Complexes with a Monohapto Bound Phosphorus Tetrahedron and Phosphaalkyne[1]

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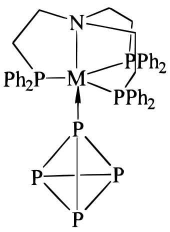
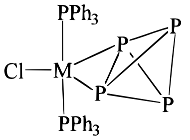
Summary: The reaction of white phosphorus with the coordinatively unsaturated [M(CO)$_3$(PR$_3$)$_2$] complexes (M = Mo, W; R = Cy, Pr^i) yields the compounds [M(CO)$_3$(PR$_3$)$_2$(η^1-P$_4$)] in which the P$_4$-tetrahedron is end-on bonded to the metal. In the same manner reacts Ar′C≡P (Ar′ = C$_6$H$_2$Bu$^t{}_3$-2,4,6) with this complex to give [W(CO)$_3$(PCy$_3$)$_2$(η^1-P≡CAr′)]. The X-ray structures of the products are discussed, and for the P$_4$-unit in [W(CO)$_3$(PCy$_3$)$_2$(η^1-P$_4$)] the librational analysis was performed to correct their translational and rotational motions.

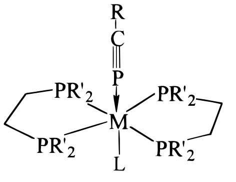
Interest has been focused on unsubstituted group 15 ligands bonded to transition metal complexes for several years.[3] Most of the P$_x$ ligand complexes are formed by reaction of white phosphorus with the appropriate transition metal complexes. However, only one type of compounds with a monohapto bound P$_4$-tetrahedron is known, the [(η^1-P$_4$)M(np$_3$)] (**1**) (M = Ni (**a**), Pd (**b**); np$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$) complexes reported by Sacconi and co-workers.[4] Moreover, Ginsberg and Lindsell suggested the occurrence of a side-on coordinated P$_4$-unit in compounds of the type [(R$_3$P)$_2$MCl(η^2-P$_4$)] (**2**) (M = Rh (**a**), Ir (**b**)).[5] 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$_4$-unit.[3,6] In a similar manner, the number of mononuclear coordination complexes formed with untransformed phosphaalkyne remains small.[7] Among them only the complexes *trans*-[Mo(η^1-P≡CAd)$_2$(depe)$_2$] **3a**[8] and *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BPh$_4$] **3b**[9] with a η^1-ligated phosphaalkyne are structurally characterized. Recently, Bedford et al. reported the synthesis of the complex [Ru(η^1-P≡CAr′)(CO)$_2$(PPh$_3$)$_2$] suggesting an η^1-coordination of the phosphaalkyne P≡CAr′ (Ar′ = C$_6$H$_2$Bu$^t{}_3$-2,4,6) to the central ruthenium atom, which was confirmed by spectroscopic data.[10]



1a: M = Ni
1b: M = Pd



2a: M = Rh
2b: M = Ir



3a: M = Mo
R = 1-Adamantyle
R' = Et
L = P≡CR
3b: M = Fe$^+$
L = H; R' =Ph
R = *t*Bu

We found that in both respects—forming η^1-complexes of P$_4$ as well as of phosphaalkynes—the electronically and coordinatively unsaturated compounds [M(CO)$_3$(PCy$_3$)$_2$] (M = Mo, W), serve as the ideal starting material. These complexes are known to coordinate numerous small molecules such as H$_2$ and N$_2$.[11]

The reaction of [M(CO)$_3$(PR$_3$)$_2$] with 1 equiv of P$_4$ in toluene at −78 °C leads to the capture of one phosphorus lone pair yielding the η^1-bonded P$_4$ complexes [M(CO)$_3$(PR$_3$)$_2$(η^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)$_4$(PR$_3$)$_2$][12] (**5a,b**) (M = W, Mo) and P$_4$. 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$_3$)$_2$(η^1-P$_4$)] with a η^1-bonded P$_4$ tetrahedron (Figure 1). The distance of the coordinated

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[1] Dedicated to Prof. Dr. O. J. Scherer in occasion of his 65th birthday.

