

Addition of a Phenyl Phosphinidene Complex to Conjugated Diynes

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Summary: Alkynyl-substituted phosphirenes are formed from the addition of $\text{PhPW}(\text{CO})_5$ to 2,4-hexadiyne, 5,7-dodecadiyne, and 2,2,7,7-tetramethylocta-3,5-diyne. No bisphosphirenes are formed. Instead, but only for the 2,4-hexadiyne derivative, a second $\text{PhPW}(\text{CO})_5$ inserts into the phosphirene ring to give a 2:1 mixture of *cis*- and *trans*-1,2-dihydro-1,2-diphosphetes. An X-ray structure determination, *ab initio* computed geometries, and NMR data are presented.

1,3-Diynes have become versatile building blocks with broad appeal in organic, organometallic, and materials chemistry.¹ Not only is the conjugated diyne unit an ideal "inert" rodlike spacer with conducting properties but its reactivity toward carbenes² and transition metals is equally multifaceted.³ Our interest concerns the susceptibility toward the transition metal-complexed phosphinidenes, of which $\text{PhPW}(\text{CO})_5$ has carbene-like properties.⁴ This species is generated *in situ* from the 7-phosphanorbornadiene precursor **1**⁵ and reacts with double and triple bonds to give $\text{W}(\text{CO})_5$ -complexed phosphiranes and phosphirenes, respectively.^{5,6} Conjugated olefins give 1,2-cycloadditions and subsequent epimerizations and rearrangements to products such as phospholenes.^{6,7} During the course of this study Mathey and co-workers reported on the addition of $\text{RPW}(\text{CO})_5$

to 1,3-diynes.⁸ Here we report our results for the addition of $\text{PhPW}(\text{CO})_5$ to a set of different 1,3-diynes. While these results are in line with Mathey's experimental observations, they do show important differences. In addition, we present an evaluation of the electronic properties of the products using *ab initio* MO theory.

Results and Discussion

Reaction of the diynes **2** ($\text{R} = \text{Me}$, *n*-Bu, *t*-Bu) with 1 equiv of **1** in toluene at 55–60 °C using CuCl as catalyst affords in all cases the expected alkynyl-substituted phosphirenes in reasonable isolated yields, i.e., 66% for **3a**, 55% for **3b**, and 52% for **3c**. The differentiation in yields illustrates the effect of steric hindrance that the alkyl substituents have on the cycloaddition efficiency. For comparison, 2-butyne reacts with **1** to give phosphirene **4** in 85% yield.⁹ Mathey reported a 55% yield for the reaction of **1** with diyne **2d** ($\text{R} = \text{Ph}$).⁸

Our next step was to add a second $\text{PhPW}(\text{CO})_5$ to the remaining and presumed readily accessible triple bond of **3** in the anticipation of forming bisphosphirenes **5**. However, none of the diynes **2a–c** underwent such an addition. Mathey made the same observation and found instead that with the diynes **3e** ($\text{R} = \text{Ph}$) and **3f** ($\text{R} = \text{CH}_2\text{OPh}$) the second $\text{R}'\text{PW}(\text{CO})_5$ group ($\text{R}' = \text{Me}$, allyl, Bz, Ph) inserts into the phosphirene ring to give 1,2-dihydro-1,2-diphosphetes with exclusive formation of the *cis* isomer.⁸ Our results differ in two important aspects. First, whereas reaction of **1** with **3a** gives indeed a C–P insertion, the resulting 1,2-dihydro-1,2-diphosphete (**6a**) is formed under the reaction conditions (55 °C) in a 2:1 mixture of *cis* and *trans* isomers. Heating the mixture increases this ratio to 4:1, which suggests that the thermodynamically favored *cis* isomer is formed (in part) by epimerization of one of the P-centers. Apparently the insertion reaction leading to the *cis* isomer does not go with the high regio- and stereoselectivity as has been suggested.⁸ Second, the alkynes **3b** and **3c** give neither a C–P insertion (like **3a**) nor a 1,2-addition in detectable yields. This lack of

