

one considers the order of bond strengths⁴¹ $M-C > M-O > M-N$ together with the order $N-H > O-H > C-H$, we conclude that catalytic amination of olefins by the mechanism of Scheme I will be difficult to achieve unless the $N-H$ bond is activated (e.g., in NH_2COR).^{7,42} Heterolytic activation paths that take advantage of the inherent acidity of $N-H$ bonds are being explored in our

laboratories as an alternative mechanism for catalytic amination.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates and figures showing complete atom-numbering schemes for **2** and **7** (9 pages); tables of observed and calculated structure factors (66 pages). Ordering information is given on any current masthead page.

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Effects of $HgCl_2$ and $W(CO)_5$ Coordination on the Structure of a 1,2-Dihydrophosphete (Phosphacyclobutene)

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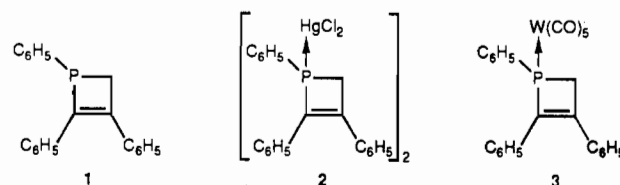
The synthesis and structural characterization of 1,3,4-triphenyl-1,2-dihydrophosphete and its complexes with mercuric chloride and tungsten pentacarbonyl are reported. Changes in bond lengths and angles upon metal coordination are consistent with an increased bonding contribution from the phosphorus s orbital. This rehybridization is supported by 1H , ^{13}C , and ^{31}P NMR spectral studies. Metal coordination does not lead to any significant skewing of the geometry of the phosphacyclobutene ring toward the corresponding ring-opened 1-phosphabutadiene form, and in fact may have the reverse effect.

Introduction

Small-ring carbocyclic and heterocyclic compounds continue to be of considerable interest. Questions about ring strain in these materials make them fertile ground for physical study, while the rich reaction chemistry of such compounds, frequently driven by relief of this ring strain, makes them key targets for synthetic study. Preliminary accounts suggest that phosphacyclobutenes (1,2-dihydrophosphetes) may provide convenient synthetic entry into unusual new classes of phosphorus heterocycles.¹⁻⁸ However, work in this area has been hampered by the lack of a simple, general route to the phosphacyclobutene ring system. Until recently, only a single representative, bearing a P -amino substituent, had been prepared in its uncomplexed form,⁵ while several other phosphacyclobutenes had been isolated in the form of their tungsten pentacarbonyl complexes or their P -oxides.² We have developed^{9,10} a simple and efficient synthesis of a variety of uncomplexed, trivalent, non-heteroatom-substituted phosphacyclobutenes and have taken advantage of this unique opportunity to embark on an examination of the structure and reactivity of these simple phosphorus heterocycles.

Reactivity of tungsten-coordinated phosphacyclobutenes consistent with electrocyclic ring opening to 1-phosphabutadienes, followed by $[4 + 2]$ cycloaddition with added dienophiles, has been reported.³ Indeed, on the basis of results of an X-ray diffraction analysis of one of these tungsten complexes, some distortion of the ground-state structure of the phosphacyclobutene toward the corresponding ring-opened form has been inferred.^{2,11} Although similar propensity toward ring opening has been documented in other small-ring heterocycles,¹²⁻¹⁵ our initial studies¹⁶ of the reactivity of a simple, uncomplexed representative of this class of compounds, phosphacyclobutene **1**, appeared to be inconsistent with this proposal. In light of the differences between the reactivity of uncomplexed phosphacyclobutene **1** and that of one of the reported tungsten complexes, we felt it was critical to study the effects of metal coordination on both the structure and reactivity of **1**. For this comparison, we chose to examine two quite different metal complexes—the mercuric chloride complex (**2**), to permit

an assessment of the importance of metal electrophilicity on complex structure and reactivity, and the tungsten pentacarbonyl complex (**3**), to facilitate comparison with literature reports. Herein, we report the synthesis and structural characterization of uncomplexed phosphacyclobutene **1** and its metal complexes, **2** and **3**.



Results

Addition of 1 equiv of phenyldichlorophosphine to a solution of 2,3-diphenyl-1-titanacyclobut-2-ene¹⁷ in benzene results in

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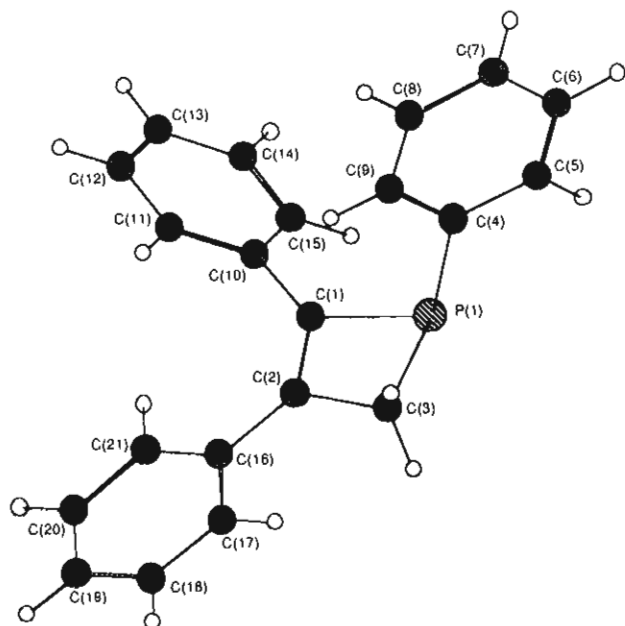
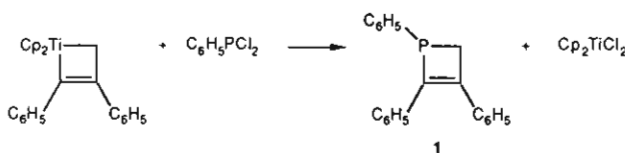


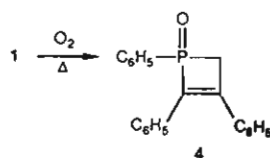
Figure 1. Molecular structure of 1,3,4-triphenyl-1,2-dihydrophosphete (1).

immediate precipitation of a red microcrystalline solid (Cp_2TiCl_2). Filtration of the reaction mixture through a short column of basic alumina, eluting with diethyl ether, affords 1,3,4-triphenyl-1,2-dihydrophosphete (1) as a white solid in 66% yield.



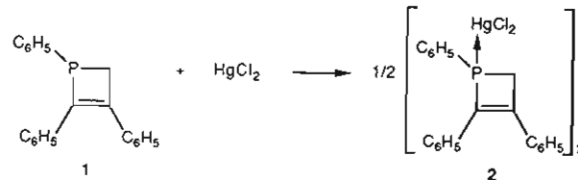
The ^1H NMR spectrum of 1 in C_6D_6 displays, in addition to multiplets for the aromatic protons, a doublet of doublets at δ 2.37 (1 H, $J_{\text{HH}} = 14.4$ Hz, $J_{\text{PH}} = 4.2$ Hz) and a doublet of doublets at δ 2.71 (1 H, $J_{\text{HH}} = 14.4$ Hz, $J_{\text{PH}} = 9.6$ Hz). The ^{13}C NMR spectrum of 1 displays a phosphorus-coupled doublet at δ 28.1 ($J_{\text{CP}} = 7.1$ Hz), and the ^{31}P spectrum shows a single resonance at δ -16.04. Crystallization of 1 from toluene/pentane affords colorless platelets. X-ray crystallographic analysis confirms the formulation of 1 as a phosphacyclobutene (Figures 1 and 2).