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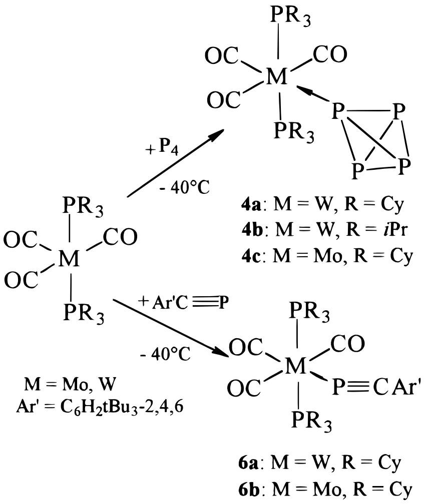

phosphorus to the central tungsten atom is of 2.463(2) Å, which is shorter than the P−W bond lengths of the two tricyclohexylphosphine phosphorus atoms which increase from 2.463(1) and 2.494(1) Å in the starting complex to 2.520(2) and 2.525(2) Å upon coordination of P_4.

There are substantial differences in the bond distances within the P_4-tetrahedron compared to those in **1a** reported by Sacconi and co-workers.[4a] 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−P bond 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_4 unit to correct the shortened bond length due to translational and rotational motions of the P atoms.[13] By using a "dummy atom" as described for β-P_4[14] 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^+ attached P_4 tetrahedron longer basal P−P bonds of 2.269 Å and shorter apical ones of 2.122 Å.[15]

^{31}P NMR data of the isostructural complexes **4a**−**c** reveals three different groups of signals as an A_2MX_3 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 η^1-bound P_4-tetrahedron. No WP-coupling can be observed in the quartet resonance of the coordinated P_M-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 $^1J_{P(M),P(X)}$ values, ranging from 206 (**4b**) to 185 (**4c**) 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.

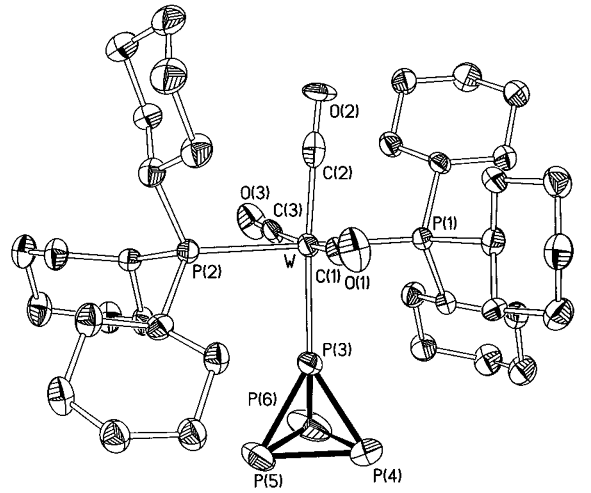

Figure 1. Molecular structure of **4a** (ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (deg) [by librational analysis corrected distances]: W−P(1) 2.520(2), W−P(2) 2.525(2), W−P(3) 2.463(2), P(3)−P(4) 2.162(3) [2.187], P(3)−P(5) 2.181(3) [2.199], P(3)−P(6) 2.172(3) [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).