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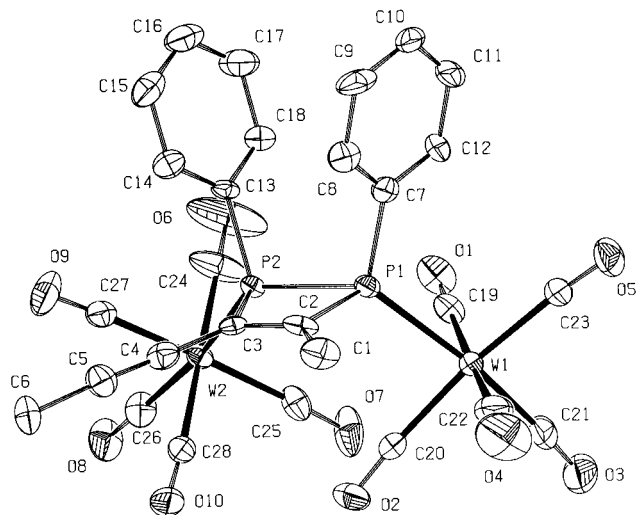
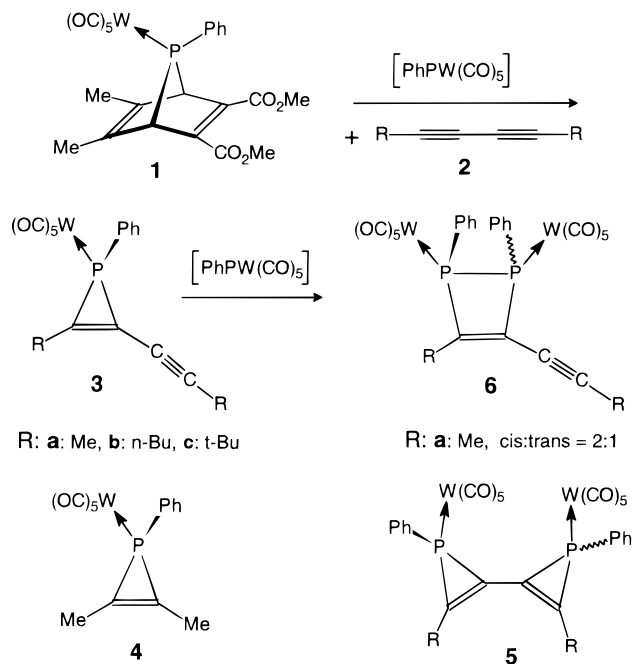
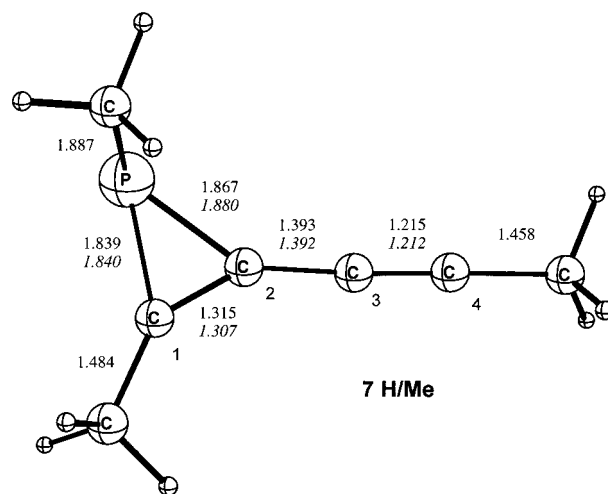


Figure 1. ORTEP drawing of the molecular structure of **6a**. Selected bond lengths (in Å) and bond angles (in deg): W_1-P_1 2.482(2), W_2-P_2 2.482(2), P_1-P_2 2.271(3), P_1-C_2 1.824(9), P_2-C_3 1.833(8), C_1-C_2 1.492(13), C_2-C_3 1.340(12), C_3-C_4 1.407(12), C_4-C_5 1.200(13), C_5-C_6 1.465(15), $P_1-C_2-C_3$ 104.9(6), $P_2-C_3-C_2$ 104.6(6), $P_1-P_2-C_3$ 75.1(3), $P_2-P_1-C_2$ 75.4(3), $C_1-C_2-C_3$ 128.8(8), $C_2-C_3-C_4$ 129.7(8), $C_3-C_4-C_5$ 173.2(10), $C_4-C_5-C_6$ 177.0(10).

