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Rearrangement of a W(CO)$_5$-Complexed 7-Phosphanorbornadiene Analyzed by ab Initio MO Calculations

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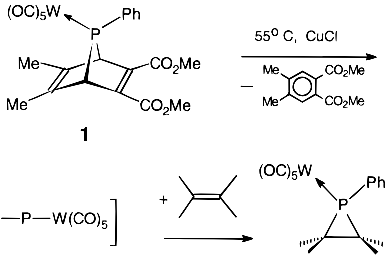
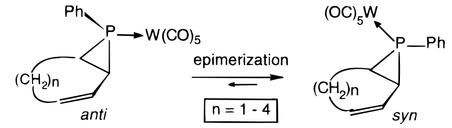
The rearrangement of W(CO)$_5$-complexed 7-phosphanorbornadiene **1** to the 7-phosphatricyclo[3.2.0^{4,6}]hept-2-ene complex **2** is investigated experimentally and with the aid of ab initio theory at MP2(fc)/6-31G*. Photochemical concerted and thermal biradical pathways are considered. Calculations on the uncomplexed parent system indicate that a thermal rearrangement is unlikely because of its 6.4 kcal/mol endothermicity. The relationship of the **1** → **2** rearrangement with the CuCl-catalyzed, thermal decomposition of **1** to generate the incipient phosphinidene complex PhPW(CO)$_5$ is discussed.

Phosphinidenes gain rapidly in popularity as versatile reagents in the syntheses of low-coordination organophosphorus compounds.[1,2] Through transition metal complexation, the otherwise triplet species[3] are stabilized to singlets.[4] Nucleophilic phosphinidenes, tailored after the Schrock complexes, use Ta and Zr in, for example, the phospha-Wittig reaction.[5] The best known electrophilic phosphinidenes, developed a decade ago by Marinetti and Mathey,[6] are stabilized by a W(CO)$_5$ group. They are generated in situ from the 7-phosphanorbornadiene precursor complex **1**.[7] In contrast to the uncomplexed triplet PhP[3a] and the nucleophilic RP=M (M = Ta, Zr complex),[5] the electrophilic RPW(CO)$_5$ has not been characterized spectroscopically. It is assumed that **1** undergoes a thermal retrocycloaddition to give the tetrasubstituted benzene and the coordinated phosphinidene, which immediately adds, for example, to olefins to give phosphiranes (eq 1).[6−10] This phosphinidene−olefin cycloaddition is a first-order process in the thermal decomposition of **1** at ∼90−110 °C, which can be catalyzed by CuCl to occur at ∼55 °C.[6]



(1)

In analogy with the chemistry of carbenes, generated from diazirines,[11] there is the lingering question whether RPW(CO)$_5$ phosphinidenes are formed from **1** in a concerted or a stepwise process. The possible existence of biradical intermediates surfaced in our recent observation that W(CO)$_5$-complexed vinylphosphiranes P-epimerize under mild reaction conditions (eq 2).[12]



(2)

Mathey[1a] argued that if **1** were to give a biradical thermally it would rearrange to a cyclophosphaheptatriene (phosphepine), which has never been observed