As a solid, 1 appears to be indefinitely stable to atmospheric oxygen and moisture. In benzene solution, 1 reacts slowly with oxygen at room temperature, or rapidly at 150 $^\circ\text{C}$, to form the corresponding *P*-oxide (4), displaying a similar, but shifted, ^1H NMR spectrum (doublets of doublets at δ 2.8 and 3.3), a ^{31}P resonance at δ 18.39, and a ^{13}C resonance at δ 42.7 ($J_{\text{PC}} = 59.2$ Hz). Infrared ($\nu_{\text{P=O}} = 1230$ cm^{-1}), high-resolution mass spectral, and elemental analyses are also consistent with this structural assignment for 4.

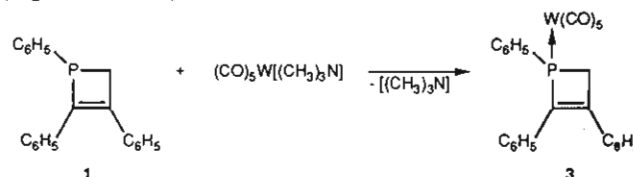


Treatment of 1 with 1 equiv of HgCl_2 in dry benzene affords a sparingly soluble white solid, 2, which displays a new pair of doublets in its ^1H NMR spectrum, at δ 3.01 (1 H, $J_{\text{HH}} = 16.0$ Hz, $J_{\text{PH}} = 14.1$ Hz) and δ 4.68 (1 H, $J_{\text{HH}} = 16.0$ Hz, $J_{\text{PH}} = 9.7$ Hz). Corresponding shifts are observed in the ^{13}C and ^{31}P NMR spectra of 2, with the methylene carbon appearing as a phosphorus-coupled doublet at δ 33.9 ($J_{\text{CP}} = 39.2$ Hz) and the

phosphorus giving rise to a singlet at δ 35.45. Complex 2 may be crystallized in the form of colorless laths from mixtures of benzene and tetrahydrofuran. X-ray analysis shows 2 to be a dimeric 1:1 complex in the solid state (Figures 3 and 4).



Phosphacyclobutene 1 reacts with $\text{W}(\text{CO})_5(\text{Me}_3\text{N})^{18}$ in toluene to afford a new complex, 3, displaying a new pair of doublets in its ^1H NMR spectrum, at δ 2.51 (1 H, $J_{\text{HH}} = 15.4$ Hz, $J_{\text{PH}} = 9.8$ Hz) and δ 3.16 (1 H, $J_{\text{HH}} = 15.4$ Hz, $J_{\text{PH}} = 2.8$ Hz). The methylene carbon resonance is shifted downfield from that observed for the uncomplexed phosphacyclobutene, appearing at δ 35.5 as a phosphorus-coupled doublet ($J_{\text{CP}} = 38.5$ Hz). The ^{31}P NMR spectrum of 3 shows a single resonance at δ 16.9, with satellites due to coupling to ^{183}W evident ($J_{\text{PW}} = 231$ Hz). Complex 3 crystallizes from heptane, forming irregular crystals suitable for X-ray diffraction analysis. Crystallographic study shows the phosphacyclobutene ring is maintained in this complex (Figures 5 and 6).

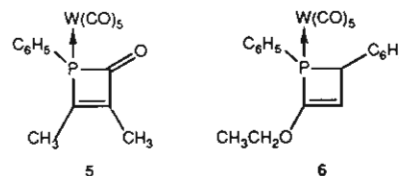


Discussion

Synthesis and Structure of Uncomplexed Phosphacyclobutene

1. The diphenyltitanacyclobutene, readily preparable from $\text{Cp}_2\text{TiCH}_2\text{Al}(\text{CH}_3)_2\text{Cl}$ and diphenylacetylene,¹⁷ reacts immediately with phenyldichlorophosphine at room temperature, precipitating titanocene dichloride and forming 1,3,4-triphenyl-1,2-dihydrophosphete (1). This reaction, of a type first reported for the formation of phosphole derivatives from zirconacyclopentadienes,¹⁹ is in fact quite general. A number of other alkyl- and alkoxydichlorophosphines react analogously,^{9,20} providing access to a variety of functionalized 1,2-dihydrophosphetes (phosphacyclobutenes). For the purposes of this discussion, we have focused only on the triphenyl derivative, 1.

The phosphacyclobutene ring system is comparatively rare. Neilson has reported the synthesis of a *P*-amino analogue as a mixture with its corresponding ring-opened 1-phosphabutadiene,^{5,11} while Mathey has prepared several phosphacyclobutenes as their tungsten pentacarbonyl complexes. Complexes 5⁴ and 6,² for example, have been characterized by X-ray diffraction analysis.



Oxidative workup of complexes such as 6 liberates the heterocycle. However, these conditions for liberation of the heterocycles have thus far allowed isolation of only the corresponding *P*-oxides. Given this apparent ease of oxidation of phosphacyclobutenes to their *P*-oxides, phosphacyclobutene 1 was anticipated to be highly reactive toward oxygen. In fact, however, it is quite inert to

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Table I. Details of Crystallographic Data Collection for 1-3

compd	1	2	3
chem formula	C ₂₁ H ₁₇ P	C ₄₂ H ₃₄ Cl ₄ Hg ₂ P ₂ ·0.5C ₆ H ₆	C ₂₆ H ₁₇ O ₅ PW
fw	300.343	1143.679	624.246
temp, K	298	294	140
cryst size, mm	0.28 × 0.15 × 0.48	0.30 × 0.15 × 0.10	0.03 × 0.12 × 0.16
appearance	colorless platelet	colorless lath	colorless sliver
radiation	Cu Kα (graphite monochromator)	Mo Kα (graphite monochromator)	Cu Kα (Ni filter)
wavelength, Å	1.541 78	0.710 69	1.541 78
space group	P2 ₁ /n	P2 ₁ /c	P $\bar{1}$
a, Å	9.265 (4)	18.465 (5)	9.373 (5)
b, Å	6.863 (3)	10.624 (4)	11.464 (9)
c, Å	26.082 (11)	23.507 (4)	12.976 (7)
α, deg	90	90	114.29 (5)
β, deg	93.826 (11)	94.62 (2)	96.60 (4)
γ, deg	90	90	109.03 (5)
V, Å ³	1655	4597 (4)	1150.1 (13)
Z	4	4	2
ρ _{calcd} , g cm ⁻³	1.2	1.708	1.802
μ, cm ⁻¹	13.0	70.0	104
scan width below Kα ₁ , deg	1.3	(1.00 + 0.30 tan θ)	1° total
scan width above Kα ₂ , deg	1.6	(1.00 + 0.30 tan θ)	
scan rate, deg min ⁻¹	4.5	16	58.6
no. of unique reflcns	1707	8862	2762
no. of obsd reflcns [I > 3σ(I)]	1471	4498	2155
2θ max, deg	100	50	108
data collected	+h,+k,±l	+h,+k,±l	±h,±k,+l
no. of params refined	164	241	264
R, R _w , GOF	0.050, 0.073, 2.87	0.044, 0.051, 1.53	0.082, 0.109, 0.87
max Δ/σ, last cycle	0.003	0.11	0.03
max, min in final diff map, e Å ⁻³	+0.25, -0.25	+1.03, -0.97	+2.1, -1.5