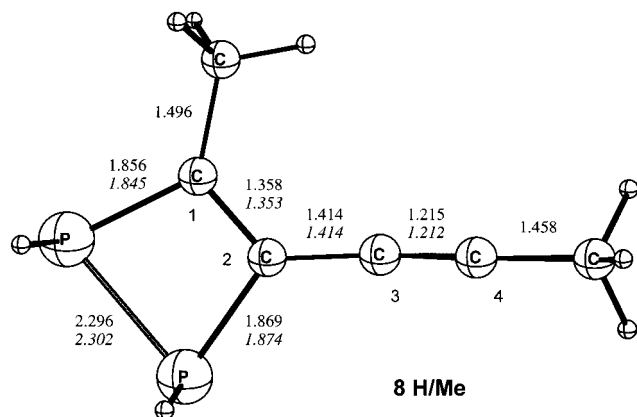
reactivity of both the alkynyl and the phosphirene group is most surprising.



We resorted to computations, using density functional theory, and an X-ray structure determination of **6a** (Figure 1) for investigation of the structural and electronic properties. To bring the scope of the calculations within manageable proportions, we eliminated the $W(CO)_5$ groups, replaced the P-Ph group for P-H or P-Me, and used $\equiv C-CH_3$ or $\equiv C-H$ substituents to compute **7** and **8** at the B3LYP/6-31G* level of theory (Figure 2). These changes do not affect the analyses of the electronic properties in these systems; the absence of the transition metal complex merely elongates both P-C bonds. Structure **7H** shows delocalization between



7 H/Me



8 H/Me

Figure 2. B3LYP/6-31G* optimized structures for **7** and **8**. Upper values are bond lengths (in Å) for the methyl derivatives (as shown), while the lower italic values are for the structures without methyl groups.

the phosphirene ring and its alkynyl substituent. This is evident from the 1.392 Å short C(2)-C(3) bond, which connects the alkynyl group ($d(C\equiv C) = 1.215$ Å) with the phosphirene ring ($d(C=C) = 1.307$ Å), and from the 0.040 Å large difference in the two ring P-C bond lengths, of which the PC(2) bond is the longest (1.880 Å). Methyl substitution has little effect, although the P-Me group does reduce the longer PC(2) bond slightly (i.e., by 0.013 Å). The reported X-ray structure for **3d** (R = Ph; $>PPhW(CO)_5$)⁸ gives a difference in PC bond lengths of 0.017 Å and thus compares well with the computed structure **7Me** (R = Me; $>PH$). This suggests that indeed the alkynyl-induced conjugative weakening of the *proximal* PC(2) bond underlies the ability of $PhPW(CO)_5$ to insert into the phosphirene ring of **3a**. As an aside we note, however, that this P-C insertion to form phosphetes is by no means common. For example, the related conjugative weakening of the *distal* PC bond in alkylidenephosphiranes does not lead to insertion of a phosphinidene.¹⁰ This may suggest that the closeness of the weakened proximal PC bond with the conjugated alkynyl group underlies the insertion reaction of **3a**. However, it is remarkable that neither the *n*-butyl (**3b**) nor *tert*-butyl (**3c**) derivatives give phosphinidene insertion into the phosphirene ring nor