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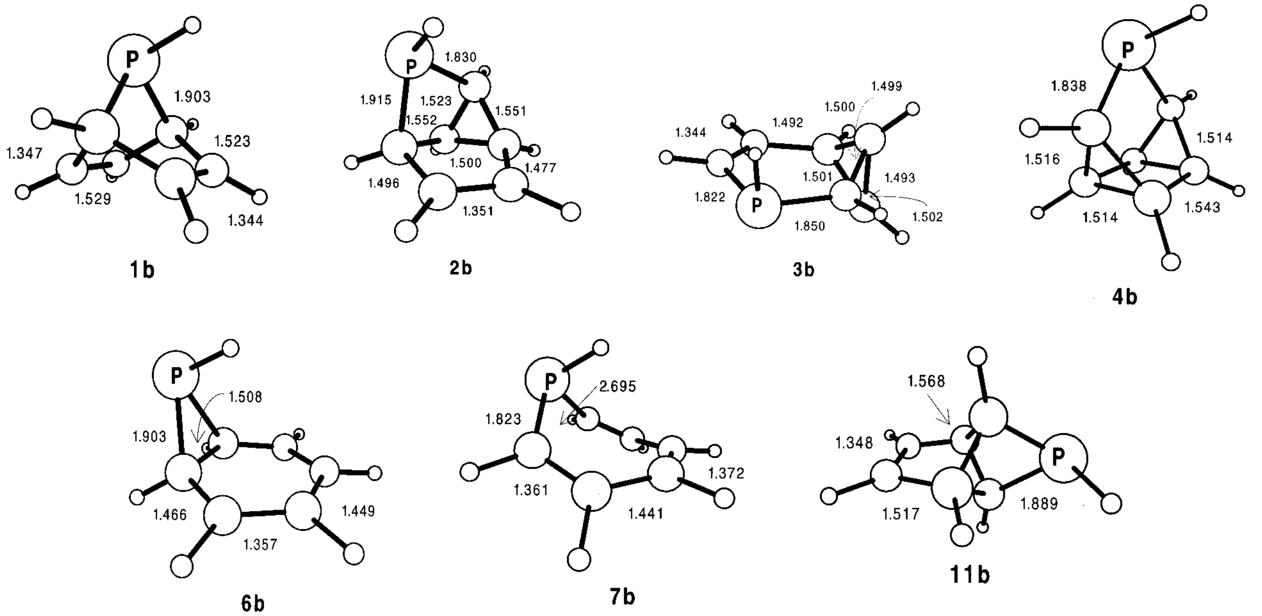
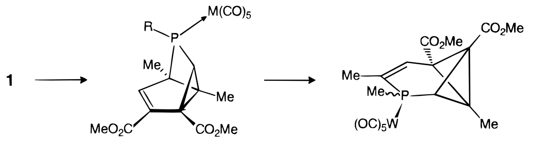


Figure 1. MP2/6-31G* geometries for **1b**, **2b**, **3b**, **4b**, **6b**, **7b**, and **11b**.

in these reactions. Marinetti and Mathey did show that **1**, when exposed to sunlight for 2 weeks, rearranges to the tricyclic compound, **2**, which rearranges further to **3** when the P atom carries a Me instead of a Ph substituent (eq 3).[13]



(3)

2 R = Ph, Me; M = W, Cr **3**

To understand in more detail the reaction channels available to **1** and the relationship with its isomers, we investigated the **1** → **2** rearrangement and computed by ab initio quantum mechanical methods isomeric model structures that are devoid of substituents and of the metal group.

Computational Methods

The *ab initio* calculations[14] were carried out using the Gaussian 94 suite of programs[15] for the parent unsubstituted and uncomplexed organophosphorus compounds. These are identified with the index **b**. Geometries of **1b**–**4b**, **6b**, **7b**, and **11b** were optimized at the SCF level with the d-polarized split-valence 6-31G* basis set and with inclusion of the effects of valence electron correlation by using Møller–Plesset perturbation theory at second order (MP2(fc)); no activation barriers were determined. Force constant matrices and zero-point vibrational energies (ZPVE) were calculated analytically for the geometries. MP2(fc)/6-31G* absolute, relative, and ZPVE energies are given in Table 1, and the geometries are shown in Figure 1. Table 1 also lists the PMP2(fc)/6-31G* energies for the C_6H_7 radicals **9** and **10**. Throughout the text we will use relative energies, corrected for ZPVEs.

