sup>(17)</sup> Furthermore the reaction of  $Bu^{t}C \equiv P$  with  $[W(CO)_{3}(PCy_{3})_{2}]$ leads to a mixture of products inseparable by chromatography. The <sup>31</sup>P{<sup>1</sup>H} NMR studies reveal resonances indicating primary products with oligomerized phosphaalkynes. Within the resonances a doublet at  $\delta$  25.4 ppm and a triplet at  $\delta$  18.2 ppm with a small PP-coupling of 4.4 Hz appear, which can be assigned to the compound [W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>- $(\eta^1 - P \equiv CBu^t)]$  (6c).

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Synthesis of  $[M(CO)_3(PR_3)_2(\eta^1-P_4)]$  (4a-c). To a solution of  $[M(CO)_3(PR_3)_2]$  (M = W, R = Cy: 140 mg, 0.17 mmol) in toluene at -78 °C was added 1 equiv of P<sub>4</sub> (21 mg, 0.17 mmol) in toluene over a period of 30 min. On warming up to -20 °C the solution changed color from violet to green. On concentrating the solution in vacuo and storing it at -30 °C, orangeyellow crystalline product could be obtained. Solutions of 4a-c decompose above 0-5 °C, whereas the crystalline solids are stable under argon at ambient temperature. 4a (65% yield): <sup>31</sup>P{<sup>1</sup>H} NMR [101.26 MHz, 244 K, toluene- $d_8$ , A = P(1), P(2); M = P(3); X = P(4), P(5), P(6)]:  $\delta$  26.5 (P<sub>A</sub>) (d, 11 Hz, <sup>1</sup>J<sub>WP</sub> 262 Hz),  $\delta -422$  (P<sub>M</sub>) (q, <sup>1</sup>*J*<sub>MX</sub> 204 Hz, <sup>2</sup>*J*<sub>AM</sub> and <sup>1</sup>*J*<sub>WP</sub> not resolved);  $\delta$  -473 (P<sub>X</sub>) (d, <sup>1</sup>J<sub>MX</sub> 204 Hz). IR (KBr, cm<sup>-1</sup>): 1951 s, 1922 w, 1836 vs [ $\nu$  (CO)]. EI MS: m/z (%) = 952.6 (1) [M]<sup>+</sup>, 828.7 (1.5) [M-P<sub>4</sub>]<sup>+</sup>, 123.9 (74) [P<sub>4</sub>]. **4b** (58% yield): <sup>1</sup>H NMR (250.13) MHz, 244 K, toluene-*d*<sub>8</sub>): δ 1.12 (dd, 36H, *J*<sub>HH</sub> 7.2 Hz, *J*<sub>PH</sub> 12.9 Hz),  $\delta$  2.10 (sept, 6H,  $J_{\text{HH}}$  7.2 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (101.26 MHz, 244 K, toluene- $d_8$ ):  $\delta$  33.7 (P<sub>A</sub>) (d, <sup>2</sup> $J_{AM}$  20 Hz, <sup>1</sup> $J_{WP}$  263.9 Hz),  $\delta$  -422.6 (P<sub>M</sub>) (q, <sup>2</sup>J<sub>AM</sub> 20 Hz, <sup>1</sup>J<sub>MX</sub> 206 Hz,),  $\delta$  -476.9 (P<sub>X</sub>) (d, <sup>1</sup>*J*<sub>MX</sub> 206 Hz, <sup>1</sup>*J*<sub>WP</sub> not resolved). IR (KBr, cm<sup>-1</sup>): 1964 s, 1923 w, 1844 vs [ $\nu$  (CO)]. EI MS: m/z (%) = 656.1 (5) [M - 2CO]<sup>+</sup>, 588.2 (50)  $[M - P_4]^+\!\!.$  4c (62% yield):  $^{31}P\{^1H\}$  NMR (101.26 MHz, 244 K, toluene- $d_8$ ):  $\delta$  51.2 (P<sub>A</sub>) (s),  $\delta$  -400.2 (P<sub>M</sub>) (q, <sup>1</sup>J<sub>MX</sub> 185 Hz),  $\delta$  -480.0 (P<sub>X</sub>) (d, <sup>1</sup>J<sub>MX</sub> 185 Hz). EI MS: m/z (%) = 742.4 (45)  $[M - P_4]^+$ 