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Table 1. Summary of Observed ^{31}P and ^{13}C NMR Chemical Shifts (in ppm) for **3, **4**, and **6**, and GIAO (B3LYP/6-31G*) Computed ^{13}C NMR Chemical Shifts (in ppm, Referenced against SiMe_4) for **6** and **7**^a**

compd ^b	P	C1	C2	C3	C4	CH ₃ (1)	CH ₃ (4)
4	-157.4	128.3				11.2	
3a , Me	-135.3	134.0	115.4	65.0	105.2	11.9	4.5
3b , <i>n</i> -Bu	-136.5	139.2	115.2	67.7	110.7	(29.6)	(22.3)
3c , <i>t</i> -Bu	-135.9	146.7	117.6	65.9	11.7	(35.3)	(29.5)
6a , Me	49.0, 43.0	157.2	133.5	75.0	99.8	19.7	5.0
7H		110	104	64	94		
7Me		128	107	64	99	16	6
8H		147	132	72	76		
8Me		158	126	72	85	23	6

^a The carbon labels refer to those shown in structures **7** and **8**.

^b Substituents on the alkynyl and phosphirene/phosphete groups are given.

addition to the remaining triple bond. Because, a priori, there is no difference in electronic properties between **3b,c** and **3a**, we assume the *n*-butyl and *tert*-butyl groups to sterically inhibit the approach of $\text{PhPW}(\text{CO})_5$ to the reactive center.

The X-ray structure of the major isomer of **6a** has its two $\text{W}(\text{CO})_5$ in a *cis* orientation. The 0.009 Å difference between the two P–C bond lengths of its fully planar four-membered ring is well within the error limits. The 1.407(12) Å short C(3)–C(4) bond, which connects the alkynyl group ($d(\text{C}\equiv\text{C}) = 1.200(13)$ Å) with the 1,2-diphosphete ring ($d(\text{C}=\text{C}) = 1.340(12)$ Å), suggests some resonance stabilization which is not reflected in the P–C bond lengths. This resonance stabilization between the double and triple bonds of *cis*-**6a** is supported on comparison with the 1.44(1) Å long C(3)–C(4) bond in the reported X-ray structure of *cis*-**6d**.⁸ This lengthening of the C(3)–C(4) bond of **6d** is undoubtedly caused by the C-phenyl substituents, which provide more extended resonance stabilization. The ab initio computed structures **8H** and **8Me** compare well with the X-ray structure of *cis*-**6a**.

The ^{13}C NMR spectrum of **3a** contains four quaternary carbons with very different chemical shifts. These were assigned by long-range HETCOR experiments and confirmed by ab initio computed ^{13}C NMR chemical shifts, referenced against SiMe_4 . The GIAO chemical shifts for methyl derivative **7Me** (see Table 1), computed at B3LYP/6-31G*, are in excellent agreement with the experimental values of **3a**. This validation of assignments confirms the alkynyl carbons to have rather different chemical shifts ($\Delta\delta = 23$ – 35 ppm). Also the phosphirane carbons have markedly different chemical shifts ($\Delta\delta = 21$ – 32 ppm). The calculated values show the influence of methyl substitution (cf., **7Me** vs **7H** and **8Me** vs **8H**) to be modest and in the expected range. The comparison between the observed and GIAO carbon chemical shifts of the 1,2-dihydro-1,2-diphosphetes **6a** and **8Me** is very reasonable, with the terminal alkyne carbon having the most prominent difference in δ values, i.e., $\delta_{\text{obs}} = 100$ vs $\delta_{\text{calc}} = 85$ ppm. The influence of methyl substitution in the computed chemical shifts of this alkyne carbon is modest in both **7** and **8**.

This study confirms that 1,3-diynes undergo only a single phosphinidene addition. No other reactions are found for the di-*n*-butyl and di-*tert*-butyl derivatives. In contrast, the dimethyl derivative shows an insertion of a second $\text{PhPW}(\text{CO})_5$ into the proximal C–P bond of the

phosphirene ring with the alkynyl group playing an important supportive role. The formation of both the *cis* and *trans* isomers of the 1,2-dihydro-1,2-diphosphete illustrates this insertion reaction to occur with little regio- and stereoselectivity. In fact, the *trans* form isomerizes to the thermodynamically more stable *cis* form. Ab initio calculations of structural parameters and NMR chemical shifts in conjunction with an X-ray structure determination illustrate the special electronic effects in these systems.