Table 1. Absolute (in au) and Relative Energies (in kcal/mol) of C_6H_7P Isomers and the Hydrocarbon Radicals 7 and 8[a]

compd	MP2(fc)/6-31G*	ZPVE	ΔE^b
1b	−572.793 79	74.77	0.00
2b	−572.783 42	74.93	6.36
3b	−572.759 92	74.19	21.80
4b	−572.757 94	74.72	22.54
6b	−572.813 84	74.89	−12.70
7b	−572.801 30	74.28	−4.25
11b	−572.754 10	74.94	24.74
$C_6H_7^\bullet$ (**9**)	−231.979 87	72.72	0.00
$C_6H_7^\bullet$ (**10**)	−231.953 60	72.06	17.11

[a] PMP2 energies are given for the radicals **9** and **10**. [b] The HF/6-31G* zero-point vibrational energies (ZPVE, in kcal/mol) are scaled by 0.95 in the relative energies ΔE.

Results and Discussion

In many of the CuCl-catalyzed phosphinidene olefin cycloadditions (at 55 °C), we have observed formation of some of the $W(CO)_5$ complex of **2** ($\delta_{^{31}P}$ = 19.5 ppm), suggesting a possible thermal conversion from **1**. However, as noted, compound **2** is reportedly formed (~40%), in the absence of a catalyst, upon exposure of **1** to sunlight for 2 weeks.[13] We therefore wondered whether **2** could be formed as a side product in a stepwise, thermal retrocycloaddition of **1** that gives the incipient phosphinidene complex $RPW(CO)_5$. It should be noted that the related formation of silylenes from 7-silanorbornadiene has been discussed in terms of a mechanism involving radicals.[16] But, when **1** was heated at 55 °C in the NMR probe (*i.e.*, in the absence of light), using toluene-d_6 as solvent and with CuCl present as catalyst,

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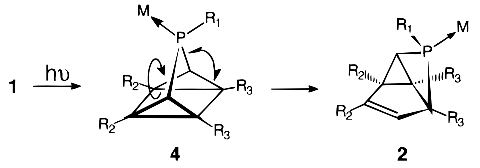
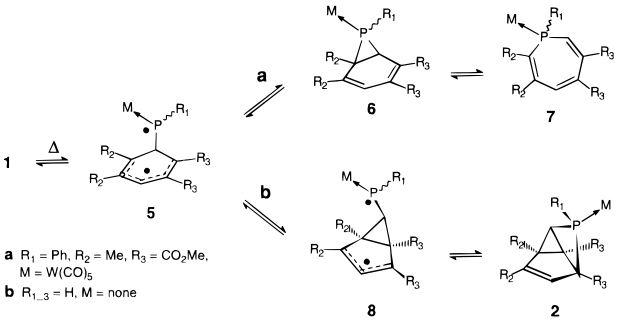
Scheme 1



Scheme 2



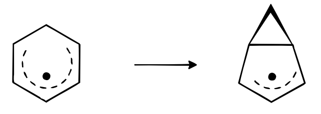
no noticeable rearrangement was observed as monitored by ^{31}P NMR. In contrast, the **1** → **2** conversion is abundant in a matter of hours in the presence of daylight or even in fluorescent light used in hoods. These observations do support a photochemical pathway for the **1** → **2** rearrangement. To ascertain the nature of this rearrangement, we conducted theoretical calculations on model systems and determined the X-ray structure of **2**.

The photochemical and thermal rearrangements to be considered for **1** are shown in Schemes 1 and 2, respectively. The photochemical pathway, suggested by Mathey, involves cyclization to P-quadricyclane **4**, followed by a disrotatory opening of a cyclopropane ring with a concurrent P-shift. A homolytic C−P bond fission is expected to be the initial step in a biradical mechanism. Ring closure of the resulting biradical **5** can give (besides **1**) phosphirane **6** (path a), which is subject to a subsequent electrocyclic ring opening to phosphepine **7**. Alternatively, a C−C bond closure of the pentadienyl radical unit in **5** (path b) affords biradical **8**, from which the observed **2** would result on C−P bond closure.

Ab initio calculations at MP2(fc)/6-31G* on the model systems **1b**−**4b**, **6b**, **7b**, and **11b**, which contain neither C- nor P-substituents nor the complexing W(CO)$_5$ group, provide support for the photochemical rearrangement of **1**. Importantly, the rearranged structure **2b** is 6.4 kcal/mol less stable than 7-phosphanorbornadiene **1b**. This endothermicity, albeit surprisingly small and despite the unknown influence of substituents and the W(CO)$_5$ coordinating group, would exclude the **1** → **2** rearrangement to occur thermally.