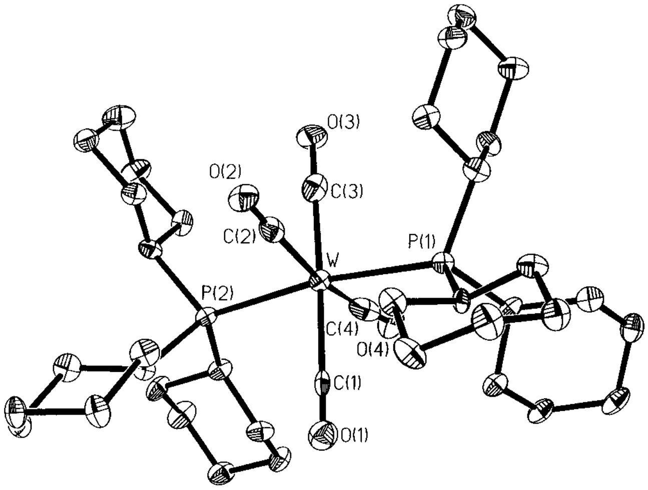

Figure 2. Molecular structure of **5a** (ellipsoids drawn at 30% probability level). Selected bond distances (Å) and angles (deg): W−P(2) 2.506(3), W−P(1) 2.525(3), W−C(1) 2.129(13), W−C(2) 2.064(13), W−C(3) 2.018(14), W−C(4) 1.99(2), P(2)−W−P(1) 170.93(8), C(4)−W−C(2) 170.0(4), C(3)−W−C(1) 177.9(5),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

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.[16] The cyclohexyl substituents are eclipsed with a slightly bent P−M−P axis. In contrast to this, the Cy groups in the P_4-complex **4a** are staggered with an almost linear P(2)−W−P(1) arrangement.

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Table 1. Crystallographic Data for 4a and 5a,b

	4a·$0.5C_7H_8$	**5a**·$0.5C_7H_8$	**5b**·$0.5C_6H_6$
formula	$C_{42.5}H_{70}O_3P_6W$	$C_{43.5}H_{70}O_4P_2W$	$C_{43}H_{69}O_4P_2Mo$
formula weight	998.15	902.79	807.86
cryst size, mm	0.15 × 0.15 × 0.08	0.15 × 0.04 × 0.02	0.12 × 0.08 × 0.02
T, K	200(1)	203(2)	200(1)
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (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)
c, Å	24.217(5)	14.799(4)	14.807(4)
α, deg	92.54(3)	66.02(2)	65.63(2)
β, deg	100.13(3)	82.91(2)	83.34(2)
γ, deg	96.20(3)	82.92(2)	83.03(2)
V, Å^3	2272.6(8)	2089.5(7)	2061.9(7)
Z	2	2	2
d_c, g/cm^3	1.459	1.435	1.301
μ_c, cm^{-1}	27.89	28.80	4.35
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
diffractometer	STOE IPDS	STOE IPDS	STOE IPDS
2θ range, deg	$4.40 \leq 2\Theta \leq 52.26$	$4.62 \leq 2\Theta \leq 52$	$3.74 \leq 2\Theta \leq 52$
hkl range	$-11 \leq h \leq 11, -12 \leq k \leq 9, -29 \leq l \leq 28$	$-11 \leq h \leq 13, -17 \leq k \leq 13, -18 \leq l \leq 15$	$-13 \leq h \leq 13, -17 \leq k \leq 17 -18 \leq l \leq 18$
data/restraints/parameters	6855/0/480	5873/14/446	7481/0/458
independent reflections with $I > 2\sigma(I)$	5866 ($R_{int} = 0.0234$)	4207 ($R_{int} = 0.0611$)	6042 ($R_{int} = 0.0363$)
goodness-of-fit on F^2	1.067	0.938	1.007
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0418, 0.1037	0.0525, 0.1168	0.0313, 0.0734
R_1,[a] wR_2[b] (all data)	0.0519, 0.1097	0.0815, 0.1266	0.0454, 0.0776
largest diff peak, hole, e/Å^3	1.250, −1.238	0.895, −1.488	0.603, −0.339

[a] $R = \sum|F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = [\sum\omega(F_0^2 - F_c^2)^2]/[\sum(F_0^2)^2]^{1/2}$; $\omega^{-1} = \sigma^2(F_0^2) + a(P)^2 + bP$; $P = [F_0^2 + 2F_c^2]/3$.

Addition of the phosphaalkyne P≡CAr′ (Ar′ = C_6H_2-Bu^t_3-2,4,6) to $[M(CO)_3(PCy_3)_2]$ (M = W, Mo) in hexane produces an orange precipitate of $[M(CO)_3(PCy_3)_2(\eta^1$-P≡CAr′)] (**6a,b**),[17] which is insoluble in nonpolar solvents, but slightly soluble in toluene, CH_2Cl_2, 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 $[W(CO)_3(PCy_3)_2]^+$. $^{31}P\{^1H\}$ NMR spectra of **6** reveal a doublet at δ 29.6 and 54.1 ppm, respectively, assigned to the two equivalent phosphine phosphorus atoms and a triplet at δ 24.4 and 57.0 ppm, respectively, due to the phosphorus atom of the η^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_3 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 η^1-ligated phosphaalkyne.[3]

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 η^1-coordination.