Computational Section

Electronic structure calculations were carried out using the GAUSSIAN 94 suite of programs (G94).¹¹ For the density functional theory calculations we used Becke's three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional, referred to as B3LYP. The structures were calculated using the 6-31G* basis set and were verified to be minima. Their NMR shielding tensors were computed with the gauge-independent atomic orbital method (GIAO), which is incorporated in G94, and these are referenced against that of tetramethylsilane.

Experimental Section

NMR spectra were recorded on Bruker ARX 300 and DRY400 FT-NMR spectrometers. Chemical shifts are referenced in ppm to internal Me_4Si for the ^1H and ^{13}C NMR spectra and to external 85% H_3PO_4 for the ^{31}P NMR spectra. Downfield shifts are reported as positive. Mass spectra were recorded on a HP 5985 at 70 eV. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All materials were handled under an atmosphere of dry, high-purity nitrogen. Reagents and solvents were used as purchased, except for toluene, which was dried over molecular sieves. Chromatographic separations were performed on silica gel columns (230–400 mesh). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (**1**) and the general procedure for the phosphinidene addition to olefins and alkynes have been described in ref 5.

3a: 66% isolated yield; mp 113–4 °C, light yellow. ^{31}P NMR: δ -135.3 ($^1J_{\text{PW}} = 271$ Hz). ^1H NMR: δ 2.02 (d, $^5J_{\text{PH}} = 3.15$ Hz, 3H, CH₃), 2.32 (d, $^3J_{\text{PH}} = 9.6$ Hz, 3H, CH₃), 7.27 (m, 5H, Ph). ^{13}C NMR: δ 4.50 (s, CH₃), 11.9 (d, $^2J_{\text{PC}} = 6.1$ Hz, CH₃), 65.0 (m, $^2J_{\text{PC}} = 6.4$ Hz, C≡), 105.3 (m, $^3J_{\text{PC}} = 3.6$ Hz, C≡), 115.4 (s, $^1J_{\text{PC}} \approx 0$ Hz, C≡), 127.4 (d, $^2J_{\text{PC}} = 10.4$ Hz, *o*-Ph), 129.7 (d, $^4J_{\text{PC}} = 2.2$ Hz, *p*-Ph), 130.3 (d, $^3J_{\text{PC}} = 15.9$ Hz, *m*-Ph), 133.9 (d, $^1J_{\text{PC}} = 13.0$ Hz, *i*-Ph), 136.8 (s, $^1J_{\text{PC}} \approx 0$ Hz, C≡), 194.7 (d, *cis* CO, $^2J_{\text{PC}} = 8.6$ Hz), 196.3 (d, *trans* CO, $^2J_{\text{PC}} = 31.7$ Hz). Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{PWO}_5$: C, 40.00; H, 2.16. Found: C, 39.33; H, 2.26.

3b: 55% isolated yield, oil. ^{31}P NMR: δ -136.5 ($^1J_{\text{PW}} = 268.5$ Hz). ^1H NMR: δ 0.89 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H, CH₃), 0.90 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, CH₃), 1.41 (m, 4H, 2CH₂), 1.56 (dp, $^3J_{\text{HH}} = 6.9$ Hz, $^5J_{\text{PH}} = 0.98$ Hz, 2H, CH₂), 1.71 (dp, $^3J_{\text{HH}} = 6.9$ Hz, $^4J_{\text{PH}} = 1.8$ Hz, 2H, CH₂), 2.49 (dt, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{PH}} = 3.0$ Hz, 2H, CH₂), 2.75 (q, $^3J_{\text{HH}} = 7.5$ Hz, 2H, CH₂), 7.21 (m, 5H, Ph). ^{13}C