The global minimum energy structure, isomeric phosphirane **6b**, is energetically favored over **1b** by a significant 12.7 kcal/mol and therefore would be the expected product from a thermal process. Formation of phosphepine **7b** from **6b** via a disrotatory ring opening is unlikely because of its 8.5 kcal/mol endothermicity, which is according to expectations. Structure **6b** has a normal phosphirane C−C bond length of 1.508 Å, while these carbons are separated by 2.695 Å in the ring-opened phosphepine **7b**—there is no indication for homoaromatic character. While the influence of substituents and of the W(CO)$_5$ group on the relative stability of these two isomers is not known, our experimental work shows no evidence for the formation of either **6** or **7**. If phosphanorbornadiene complex **1** undergoes a thermal retro-[1,4]-cycloaddition to generate the PhPW(CO)$_5$ phosphinidene, then **6** is likewise subject to a retro-[1,2]-cycloaddition. Both processes render the same thermodynamically favored benzene derivative. Because phosphinidene cycloadditions are conducted until precursor **1** is consumed, it is unlikely that **6** would survive the reaction conditions. The thermally allowed electrocyclic interconversion of **6** and **7** does not alter this picture.

If the retro-[1,4]-cycloaddition of **1** were to occur in a stepwise manner, starting with a C−P bond fission, to give the common biradical intermediate **5**, a C−C ring closure of its cyclohexadienyl radical unit provides a structural change to the bicyclo[3.1.0]hexenyl radical component in **8** (Scheme 2, path b). However, such a ring closure is estimated to be endothermic for the $C_6H_7^\bullet$ radicals (**9** → **10**) by 17.1 kcal/mol at PMP2/6-31G*.



While subsequent C−P bond formation between the phosphorus and allyl radical centers provides a direct route to the observed product, the overall conversion of **1b** to **2b** is, as noted, estimated to be endothermic by 6.4 kcal/mol. Therefore, these data suggest that the hydrocarbon framework of **2** is not formed by a radical process.

Additional evidence comes from the lack of P-epimerization of the isomers of **1**. We were able to isolate the minor syn form of **1** from the well-documented Diels−Alder reaction of 1-phenyl-3,4-dimethylphosphole W(CO)$_5$ complex and dimethylacetylenedicarboxylate.[6] This isomer, which is formed in minute amounts, does not epimerize to anti-**1**, which is used in the phosphinidene addition reactions (eq 1). Since epimerizations do occur for vinylphosphiranes (eq 2),[12] its absence in the case of **1** also argues against the stepwise formation of incipient PhPW(CO)$_5$.

Photochemical [2 + 2]-cyclizations of norbornadiene and its 7-hetero derivatives to the corresponding quadricyclanes are well established.[17] Whereas phospha derivative **4** remains elusive, Mathey suggested it as an intermediate in the formation of **2**. We estimate phosphaquadricyclane **4b** to be 22.5 kcal/mol less stable than **1b**. Structure **4b**, which contains two normal cyclopropane rings and a slightly elongated cyclobutane ring, does not show signs of additional strain on the phosphorus bridge. Its P−C bonds of 1.838 Å are even 0.065 Å shorter than those in **1b**; this difference is also reflected in the 6.5° wider CPC angle of 84.1° for **4b**. Rearrangement of **4b** to **2b** is exothermic by 16.2 kcal/mol. This energy difference reflects largely relief of ring strain.

We briefly comment on the X-ray structure of **2**, shown in Figure 2, which reveals a polycyclic product with three-, four-, five-, and six-membered rings[18] analogous to its earlier reported Cr(CO)$_5$ complex.[13] The phosphacyclobutane ring shows significant folding with

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[17] Bansal, R. C.; McCulloch, A. W.; McInnes, A. G. *Can. J. Chem.* **1969**, *47*, 2391.