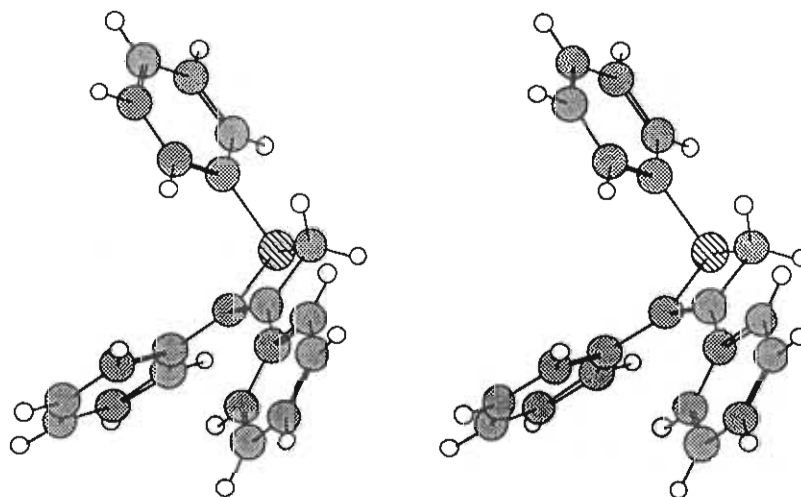
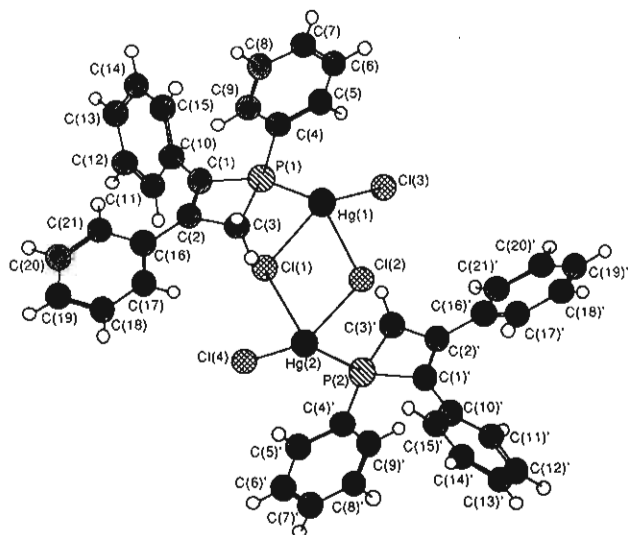


Figure 2. Stereoscopic view (crossed eye) of the molecular structure of 1,3,4-triphenyl-1,2-dihydrophosphete (1).

Figure 3. Molecular structure of the HgCl₂ complex of 1,3,4-triphenyl-1,2-dihydrophosphete (2).

oxidation, requiring prolonged reaction times or vigorous heating with oxygen to be converted to its corresponding *P*-oxide, **4**. Similarly, **1** was anticipated to undergo facile thermal ring-opening reactions driven by relief of ring strain, yet thermal reactions of **1** are for the most part sluggish at temperatures below 100 °C. Alone in an anaerobic benzene solution, **1** decomposes only slowly over a matter of several weeks at 150 °C.

Although all spectral features (*vide infra*) of **1** were consistent with formulation as a phosphacyclobutene, its relative chemical inertness cast some doubt on this structural proposal. Accordingly, we carried out a single-crystal X-ray crystallographic analysis (Tables I and II), confirming the phosphacyclobutene structure of **1** (Figures 1 and 2). Representative bond lengths and angles and dihedral angles are presented in Tables III-V. The phosphacyclobutene ring is not planar, displaying a dihedral angle of ca. 9.3°; this distortion is mirrored in the C=C double bond of the ring, which is twisted by 10.6°. The phenyl group on C(1) is twisted nearly 40° out of conjugation with the C(1)-C(2) double bond in **1**, while the phenyl group on C(2) is only 11° out of planarity, suggesting some delocalization into this aromatic ring.

The P-C(3) bond, 1.886 (4) Å, is slightly longer than the P-C bonds in trimethylphosphine²¹ (1.84 Å) or triphenylphosphine²²

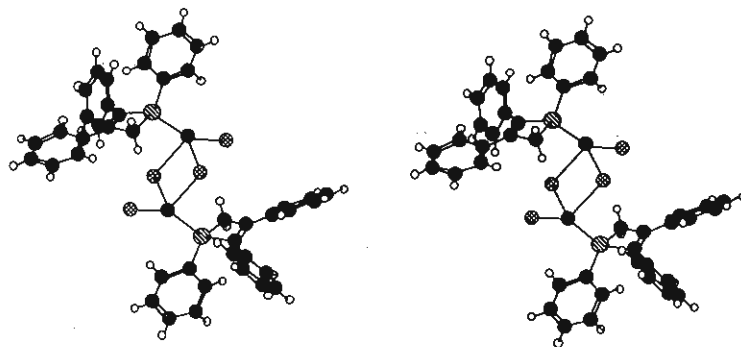


Figure 4. Stereoscopic view (crossed eye) of the molecular structure of the HgCl_2 complex of 1,3,4-triphenyl-1,2-dihydrophosphete (2).

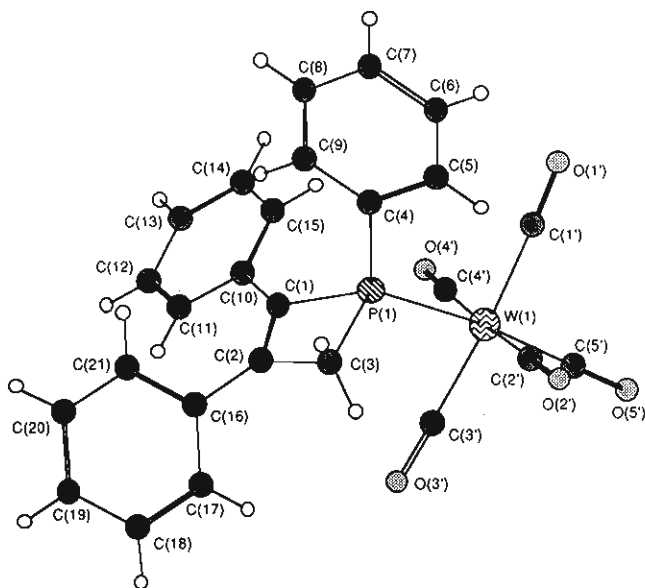


Figure 5. Molecular structure of the W(CO)_5 complex of 1,3,4-triphenyl-1,2-dihydrophosphete (3).