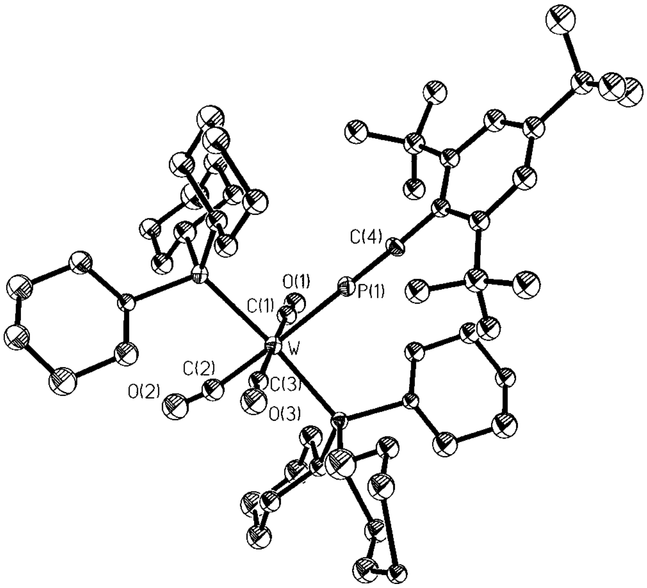

Figure 3. Molecular structure of **6a** (ellipsoids drawn at 30% probability level). Selected bond distances (Å) and angles (deg): W−P(1) 2.390(5), W−P(2) 2.523(5), W−P(3) 2.510(5), P(1)−C(4) 1.54(2), P(1)−W−P(3) 92.4(2), P(1)−W−P(2) 91.5(2), P(3)−W−P(2) 175.1(2), C(4)−P(1)−W 179.3(7), C(5)−C(4)−P(1) 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 $LiAlH_4$. Phosphaalkynes P≡CAr′,[19] P≡CBu^t [20] as well as the complexes $[M(CO)_3(PR_3)_2]$ (M = W, Mo; R = Cy, Pr^i)[11] were prepared according to modified literature methods.

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[17] Furthermore the reaction of Bu^tC≡P with $[W(CO)_3(PCy_3)_2]$ leads to a mixture of products inseparable by chromatography. The $^{31}P\{^1H\}$ NMR studies reveal resonances indicating primary products with oligomerized phosphaalkynes. Within the resonances a doublet at δ 25.4 ppm and a triplet at δ 18.2 ppm with a small PP-coupling of 4.4 Hz appear, which can be assigned to the compound $[W(CO)_3(PCy_3)_2$-(η^1-P≡CBu^t)] (**6c**).