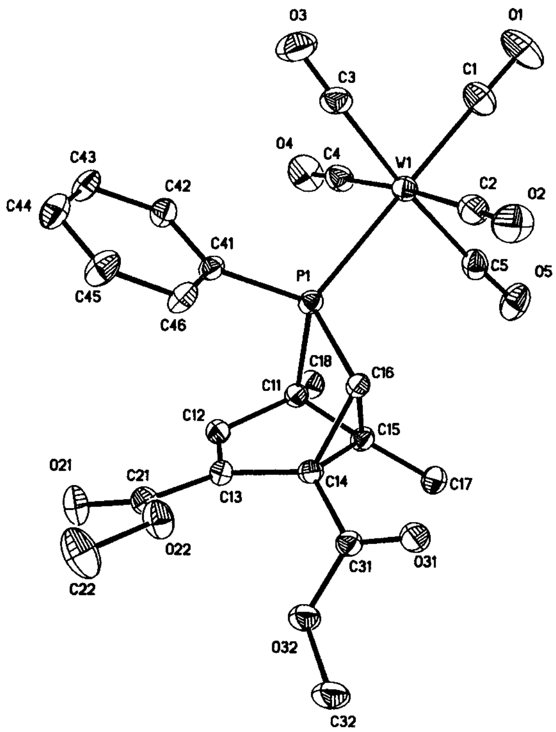


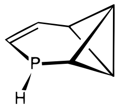
Figure 2. Ortep representation of **2a**. Selected bond distances (in Å) and angles (in degrees): P(1)–C(11) = 1.936(5), P(1)–C(16) = 1.806(4), C(11)–C(15) = 1.570(5), C(15)–C(16) = 1.517(7), C(11)–C(12) = 1.486(6), C(12)–C(13) = 1.332(6), C(13)–C(14) = 1.500(6), and C(14)–C(15) = 1.527(6); C(11)–P(1)–C(16) = 77.6(2), P(1)–C(11)–C(15) = 85.5(3), P(1)–C(16)–C(15) = 91.8(3), C(11)–C(15)–C(16) = 99.0(3), P(1)–C(11)–C(12) = 104.0(3), P(1)–C(16)–C(14) = 116.1(3).

P(1) residing 0.6477 Å out of the plane formed by C(11)–C(15)–C(16), resulting in a puckering angle of 26.4°. This is associated with an especially long P(1)–C(11) bond of 1.936(5) Å and an elongated C(11)–C(15) bond of 1.570(5) Å. These contrast the regular P(1)–C(16) bond length of 1.806(4) Å and the short bond distance of 1.517(7) Å for the C(15)–C(16) bond that is shared with the cyclopropyl ring. No strain is evident in the rest of the molecule; the cyclopentene ring is essentially planar (the average deviation from the plane is 0.09 Å) with a normal intercept of 66.5° with the cyclopropane C(14)–C(15)–C(16) plane. The computed geometry of structure **2b** is very similar to the X-ray structure. The largest difference is found in the 0.021 Å shorter P(1)–C(11) bond, which is still a sizable 1.915 Å long.

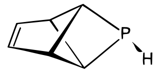
Despite its very long P(1)–C(11) bond of 1.936(5) Å, **2** is remarkably stable at temperatures up to ~75 °C. The neighboring vinyl group may contribute to the long P–C bond through hyperconjugation. This weakening of the P–C bond is expected to facilitate P-epimerization. However, because only *anti*-**2** is observed, we assume that the syn isomer is the sterically more congested of the two. As noted above (eq 2), various vinylphosphiranes have been shown to undergo P-epimerization. In addition, the syn phosphiranes of 1,3-cyclohexadienes undergo a subsequent thermal [1,3]-sigmatropic rearrangement (with inversion of the P-center) to phosphanorbornenes. Because no [1,3]-shift is observed for **2**, we assume it to be the thermodynamically more stable product. This is not unreasonable in light of the presence of the Me and CO_2Me substituents. For unsubstituted **2b**, the thermal [1,3]-shift represents a symmetry-allowed, degenerate process.