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NMR: δ 13.9 (s, CH₃), 14.1 (s, CH₃), 22.3 (d, $^4J_{PC}$ 2.0, CH₂), 22.9 (s, CH₂), 28.1 (d, $^3J_{PC}$ 5.6, CH₂), 29.6 (d, $^2J_{PC}$ 4.0, CH₂), 30.7 (s, CH₂), 30.8 (s, CH₂). ^{13}C NMR δ 67.7 (d, $^2J_{PC}$ = 6.1 Hz, C \equiv), 110.7 (d, $^3J_{PC}$ = 3.8 Hz, C \equiv), 115.2 (d, $^1J_{PC}$ = 2.8 Hz, C \equiv), 128.9 (d, $^2J_{PC}$ = 10.5 Hz, o-Ph), 131.0 (d, $^4J_{PC}$ = 2.5 Hz, p-Ph), 131.7 (d, $^3J_{PC}$ = 15.7 Hz, m-Ph), 138.6 (d, $^1J_{PC}$ = 3.1 Hz, C \equiv), 139.2 (d, $^2J_{PC}$ = 16.5 Hz, i-Ph), 196.2 (d, cis CO, $^2J_{PC}$ = 9.4 Hz), 198.4 (d, trans CO, $^2J_{PC}$ = 31.7 Hz).

3c: 52% isolated yield, mp 68–9 °C, light yellow. ^{31}P NMR: δ -136.7 ($^1J_{PW}$ = 270 Hz). 1H NMR: δ 1.16 (s, 3CH₃), 1.19 (s, CH₃), 1.24 (s, 2CH₃), 7.35 (m, 5H, Ph). ^{13}C NMR: δ 28.3 (s, CH₃), 29.0 (d, $^3J_{PC}$ = 2.7, CH₃), 29.5 (s, C-CH₃), 30.7 (s, CH₂), 30.9 (s, CH₃), 31.0 (s, CH₃), 35.3 (d, $^2J_{PC}$ = 5.0, C-CH₃), 65.9 (d, $^2J_{PC}$ = 5.9 Hz, C \equiv), 111.4 (s, C \equiv), 117.6 (d, $^1J_{PC}$ = 3.8 Hz, C \equiv), 128.8 (d, $^2J_{PC}$ = 10.5 Hz, o-Ph), 131.0 (d, $^2J_{PC}$ = 2.3 Hz, p-Ph), 131.5 (d, $^3J_{PC}$ = 15.8 Hz, m-Ph), 139.2 (d, $^1J_{PC}$ = 3.4 Hz, C \equiv), 146.8 (d, $^1J_{PC}$ = 20.2 Hz, i-Ph), 196.4 (d, cis CO, $^2J_{PC}$ = 8.6 Hz), 198.3 (d, trans CO, $^2J_{PC}$ = 32.0 Hz). Anal. Calcd for C₂₃H₂₃PWO₅: C, 46.46; H, 3.87. Found: C, 45.82; H, 3.88.

4: 85% isolated yield, mp 69–71 °C, light yellow. ^{31}P NMR: δ -157.4 ($^1J_{PW}$ = 266 Hz). 1H NMR: δ 2.20 (d, $^5J_{PH}$ = 39.6 Hz, 6H, CH₃), 7.20 (m, 5H, Ph). ^{13}C NMR: δ 11.2 (d, $^2J_{PC}$ = 27.9 Hz, CH₃), 128.3 (d, $^1J_{PC}$ = 9.7 Hz, i-Ph), 128.9 (d, $^2J_{PC}$ = 10.3 Hz, o-Ph), 130.7 (d, $^2J_{PC}$ = 3.2 Hz, p-Ph), 131.6 (d, $^3J_{PC}$ = 15.9 Hz, m-Ph), 139.0 (d, $^2J_{PC}$ = 3.4 Hz, C \equiv), 196.8 (d, cis CO, $^2J_{PC}$ = 8.8 Hz), 198.8 (d, trans CO, $^2J_{PC}$ = 29.8 Hz). Anal. Calcd for C₁₅H₁₁PWO₅: C, 37.04; H, 2.26. Found: C, 37.00; H, 2.35.