(1.83 Å) but is slightly shorter than that reported by Mathey for the analogous bond in complexes **5** (1.93 Å) and **6** (1.902 Å). Mathey has suggested^{2,3} that since this bond is lengthened (and thus presumably weakened), the phosphacyclobutene ring in **6** may undergo facile electrocyclic ring-opening to produce the corresponding 1-phosphabutadiene. Observation of a somewhat shortened P-C(1) bond in both **1** (1.821 Å) and **6** (1.815 Å) is consistent with some distortion of the ground-state structure toward the corresponding 1-phosphabutadiene form. However, whereas other bond lengths within the phosphacyclobutene ring of **6** are also consistent with such a distortion, the structure of **1** is not readily interpretable in this light—e.g., the C(1)–C(2) double bond appears normal at 1.366 Å, while the C(2)–C(3) bond, at 1.517 Å, is if anything slightly longer than expected for such a bond. Our studies on structural effects of coordination to tungsten (vide infra) suggest that metal coordination is not responsible for the elongated P–C(3) bond in **6**, which is perhaps a consequence of the phenyl substituent on C(3) of this complex.

The C(1)–P–C(3) angle in **1**, at 74°, is essentially the same as that seen in tungsten complexes **5** (71.9°) and **6** (74°), and somewhat smaller than that for the less-strained phosphacyclobutanes (phosphetanes, 79–83°).²³ Similarly, the angle between the *P*-phenyl bond and the phosphacyclobutene ring P–C bonds averages 104° in **1** and is nearly the same in **6** (104.5°) and triphenylphosphole (105°).²⁴ Such bond angles are consistent

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) [$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cos \alpha_{ij}$] for **1**^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
C(1)	3487 (4)	2543 (5)	6190 (1)	3.8 (2)
C(2)	4699 (4)	1432 (5)	6152 (1)	3.9 (2)
C(3)	4239 (4)	0133 (6)	5699 (1)	5.3 (2)
P(1)	2350 (1)	1128 (1)	5731.2 (4)	4.80 (6)
C(4)	2088 (2)	2733 (5)	5167 (1)	4.6 (2)
C(5)	3098 (2)	4141 (5)	5047 (1)	7.7 (3)
C(6)	2845 (2)	5305 (5)	4612 (1)	9.2 (3)
C(7)	1582 (2)	5061 (5)	4296 (1)	6.9 (3)
C(8)	0572 (2)	3654 (5)	4416 (1)	6.2 (2)
C(9)	0825 (2)	2489 (5)	4851 (1)	5.5 (2)
C(10)	3089 (2)	4242 (3)	6499 (1)	3.6 (2)
C(11)	1685 (2)	4306 (3)	6661 (1)	4.6 (2)
C(12)	1233 (2)	5906 (3)	6938 (1)	5.8 (3)
C(13)	2186 (2)	7442 (3)	7054 (1)	6.0 (3)
C(14)	3590 (2)	7378 (3)	6892 (1)	5.6 (3)
C(15)	4042 (2)	5778 (3)	6615 (1)	4.7 (2)
C(16)	6096 (2)	1263 (3)	6458 (1)	4.0 (2)
C(17)	6319 (2)	2140 (3)	6939 (1)	4.5 (2)
C(18)	7658 (2)	1974 (3)	7214 (1)	5.1 (2)
C(19)	8774 (2)	0931 (3)	7007 (1)	5.3 (2)
C(20)	8551 (2)	0055 (3)	6525 (1)	5.7 (2)
C(21)	7212 (2)	0221 (3)	6251 (1)	5.0 (2)

^a B_{eq} defined by Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

with a large proportion of phosphorus p character in these bonds, leaving the phosphorus lone pair in an orbital of significant s character. Similar conclusions have been reached²⁵ for simpler phosphines on the basis of a comparison of their structures^{21,22} with those of the corresponding amines.^{26,27}

Synthesis and Structure of HgCl_2 Complex 2. Crystallographic analysis (Tables I and VI) shows the HgCl_2 complex to be a dimer in the solid state (Figures 3 and 4). Representative bond lengths and angles and dihedral angles are presented in Tables III–V, VII, and VIII. As in **1**, the phosphacyclobutene ring is slightly twisted from planarity (1° and 5°, respectively, for the two phosphacyclobutenes in the dimer). Again, this distortion is mirrored in the C=C double bond twist (5.6° and 8.2°, respectively, for the two units in the dimer). The phenyl group on C(1) is twisted even more out of conjugation (average ca. 53°) than is the corresponding group in **1** (40°), while the phenyl group on C(2) displays a relatively small twist from coplanarity (average ca. 16°), analogous to that observed in **1** (11°).

Interestingly, the dimer, which has an effective center of symmetry, is made up of an RS pair of phosphacyclobutenes (chiral at phosphorus). Although reasonably close contacts between the

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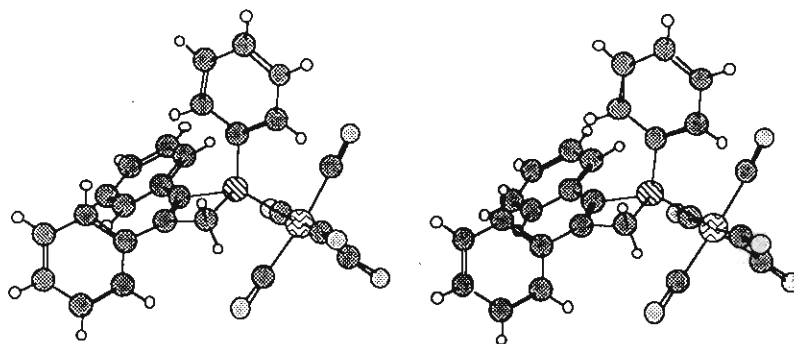


Figure 6. Stereoscopic view (crossed eye) of the molecular structure of the $\text{W}(\text{CO})_5$ complex of 1,3,4-triphenyl-1,2-dihydrophosphete (**3**).

Table III. Bond Lengths^a (Å) for the Phosphacyclobutene Core of **1-3**, **5**,^b and **6**^c

	1	2		3	5	6
P(1)-C(1)	1.821 (3)	1.80 (1)	1.80 (1)	1.816 (19)	1.83 (1)	1.815 (4)
P(1)-C(3)	1.886 (4)	1.82 (1)	1.80 (1)	1.813 (24)	1.93 (1)	1.902 (5)
P(1)-C(4)	1.842 (3)	1.79 (1)	1.81 (1)	1.801 (10)	1.85 (1)	1.820 (4)
C(1)-C(2)	1.366 (5)	1.34 (2)	1.34 (2)	1.358 (31)	1.36 (1)	1.331 (7)
C(1)-C(10)	1.477 (4)	1.48 (2)	1.46 (2)	1.477 (27)	1.46 (1)	
C(2)-C(3)	1.517 (5)	1.50 (2)	1.52 (2)	1.516 (29)	1.48 (1)	1.517 (7)
C(2)-C(16)	1.480 (4)	1.46 (2)	1.48 (2)	1.422 (24)	1.52 (1)	

^a Values for the two independent units in dimer **2** are reported separately. ESD values are given in parentheses, in units of least significant digit of the corresponding value. ^b Values for **5** taken from ref 4. ^c Values for **6** derived from data presented in ref 2.