Interestingly, Mathey reported that the anti form of the $W(CO)_5$-complexed P-methyl isomer **2**, but not the P-phenyl derivative, gives a photochemically induced suprafacial [1,3]-sigmatropic rearrangement to **3** (eq 3). This process was argued to make use of the relative weak C(11)–C(15) bond of 1.560 Å. However, it is not at all clear why the P–Ph and the P–Me group influence the photochemical stability of **2** differently, although the through-bond Ph-conjugative stabilizing may be a contributing factor. The computed structure **3b** is estimated to be a large 15.4 kcal/mol less stable than **2b** and only marginally more stable (by 0.7 kcal/mol) than P-quadricyclane **4b**.

To further explore accessible isomers, we also calculated structure **11b**. This structure contains two phosphetane rings with P–C bond lengths of 1.889 Å, a CPC bond angle of 62.8°, and a puckering angle of 39.6°. Isomer **11b** is estimated to be only 2.2 kcal/mol less stable than P-quadricyclane **4b**; the energy difference with **2b** amounts to 18.4 kcal/mol. These data suggest that appropriately substituted phosphorus-containing dihydropropellane may be synthetically accessible.



3b



11b

The important conclusion reached from this study is that no evidence is found for the intermediacy of biradicals in the formation of $W(CO)_5$-complexed phosphinidene from the CuCl-catalyzed decomposition of its 7-phosphanorbornadiene precursor **1**. The rearrangement of **1** giving **2** occurs only in light, thereby eliminating a thermal multistep process. Support for this interpretation is obtained from theoretical ab initio calculations on the parent uncomplexed systems. These show the rearrangement to be endothermic. The calculations show both isomeric structures **6** and **7** to be more stable than **1**. Because no experimental evidence is found for their presence, it follows that the CuCl-catalyzed generation of $PhPW(CO)_5$ from complexed 7-phosphanorbornadiene is likely a concerted retro-[1,4]-cycloaddition.

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore FT-NMR spectrometer. Chemical shifts are referenced in ppm to internal $(CH_3)_4Si$ for the ^1H and ^{13}C NMR spectra and external 85% H_3PO_4 for the ^{31}P NMR spectra. Downfield shifts are reported as positive. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Reagents and solvents were used as purchased, except for THF, which was distilled from sodium–benzophenone prior to use. Chromatographic separations were performed on silica gel columns (230–400 mesh, EM Science). The synthesis of *anti*-[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (**1**) is described in ref 7. We isolated **2** as a side product from the addition reactions of **1** with various olefins.

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(18) For a related, less distorted diphospha structure with two bridgehead phosphor atoms, see: Breit, B.; Boese, R.; Regitz, M. *J. Organomet. Chem.* **1994**, *464*, 41.