**Synthesis of [M(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>(\eta^{1}-P=CAr')] (6a,b).** To a solution of [M(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>] (M = W: 166 mg, M = Mo: 148 mg, 0.2 mmol) in hexane at -20 °C was added an equimolar solution of P=CAr' (58 mg, 0.2 mmol) in hexane dropwise over a period of 30 min. The violet solution changed color to bright red, and upon being warmed, a microcrystalline orange precipitate formed, which was filtered off, washed with hexane, and dried in vacuo (yields are about 76–85%). **6a**: <sup>1</sup>H NMR (250.13 MHz, 300 K, THF-*d*<sub>8</sub>):  $\delta$  1.26–2.21 (m, 93H),  $\delta$  7.35 (s, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (101.26 MHz, 300 K, THF-*d*<sub>8</sub>):  $\delta$  24.4 (t, <sup>2</sup>*J*<sub>PP</sub> 25 Hz, <sup>1</sup>*J*<sub>WP</sub> 280 Hz),  $\delta$  29.6 (d, <sup>2</sup>*J*<sub>PP</sub> 25 Hz, <sup>1</sup>*J*<sub>WP</sub> 260 Hz). IR (KBr): 1975 w, 1965 s, 1859 vs cm<sup>-1</sup> [ $\nu$  (CO)]. EI MS: *m/z* (%) = 828.75 (1) [M – PCAr']<sup>+</sup>, 288.2 (72) [PCAr']<sup>+</sup>. **6b**: <sup>1</sup>H NMR (250.13 MHz, 300 K, THF-*d*<sub>8</sub>):  $\delta$  1.25–2.20 (m, 93H),

δ 7.42 (s, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): δ 54.1 (d, <sup>2</sup>*J*<sub>PP</sub> 31 Hz), δ 57.0 (t, <sup>2</sup>*J*<sub>PP</sub> 31 Hz). IR (KBr): 1979 s, 1960 w, 1881 vs cm<sup>-1</sup> [ν (CO)]. EI MS: *m*/*z* (%) = 1030.56 (3) [M]<sup>+</sup>, 742.34 (12) [M – PCAr']<sup>+</sup>.

**X-ray Structure Determination and Details of Refinement.** Data were collected on a Stoe IPDS diffractometer using Mo K $\alpha$  ( $\lambda = 0.71069$  Å) radiation, no absorption corrections were performed. Machine parameters, crystal data, and data collection parameters are summarized in Table 1. The structures were solved by direct methods using SHELXS-86<sup>21a</sup> and a full-matrix-least-squares refinement on  $F^2$  in SHELXL-93<sup>21b</sup> with anisotropic displacement for non-H atoms. Hydrogen atoms were placed in idealized positions and refined isotropically according to the riding model.

[W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>(η<sup>1</sup>-P=CAr)] (**6a**): C<sub>58</sub>H<sub>62</sub>O<sub>3</sub>P<sub>3</sub>W, M= 1083.83, crystal dimensions 0.2 × 0.15 × 0.03 mm, triclinic, space group P1, unit cell parameters a = 10.114(2), b = 16.904(3), c = 19.054(4) Å,  $\alpha = 92.11(3)$ ,  $\beta = 101.71(3)$ ,  $\gamma = 97.69(3)^{\circ}$ , Z = 2, V = 3154.2(11) Å<sup>3</sup>, T = 200(1) K,  $D_c = 1.176$  mg m<sup>-3</sup>,  $\mu$ (Mo  $K_{\alpha}) = 19.44$  cm<sup>-1</sup>, 14230 independent reflections ( $2\theta_{max} = 56.66^{\circ}$ ), 8115 observed with  $F_o \ge 4\sigma$  ( $F_o$ ); 296 parameter,  $R_1 = 0.1584$ ,  $wR_2 = 0.4074$ . Only the W, P, and the C(4)-atom were refined anisotropically. Several attempts to receive crystals of better quality of **6a** and **6b**, respectively, remained unsuccessful.

**Acknowledgment.** The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

**Supporting Information Available:** Complete tables of atomic coordinates, H-atom parameters, bond distances and anisotropic displacement parameters, and fully labeled figures for **4a**, **5a**,**b**, and **6a** (38 pages). Ordering information is given on any current masthead page.

## OM9806794

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