cis/trans-6a. Reaction of **1** with isolated **3a** in a 1:1 ratio in toluene for 2 h at 55–60 °C, following the same procedure as the alkyne additions, afforded a 2:1 mixture of *cis*- and *trans*-**6a** in 75% isolated yield. *cis*-**6a**: mp 168–70 °C, yellow. ^{31}P NMR: δ 49.0 ($^1J_{PP}$ = 34.3 Hz, $^1J_{PW}$ = 240 Hz), 43.0 ($^1J_{PP}$ = 34.3 Hz, $^1J_{PW}$ = 237 Hz). 1H NMR: δ 2.37 (d, $^3J_{PH}$ = 11.0 Hz, 3H, CH₃), 2.07 (d, $^3J_{PH}$ = 3.7 Hz, 3H, CH₃), 7.61 (m, 10H, Ph). ^{13}C NMR: δ 4.96 (d, $^4J_{PC}$ = 1.31 Hz, CH₃), 19.7 (dd, $^2J_{PC}$ = 2.86 Hz, $^3J_{PC}$ = 5.28 Hz, CH₃), 75.0 (dd, $^2J_{PC}$ = 8.2 Hz, $^3J_{PC}$ = 10.1 Hz, C \equiv), 99.8 (d, $^3J_{PC}$ = 5.3 Hz, C \equiv), 128–131 (m, C_{PH}), 133.5 (dd, $^1J_{PC}$ = 33.7 Hz, $^2J_{PC}$ = 19.9 Hz, C \equiv), 157.2 (dd, $^1J_{PC}$ = 41.9 Hz, $^2J_{PC}$ = 24.4 Hz, C \equiv), 196.1 (d, cis CO, $^2J_{PC}$ = 6.9 Hz), 196.2 (d, cis CO, $^2J_{PC}$ = 7.5 Hz), 197.7 (d, trans CO, $^2J_{PC}$

= 26.0 Hz), 198.2 (d, trans CO, $^2J_{PC}$ = 27.2 Hz). Anal. Calcd for C₂₈H₁₆P₂W₂O₁₀: C, 35.67; H, 1.70. Found: C, 35.80; H, 1.74. *trans*-**6a**: ^{31}P NMR: δ 50.8 ($^1J_{PP}$ = 32.2 Hz, $^1J_{PW}$ = 222.6 Hz), 45.5 ($^1J_{PP}$ 32.2, $^1J_{PW}$ = 227.2 Hz).

Crystal data for 6a: C₂₈H₁₆P₂W₂O₁₀, M_r = 942.06, yellowish block-shaped crystals (0.20 × 0.30 × 0.50 mm), monoclinic, space $P2_1/c$ (no. 14), with a = 15.5821(9) Å, b = 11.0693(10) Å, c = 17.6238(13) Å, β = 91.491(6)°, V = 3038.8(4) Å³, Z = 4, ρ_c = 2.059 g/cm³, $F(000)$ = 1768, μ (Mo K α) = 77.2 cm⁻¹, 7202 measured reflections, 6970 independent, $R(int)$ = 0.055, θ_{max} = 27.5°, ω scan, T = 150 K, Mo K α -radiation, graphite monochromator, λ = 0.710 73 Å, Enraf-Nonius CAD4T diffractometer on rotation anode. Reflection data were corrected for absorption using ψ -scan data (transmission range 0.56–0.98). The structure was solved by Patterson techniques (DIRDIF96) and refined on F^2 using SHELXL97. Convergence was reached at $R1$ = 0.0449 for 5329 reflections with $I > 2\sigma(I)$ ($wR2$ = 0.129). A final difference map did not show significant features other than residual absorption artifacts near W.

Atom coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number.

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Supporting Information Available: Crystal data, bond lengths and angles, hydrogen atom positions, and isotropic and anisotropic displacement parameters (25 pages). Ordering information is given on any current masthead page.

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