Table IV. Bond Angles^a (deg) for the Phosphacyclobutene Core of **1-3**, **5**,^b and **6**^c

	1	2		3	5	6
C(1)-P(1)-C(3)	74.0 (2)	76.8 (6)	77.9 (6)	75.4 (10)	71.9 (5)	74.0 (2)
C(1)-P(1)-C(4)	104.3 (1)	111.9 (6)	115.4 (6)	107.1 (7)	<i>d</i>	105.7 (2)
C(3)-P(1)-C(4)	104.7 (1)	114.7 (6)	112.4 (6)	105.8 (8)	<i>d</i>	104.4 (2)
P(1)-C(1)-C(2)	95.5 (2)	91.8 (9)	91 (1)	94.3 (15)	97.0 (7)	95.9 (3)
P(1)-C(1)-C(10)	128.6 (2)	132 (1)	134 (1)	129.7 (14)		
C(2)-C(1)-C(10)	135.8 (3)	136 (1)	135 (1)	135.6 (15)		
C(1)-C(2)-C(3)	101.3 (3)	105 (1)	105 (1)	100.9 (17)	102.2 (9)	103.4 (4)
C(1)-C(2)-C(16)	134.3 (3)	129 (1)	131 (1)	133.2 (18)		
C(3)-C(2)-C(16)	124.3 (3)	126 (1)	124 (1)	125.8 (19)		
P(1)-C(3)-C(2)	88.0 (2)	86.0 (8)	86.0 (8)	89.3 (14)	88.8 (7)	86.5 (3)

^a Values for the two independent units in dimer **2** are reported separately. ESD values are given in parentheses, in units of least significant digit of the corresponding value. ^b Values for **5** taken from ref 4. ^c Values for **6** derived from data presented in ref 2. ^d Values not reported.

Table V. Dihedral Angles^a (deg) for the Phosphacyclobutene Core of **1-3** and **6**^b

	1	2		3	6
P(1)-C(1)-C(2)-C(3)	9.3	-5.2	-1.0	2.3	3.9
C(1)-P(1)-C(4)-C(5)	27.9	-47.2	45.1	-0.8	-16.6
C(1)-P(1)-C(4)-C(9)	-152.6	133.6	-141.4	177.9	163.6
C(3)-P(1)-C(4)-C(5)	-49.0	37.9	-41.6	-80.0	-93.7
C(3)-P(1)-C(4)-C(9)	130.5	-141.4	131.9	98.8	86.5
P(1)-C(1)-C(10)-C(11)	32.8	-52.4	-66.7	-15.6	
P(1)-C(1)-C(10)-C(15)	-145.0	128.2	115.5	160.2	
C(2)-C(1)-C(10)-C(11)	-143.2	130.0	121.2	173.4	
C(2)-C(1)-C(10)-C(15)	38.9	-49.4	-56.5	-10.9	
C(1)-C(2)-C(16)-C(17)	11.0	-26.6	-7.0	-53.3	
C(1)-C(2)-C(16)-C(21)	-167.9	154.7	172.6	129.3	
C(3)-C(2)-C(16)-C(17)	-163.7	152.1	174.4	123.0	
C(3)-C(2)-C(16)-C(21)	17.3	-26.7	-6.0	-54.5	

^a Values for the two independent units in dimer **2** are reported separately. ^b Values for **6** derived from data presented in ref 2.

two phosphacyclobutenes in the dimer may provide an energetic preference for formation of this dimer, this may in fact be merely an artifact of crystallization. We have not determined if the dimer structure is maintained intact in solution, where a monomer-dimer equilibrium or phosphine exchange may be quite facile.

The two phosphacyclobutene rings in dimer **2** display nearly identical metrical parameters; average values for the two rings will be used in the following discussion. At 1.81 Å, the P-C(3) bond in **2** is considerably shorter than the corresponding bond in the uncomplexed compound (1.886 Å). This bond is also shorter than typical P-C bonds in trialkylphosphines,²⁸ although it is

comparable to P-C bonds observed in other phosphine complexes of mercuric chloride.²⁹ To whatever extent the 1-phosphabutadiene form contributes to the structure of **1**, as potentially mirrored in the P-C(3) bond length, complex **2** would appear to be even less distorted toward such a ring-opened form. The other P-C

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Table VI. Atomic Coordinates ($\times 10^4$; Hg $\times 10^3$) and Equivalent Isotropic Thermal Parameters (\AA^2)
 $[B_{eq} = (8\pi^2/3)\Sigma_i U_{ij} a_i^* a_j^* \mu_i \mu_j]$ for **2**^a

atom	x	y	z	B_{eq}
Hg(1)	73341 (3)	16165 (5)	28181 (2)	4.11 (3)
Hg(2)	76108 (3)	45886 (5)	19215 (3)	4.38 (3)
Cl(1)	7467 (2)	4054 (3)	3043 (2)	5.2 (2)
Cl(2)	7467 (2)	2086 (3)	1714 (2)	4.8 (2)
Cl(3)	6086 (2)	1221 (4)	2813 (2)	6.4 (2)
Cl(4)	8868 (2)	4903 (4)	1957 (2)	6.0 (2)
P(1)	8544 (2)	1003 (3)	3137 (2)	3.4 (2)
P(2)	6382 (2)	5085 (3)	1622 (2)	3.9 (2)
C(1)	9011 (7)	1797 (11)	3736 (6)	3.6 (6)
C(2)	9456 (7)	2379 (11)	3399 (6)	3.4 (6)
C(3)	9273 (7)	1838 (12)	2817 (5)	4.3 (7)
C(1')	5939 (7)	4103 (12)	1073 (6)	4.0 (7)
C(2')	5474 (7)	3662 (12)	1434 (6)	3.8 (7)
C(3')	5698 (7)	4305 (12)	1998 (6)	4.6 (7)
C(4)	8660 (6)	-0668 (11)	3180 (5)	3.3 (6)
C(5)	9332 (7)	-1185 (13)	3306 (6)	4.3 (7)
C(6)	9424 (8)	-2463 (16)	3338 (6)	5.4 (8)
C(7)	8838 (11)	-3233 (14)	3230 (7)	6 (1)
C(8)	8159 (11)	-2771 (15)	3106 (7)	7 (1)
C(9)	8056 (8)	-1461 (13)	3077 (6)	5.2 (8)
C(10)	8922 (8)	1747 (12)	4355 (6)	4.0 (7)
C(11)	9525 (9)	1522 (15)	4724 (7)	6.0 (9)
C(12)	9451 (12)	1463 (18)	5308 (8)	8 (1)
C(13)	8803 (15)	1642 (21)	5496 (8)	8 (1)
C(14)	8236 (13)	1875 (30)	5146 (10)	13 (2)
C(15)	8284 (9)	1920 (23)	4580 (7)	10 (1)
C(16)	9999 (7)	3351 (12)	3541 (6)	3.9 (6)
C(17)	10587 (8)	3504 (14)	3220 (6)	5.4 (8)
C(18)	11084 (8)	4438 (17)	3366 (7)	6 (1)
C(19)	11014 (9)	5231 (14)	3837 (9)	7 (1)
C(20)	10417 (9)	5082 (14)	4147 (7)	5.5 (8)
C(21)	9921 (7)	4171 (13)	4007 (6)	4.7 (7)
C(4')	6213 (7)	6753 (12)	1542 (6)	4.3 (7)
C(5')	5519 (9)	7168 (16)	1404 (8)	7 (1)
C(6')	5374 (10)	8452 (16)	1343 (10)	9 (1)
C(7')	5921 (12)	9269 (15)	1472 (9)	8 (1)
C(8')	6592 (11)	8872 (16)	1646 (9)	8 (1)
C(9')	6735 (9)	7598 (14)	1667 (7)	6.1 (9)
C(10')	6085 (7)	3812 (14)	0487 (6)	4.6 (8)
C(11')	6261 (9)	2599 (15)	0353 (8)	6 (1)
C(12')	6377 (10)	2313 (20)	-0222 (11)	8 (1)
C(13')	6308 (12)	3195 (28)	-0644 (9)	9 (1)
C(14')	6153 (12)	4388 (24)	-0495 (8)	9 (1)
C(15')	6030 (9)	4687 (17)	0064 (8)	7 (1)
C(16')	4875 (7)	2745 (13)	1350 (7)	4.5 (7)
C(17')	4649 (8)	2262 (16)	0819 (7)	6 (1)
C(18')	4073 (10)	1408 (19)	0779 (9)	8 (1)
C(19')	3724 (10)	0982 (18)	1231 (9)	8 (1)
C(20')	3960 (9)	1449 (17)	1755 (9)	8 (1)
C(21')	4516 (9)	2328 (15)	1819 (7)	6 (1)