η^1(P)-{3,4-Diethoxycarbonyl-1,5-dimethyl-7-phenyl-7-phosphatricylo[3.2.0^{4,6}]hept-2-ene}pentacarbonyltungsten (2). yellow crystals; mp 128−130 °C; ^{31}P NMR (C_6H_6) δ 19.5 ($^1J(^{31}P-^{183}W) = 240.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 197.9 (d, $^2J(C-P) = 31.4$ Hz, trans CO), 195.9 (d, $^2J(C-P) = 6.9$ Hz, cis CO),167.6 (s, $\mathit{C}O_2CH_3$), 164.1 (s, $\mathit{C}O_2CH_3$), 146.1 (d, $^3J(C-P) = 9.9$ Hz, C═), 137.1 (d, $^2J(C-P) = 16.0$ Hz, CH═), 128.2−130.3 (m, Ph), 60.9 (d, $^1J(C-P) = 25.7$ Hz, CP), 55.7 (d, $^2J(C-P) = 7.8$ Hz, $\mathit{C}CO_2CH_3$), 52.8 (s, $\mathit{C}CH_3$), 51.7 (s, $CO_2\mathit{CH_3}$), 51.2 (d, $^2J(C-P) = 10.1$ Hz, $CO_2\mathit{CH_3}$), 30.4 (d, $^1J(C-P) = 49.2$ Hz, CHP), 17.0 (d, $^2J(C-P) = 7.8$ Hz, CH_3), 9.6 (d, $^3J(C-P) = 4.8$ Hz, CH_3); ^{1}H NMR ($CDCl_3$) δ 7.1−7.5 (m, 5H, phenyl), 5.81 (d, $^3J(H-P) = 3.91$ Hz, 1H, CH═), 3.89 (s, 3H, CO_2CH_3), 3.57 (s, 3H, CO_2CH_3), 3.24 (d, $^1J(H-P) = 23.9$ Hz, 1H, CHP), 1.68 (d, $^3J(H-P) = 21.1$ Hz, 3H, CH_3), 1.33 (s, 3H, CH_3). Anal. Calcd for $C_{23}H_{19}O_9PW$: C, 42.20; H, 2.90. Found: C, 42.06; H, 2.98.

***syn*-[5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (1).** yellow crystals; mp 144−146 °C; ^{31}P NMR (C_6H_6) δ 230 ($^1J(^{31}P-^{183}W) = 229.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 199.1 (d, $^2J(C-P) = 25.6$ Hz, trans CO), 196.2 (d, $^2J(C-P) = 6.5$ Hz, cis CO),145.4 (d, $^3J(C-P) = 19.4$ Hz, $\mathit{C}O_2CH_3$), 141.5 (d, $^3J(C-P) = 14.5$ Hz, $\mathit{C}CH_3$), 139.4 (d, $^3J(C-P) = 3.6$ Hz, $\mathit{C}CO_2CH_3$), 129.8 (s, p-Ph), 128.9 (d, $^2J(C-P) = 7.6$ Hz, o-Ph), 127.4 (d, $^3J(C-P) = 9.5$ Hz, m-Ph), 60.7 ($^2J(C-P) = 21.2$ Hz, CHP), 52.9 (s, OCH_3), 15.9 (s, CH_3); ^{1}H NMR ($CDCl_3$) δ 7.0−7.3 (m, 5H, phenyl), 3.93 (d, $^2J(H-P) = 2.2$ Hz, 2H, CHP), 3.78 (s, 6H, CO_2CH_3), 1.53 (s, 6H, CH_3).

Crystal Data for 2. $C_{23}H_{19}O_9PW$, MW = 654.2, triclinic, $a = 10.1445(19)$ Å, $b = 10.9093(8)$ Å, $c = 11.5289(15)$ Å, $\alpha = 85.072(8)°$, $\beta = 81.254(10)°$, $\gamma = 76.385(8)$, $V = 1223.9(3)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.775$ Mg/m^3, crystal dimensions 0.30 × 0.25 × 0.25 mm, and absorption coefficient $\mu = 4.888$ mm^{-1}. Data were collected on an Enraf Nonius CAD4/V at 298 K with Mo Kα ($\lambda = 0.710\ 73$ Å, ω scan, $2\theta_{max} = 45.0°$). Of the 3412 reflections measured with index ranges of $0 \le h \le 10$, $-11 \le k \le 11$, and $-12 \le l \le 12$, 3192 were unique ($R_{int} = 1.04\%$). Their refinement against 307 parameters converged (largest $\Delta/\sigma = 0.001$) with $R = 2.45\%$ and $R_w = 3.14\%$; $R = 2.22\%$ and $R_w = 3.00\%$ for those 2959 reflections with $|F| > 6.0\sigma(|F|)$. Largest features left on the difference Fourier map were a peak of 0.46 e Å^{-3} and a hole of −0.31 e Å^{-3}.

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Supporting Information Available: Listings of positional and thermal parameters and a complete listing of bond lengths and angles for **2** (8 pages). Ordering information is given on any current masthead page.

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