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Synthesis of $[M(CO)_3(PR_3)_2(\eta^1\text{-}P_4)]$ (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_4 (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, orange-yellow 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): $^{31}P\{^1H\}$ NMR [101.26 MHz, 244 K, toluene-d_8, A = P(1), P(2); M = P(3); X = P(4), P(5), P(6)]: δ 26.5 (P_A) (d, 11 Hz, $^1J_{WP}$ 262 Hz), δ −422 (P_M) (q, $^1J_{MX}$ 204 Hz, $^2J_{AM}$ and $^1J_{WP}$ not resolved); δ −473 (P_X) (d, $^1J_{MX}$ 204 Hz). IR (KBr, cm^{-1}): 1951 s, 1922 w, 1836 vs [ν (CO)]. EI MS: m/z (%) = 952.6 (1) [M]$^+$, 828.7 (1.5) [M−P$_4$]$^+$, 123.9 (74) [P$_4$]. **4b** (58% yield): ^1H NMR (250.13 MHz, 244 K, toluene-d_8): δ 1.12 (dd, 36H, J_{HH} 7.2 Hz, J_{PH} 12.9 Hz), δ 2.10 (sept, 6H, J_{HH} 7.2 Hz). $^{31}P\{^1H\}$ NMR (101.26 MHz, 244 K, toluene-d_8): δ 33.7 (P_A) (d, $^2J_{AM}$ 20 Hz, $^1J_{WP}$ 263.9 Hz), δ −422.6 (P_M) (q, $^2J_{AM}$ 20 Hz, $^1J_{MX}$ 206 Hz,), δ −476.9 (P_X) (d, $^1J_{MX}$ 206 Hz, $^1J_{WP}$ not resolved). IR (KBr, cm^{-1}): 1964 s, 1923 w, 1844 vs [ν (CO)]. EI MS: m/z (%) = 656.1 (5) [M − 2CO]$^+$, 588.2 (50) [M − P$_4$]$^+$. **4c** (62% yield): $^{31}P\{^1H\}$ NMR (101.26 MHz, 244 K, toluene-d_8): δ 51.2 (P_A) (s), δ −400.2 (P_M) (q, $^1J_{MX}$ 185 Hz), δ −480.0 (P_X) (d, $^1J_{MX}$ 185 Hz). EI MS: m/z (%) = 742.4 (45) [M − P$_4$]$^+$.

Synthesis of $[M(CO)_3(PCy_3)_2(\eta^1\text{-}P{\equiv}CAr')]$ (6a,b). To a solution of $[M(CO)_3(PCy_3)_2]$ (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**: ^1H NMR (250.13 MHz, 300 K, THF-d_8): δ 1.26−2.21 (m, 93H), δ 7.35 (s, 2H). $^{31}P\{^1H\}$ NMR (101.26 MHz, 300 K, THF-d_8): δ 24.4 (t, $^2J_{PP}$ 25 Hz, $^1J_{WP}$ 280 Hz), δ 29.6 (d, $^2J_{PP}$ 25 Hz, $^1J_{WP}$ 260 Hz). IR (KBr): 1975 w, 1965 s, 1859 vs cm^{-1} [ν (CO)]. EI MS: m/z (%) = 828.75 (1) [M − PCAr′]$^+$, 288.2 (72) [PCAr′]$^+$. **6b**: ^1H NMR (250.13 MHz, 300 K, THF-d_8): δ 1.25−2.20 (m, 93H), δ 7.42 (s, 2H). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 54.1 (d, $^2J_{PP}$ 31 Hz), δ 57.0 (t, $^2J_{PP}$ 31 Hz). IR (KBr): 1979 s, 1960 w, 1881 vs cm^{-1} [ν (CO)]. EI MS: m/z (%) = 1030.56 (3) [M]$^+$, 742.34 (12) [M − PCAr′]$^+$.

X-ray Structure Determination and Details of Refinement. Data were collected on a Stoe IPDS diffractometer using Mo Kα (λ = 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[21a] and a full-matrix-least-squares refinement on F^2 in SHELXL-93[21b] with anisotropic displacement for non-H atoms. Hydrogen atoms were placed in idealized positions and refined isotropically according to the riding model.

$[W(CO)_3(PCy_3)_2(\eta^1\text{-}P{\equiv}CAr')]$ (**6a**): $C_{58}H_{62}O_3P_3W$, M = 1083.83, crystal dimensions 0.2 × 0.15 × 0.03 mm, triclinic, space group $P\bar{1}$, unit cell parameters a = 10.114(2), b = 16.904(3), c = 19.054(4) Å, α = 92.11(3), β = 101.71(3), γ = 97.69(3)°, Z = 2, V = 3154.2(11) Å^3, T = 200(1) K, D_c = 1.176 mg m^{-3}, μ(Mo K_α) = 19.44 cm^{-1}, 14230 independent reflections ($2\theta_{max}$ = 56.66°), 8115 observed with $F_o \geq 4\sigma(F_o)$; 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.

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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.

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(21) (a) Sheldrick, G. M. *SHELXS-86*, University of Göttingen, 1986. (b) Sheldrick, G. M. *SHELXL-93*, University of Göttingen, 1993.