^a B_{eq} defined by Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609-610. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Table VII. Bond Lengths (\AA) for the HgCl_2 Dimer Core of **2**^a

Hg(1)-Cl(1)	2.651 (3)	Hg(2)-Cl(1)	2.732 (4)
Hg(1)-Cl(2)	2.673 (4)	Hg(2)-Cl(2)	2.712 (3)
Hg(1)-Cl(3)	2.342 (4)	Hg(2)-Cl(4)	2.339 (4)
Hg(1)-P(1)	2.389 (3)	Hg(2)-P(2)	2.381 (4)

^a Esd values are given in parentheses, in units of least significant digit of the corresponding value.

and C-C bonds within the phosphacyclobutene rings of **2** display lengths that are within 0.02 \AA of the values observed for uncomplexed **1**, while the P-C(4) bond (1.80 \AA) is slightly shorter than the analogous *P*-phenyl bond in **1** (1.84 \AA).

All intraring bond angles in complex **2** are within ca. 4° of those in the uncomplexed phosphacyclobutene **1**. However, the angle between the *P*-phenyl bond and the phosphacyclobutene ring P-C bonds is considerably larger (ca. 9°) in **2** than in **1**. This distortion toward tetrahedral geometry and sp^3 hybridization, previously observed for the HgCl_2 complexes of triphenylphosphole²⁹ and

Table VIII. Bond Angles (deg) for the HgCl_2 Dimer Core of **2**^a

Cl(1)-Hg(1)-Cl(2)	89.8 (1)	Cl(2)-Hg(2)-Cl(4)	103.2 (1)
Cl(1)-Hg(1)-Cl(3)	104.6 (1)	Cl(2)-Hg(2)-P(2)	95.0 (1)
Cl(1)-Hg(1)-P(1)	97.7 (1)	Cl(4)-Hg(2)-P(2)	153.9 (1)
Cl(2)-Hg(1)-Cl(3)	101.3 (1)	Hg(1)-Cl(1)-Hg(2)	91.4 (1)
Cl(2)-Hg(1)-P(1)	101.5 (1)	Hg(1)-Cl(2)-Hg(2)	91.4 (1)
Cl(3)-Hg(1)-P(1)	148.0 (1)	Hg(1)-P(1)-C(1)	119.6 (4)
Cl(1)-Hg(2)-Cl(2)	87.4 (1)	Hg(1)-P(1)-C(3)	116.2 (5)
Cl(1)-Hg(2)-Cl(4)	99.7 (1)	Hg(1)-P(1)-C(4)	113.1 (4)
Cl(1)-Hg(2)-P(2)	99.6 (1)		

^a Esd values are given in parentheses, in units of least significant digit of the corresponding value.

triphenylphosphine²⁹ and for the NiCl_2 complexes of phosphorinanes,³⁰ increases the *p* character of the phosphorus lone pair orbital, allowing for better bonding in the metal complexes.

The phosphorus-mercury bonds in **2** (average 2.38 \AA) are somewhat shorter than those in the complexes of triphenylphosphole²⁹ and triphenylphosphine²⁹ with mercuric chloride (2.438 and 2.406 \AA , respectively) but longer than those in the complexes of triethylphosphine³¹ and tributylphosphine²⁹ (2.36 and 2.35 \AA , respectively). This bond length appears to correspond qualitatively with phosphine basicity; however, a similar ordering of P-Hg bond lengths might also be predicted simply on the basis of phosphine steric bulk, with simple models suggesting that **1** has a cone angle³² intermediate to those for trimethylphosphine and tributylphosphine.

The P-Hg-Cl_{terminal} bond angle in complex **2**, averaging 150°, is noteworthy. The dimeric complexes of triphenylphosphole and triphenylphosphine with mercuric chloride exhibit P-Hg-Cl_{terminal} angles of 127.8 and 128.7°, respectively,²⁹ while the mercuric chloride complexes of trimethylphosphine²⁹ and triethylphosphine³¹ display much larger P-Hg-Cl_{terminal} angles of 145.5 and 161.8°, respectively. The latter complexes, however, are not simple dimers but rather extended structures in which each mercuric ion has an overall coordination number of 5. No intermolecular Cl-Hg distances in the structure of **2** are less than 3.8 \AA , so penta-coordination is presumably not responsible for the large P-Hg-Cl_{terminal} angle observed.

Synthesis and Structure of $\text{W}(\text{CO})_5$ Complex 3. A ligand-exchange reaction between phosphacyclobutene **1** and $(\text{CO})_5\text{W}(\text{Me}_3\text{N})$ ^{18,33} produces the $\text{W}(\text{CO})_5$ complex, **3**. Despite their poor form, crystals of complex **3** displayed satisfactory X-ray diffraction, allowing determination of its molecular structure (Tables I and IX, Figures 5 and 6). Representative bond lengths and angles and dihedral angles are presented in Tables III-V, X, and XI. The phosphacyclobutene ring is very nearly planar, with a dihedral of slightly more than 2°. The C=C double bond twist, as measured by the dihedral angle for the two phenyl substituents, is 7.7°, comparable to that seen in **1** and **2**. Interestingly, it is the phenyl substituent on C(1) that is nearly coplanar with the phosphacyclobutene ring, twisted out of plane by only ca. 11°, while the C(2) phenyl group is twisted over 53° from the plane of the phosphacyclobutene ring.

The relatively poor quality of the crystals of complex **3** limits any detailed structural comparisons. Complexation with tungsten pentacarbonyl appears to result in shorter P-C(3) and P-C(4) bonds than in uncomplexed phosphacyclobutene **1**. Other bond lengths in the phosphacyclobutene ring of **3** are similar to those in **1** and are within 3 σ of the P-C bond lengths in $(\text{Me}_3\text{P})\text{W}(\text{CO})_5$ (average P-C = 1.85 \AA)³⁴ and $(t\text{-Bu}_3\text{P})\text{W}(\text{CO})_5$ (average P-C = 1.93 \AA).³⁵

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Table IX. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (\AA^2) [$B_{\text{eq}} = (8\pi^2/3)\sum_i \sigma_i^2 U_{ii} a_i^* a_i^* \rho_i \rho_i$] for **3**^a

atom	x	y	z	B_{eq}
P(1)	2031 (6)	3968 (5)	2150 (4)	7.0 (2)
W(1)	1004 (1)	2349 (1)	2967 (1)	6.9 (1)
C(1)	2543 (22)	3385 (18)	772 (14)	6.7 (7)
C(2)	1357 (21)	3511 (18)	180 (15)	6.8 (8)
C(3)	631 (22)	4088 (18)	1153 (16)	7.2 (8)
C(4)	3449	5745	3123	7.3 (9)
C(5)	3293 (13)	6465 (12)	4240 (10)	7.7 (9)
C(6)	4358	7851	5002	7.6 (9)
C(7)	5580	8518	4648	9.3 (11)
C(8)	5736	7798	3531	8.2 (9)
C(9)	4670	6412	2769	7.8 (9)
C(10)	3733	2826	454	7.3 (8)
C(11)	4906 (14)	3001 (12)	1339 (7)	7.4 (8)
C(12)	5969	2394	1040	7.2 (9)
C(13)	5859	1613	-144	8.6 (12)
C(14)	4686	1438	-1030	8.4 (9)
C(15)	3623	2045	-731	8.3 (10)
C(16)	878	3274	-995	7.3 (9)
C(17)	1964 (12)	3918 (13)	-1453 (10)	8.0 (9)
C(18)	1479	3729	-2590	9.7 (13)
C(19)	-91	2897	-3267	9.5 (13)
C(20)	-1177	2253	-2808	8.5 (9)
C(21)	-692	2442	-1672	7.8 (9)
C(1')	2540 (19)	3631 (17)	4525 (10)	6.9 (8)
C(2')	-380 (21)	3317 (20)	3449 (16)	7.9 (9)
C(3')	-416 (20)	1129 (17)	1379 (11)	6.9 (8)
C(4')	2415 (19)	1386 (16)	2542 (14)	6.8 (7)
C(5')	-34 (23)	979 (17)	3459 (17)	8.1 (9)
O(1')	3513 (14)	4443 (13)	5441 (10)	8.0 (7)
O(2')	-1269 (16)	3830 (16)	3761 (13)	9.0 (7)
O(3')	-1278 (14)	478 (14)	407 (10)	8.8 (7)
O(4')	3252 (16)	790 (14)	2323 (12)	8.2 (6)
O(5')	-690 (18)	207 (14)	3804 (12)	9.4 (7)

^a B_{eq} defined by Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609-610. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Table X. Bond Lengths^a (\AA) for the W(CO)₅ Core of **3** and **6**^b

	3	6		3	6
P(1)-W(1)	2.487 (7)	2.484 (1)	C(1')-O(1')	1.182 (14)	1.127
W(1)-C(1')	1.956 (11)	2.045	C(2')-O(2')	1.185 (29)	1.142
W(1)-C(2')	1.965 (24)	2.003	C(3')-O(3')	1.183 (16)	1.128
W(1)-C(3')	1.939 (12)	2.026	C(4')-O(4')	1.185 (26)	1.134
W(1)-C(4')	1.973 (20)	2.036	C(5')-O(5')	1.182 (29)	1.146
W(1)-C(5')	1.947 (23)	1.991			

^a Esd values are given in parentheses, in units of least significant digit of the corresponding value. ^b Values for **6** derived from data presented in ref 2.

Two of the P-C bonds in **3** are also shorter than those reported for other tungsten-coordinated phosphacyclobutenes, **5** and **6**. In **5**, the P-C(carbonyl) bond (1.93 \AA)⁴ in the phosphacyclobutene ring is approximately 0.1 \AA longer than either intraring P-C bond in **3**. Although the carbonyl group in **5** may distort the ring, similar differences are apparent in **6**, in which the P-C(3) bond (1.90 \AA)² is approximately 0.09 \AA longer than the corresponding bond in **3**. This difference may be caused by the phenyl substituent on C(3) in complex **6**; lengthening of the P-C(3) bond reduces steric interactions between this group and the tungsten pentacarbonyl moiety. The lengths of the other phosphacyclobutene ring bonds in **3** are nearly identical with the corresponding bonds in **5** and **6**.

The P-W bond length in **3**, 2.49 \AA , is similar to that reported for **5** (2.47 \AA)⁴ and **6** (2.48 \AA)² and shorter than that reported for (Me₃P)W(CO)₅ (2.52 \AA)³⁴ and (*t*-Bu₃P)W(CO)₅ (2.69 \AA)³⁵. Considering the small cone angle of trimethylphosphine, it is notable that the P-W bond to the phosphacyclobutene ligand is shorter than the bond to trimethylphosphine.

The comparatively poor quality of the crystals of complex **3** and the relatively low 2θ data cutoff preclude any conclusions regarding the relative trans influence³⁶ of the phosphacyclobutene

Table XI. Bond Angles^a (deg) for the W(CO)₅ Core of **3** and **6**^b

	3	6
C(1)-P(1)-W(1)	121.6 (7)	120.9 (2)
C(3)-P(1)-W(1)	118.4 (7)	125.6 (1)
C(4)-P(1)-W(1)	119.8 (6)	117.6 (1)
P(1)-W(1)-C(1')	93.7 (6)	90.4
P(1)-W(1)-C(2')	85.7 (7)	92.6
P(1)-W(1)-C(3')	83.1 (6)	92.4
P(1)-W(1)-C(4')	95.7 (6)	87.7
P(1)-W(1)-C(5')	173.2 (6)	176.7
C(1')-W(1)-C(2')	89.6 (7)	88.6
C(1')-W(1)-C(3')	176.2 (7)	177.2
C(2')-W(1)-C(3')	92.1 (8)	90.8
C(2')-W(1)-C(4')	177.9 (9)	179.3
C(3')-W(1)-C(4')	89.7 (7)	89.8
C(1')-W(1)-C(4')	88.7 (7)	90.8
C(1')-W(1)-C(5')	92.6 (7)	90.5
C(2')-W(1)-C(5')	91.7 (10)	90.6
C(3')-W(1)-C(5')	90.7 (7)	86.7
C(4')-W(1)-C(5')	87.0 (9)	89.1
W(1)-C(1')-O(1')	176.5 (17)	178.0
W(1)-C(2')-O(2')	175.4 (21)	175.7
W(1)-C(3')-O(3')	174.8 (18)	176.0
W(1)-C(4')-O(4')	177.2 (18)	177.6
W(1)-C(5')-O(5')	175.9 (17)	179.6

^a Esd values are given in parentheses, in units of least significant digit of the corresponding value. ^b Values for **6** derived from data presented in ref 2.

ring; no significant or systematic differences are apparent in the lengths of the five W-CO bonds in **3** (average W-C = 1.95 \AA). Interestingly, although (PPh₃)Cr(CO)₅ and (PPh₃)Mo(CO)₅ display a significant shortening of the M-CO_{trans} bond,³⁷ no trans influence is discernable for (Me₃P)W(CO)₅ (average W-C = 2.01 \AA)³⁴ or (*t*-Bu₃P)W(CO)₅ (average W-C = 2.00 \AA)³⁵.

Complexation with tungsten pentacarbonyl has little effect on the phosphacyclobutene ring bond angles, which are, within experimental error, the same as those in the uncomplexed phosphacyclobutene. The intraring C-P-C angle in **3** is also similar to that reported for a related complex (**6**). The angle between the *P*-phenyl substituent and the phosphacyclobutene ring in both **3** (average 106.5°) and **6** (average 105.1°)² is larger than typical C-P-C angles (ca. 100°), again suggesting rehybridization of phosphorus to give more p character to the lone pair orbital.

In complexes **3**, **5**, and **6**, the W-P-C(1) angles do not deviate significantly from 121°. Slight variations are evident in the W-P-Ph angles, with that observed for **3** (119.8°) intermediate to those of **5** (121.2°)⁴ and **6** (117.6°).² A substantial difference, however, is observed in the values of the remaining C-P-W bond angles. The C(3)-P-W angle in **6** (125.6°)² is much larger than that in **3** (118.4°) and **5** (120.5°).⁴ This is consistent with distortion in **6** to reduce steric interactions between the phenyl substituent on C(3) and the tungsten pentacarbonyl group.

¹H NMR Spectroscopy. Phosphacyclobutenes **1-3** exhibit a characteristic pattern of two doublets of doublets for the methylene protons in their ¹H NMR spectra. This pair of doublets of doublets serves as a useful diagnostic tool, appearing as a general spectral signature of all phosphacyclobutenes we have examined. Upon complexation with mercuric chloride, both absorptions are shifted downfield, while, in the tungsten pentacarbonyl complex, only one proton resonance is appreciably shifted downfield.

The geminal coupling constants for the methylene protons in **1-3** are similar (14.4, 16.0, and 15.4 Hz, respectively). Greater variations exist in the magnitude of the two-bond phosphorus-proton coupling constants. In many cyclic phosphines, α -protons cis to the phosphorus lone pair exhibit larger ² J_{PH} than do protons

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trans to the lone pair. In phosphacyclobutene **1**, the downfield methylene absorption can be assigned to the proton cis to the phosphorus lone pair, given its larger $^2J_{\text{PH}}$ (9.6 vs 4.2 Hz for the upfield resonance). In the metal-complexed phosphacyclobutenes, α -proton assignments are complicated by the coordination of metal centers to the phosphorus lone pair. In **2** and **3**, the upfield absorptions exhibit larger values for $^2J_{\text{PH}}$ (14.1 and 9.8 Hz, respectively) than the downfield absorptions (9.7 and 2.8 Hz, respectively).

^{13}C NMR Spectroscopy. In the proton-decoupled ^{13}C NMR spectra of **1–3**, the methylene carbon of the phosphacyclobutene ring appears as a phosphorus-coupled doublet. This resonance appears at δ 33.9 for mercury complex **2** and at δ 35.5 for tungsten complex **3**. Both absorptions are downfield of the resonance for the uncomplexed phosphacyclobutene **1** (δ 28.1).

The one-bond phosphorus–carbon coupling constant for the methylene carbon in **1** is quite small (7.1 Hz). Metal complexation has a marked effect on this; the tungsten pentacarbonyl complex, **3**, displays a value of 38.5 Hz, while a value of 39.2 Hz is observed for the HgCl_2 complex, **2**. This increase in $^1J_{\text{CP}}$ is consistent with increased s character in the C–P bonds. The P-oxide, **4**, displays a still larger $^1J_{\text{CP}}$ (59.2 Hz); this value is typical for simple phosphine oxides³⁸ and casts additional doubt² on one account of the synthesis of a phosphacyclobutene P-oxide⁸ reported to display a considerably smaller $^1J_{\text{CP}}$.

^{31}P NMR Spectroscopy. The ^{31}P NMR spectra of **2** (δ 35.4) and **3** (δ 16.9) show appreciable downfield shifts relative to **1** (δ –16.0). Although one-bond ^{31}P – ^{199}Hg coupling constants in the range of 6500–7500 Hz have been reported for 1:1 complexes of tertiary phosphines with mercuric chloride,^{39,40} no ^{199}Hg satellites appear in the ^{31}P NMR spectrum of **2**. The ^{31}P NMR spectrum of **3** displays ^{183}W satellites, with a ^{31}P – ^{183}W coupling constant of 231 Hz, similar to that reported for **5** (232 Hz),⁴ $(\text{Ph}_2\text{PEt})\text{W}(\text{CO})_5$ (240 Hz),⁴¹ and $(\text{PhPBu}_2)\text{W}(\text{CO})_5$ (235 Hz).⁴¹

Summary and Conclusions

We have developed a simple route for the preparation of phosphacyclobutenes, allowing for the first time a systematic comparison of their structures, both in the uncomplexed, trivalent state and as their metal complexes. Such comparisons are important in light of significant differences in reactivity observed for our uncomplexed phosphacyclobutene **1**^{16,42} and a closely related tungsten pentacarbonyl complex, **6**.³

In **1**, as in other reported phosphacyclobutenes, the P–C(3) bond, which must be broken to form the corresponding ring-opened 1-phosphabutadiene, is considerably longer than the other P–C bonds. The crystal structures of the mercury- and tungsten-coordinated phosphacyclobutenes, **2** and **3**, demonstrate a contraction of all P–C bonds, including the P–C(3) bond, relative to those in uncomplexed **1**. The C–P–C bond angles of phosphacyclobutene **1** are widened upon complexation with mercury and tungsten. These changes in bond lengths and angles are consistent with partial rehybridization of the phosphorus toward sp^3 upon metal complexation. This rehybridization is mirrored in the ^1H , ^{13}C , and ^{31}P NMR spectra of **1–3**, most notably by a dramatic increase in P–H and P–C coupling constants upon complexation.

Enlarged bond angles within a small ring generally increase the amount of ring strain. This effect could provide an energetic advantage for the ring opening of metal-coordinated phosphacyclobutenes **2** and **3** relative to the uncomplexed **1**. However, the bond contractions that also accompany metal coordination

have the opposite effect. Initial reactivity comparisons of **1** and **2** suggest that the metal complex is even less likely to undergo electrocyclic ring opening than the uncomplexed phosphacyclobutene. It seems likely that the structure and reactivity differences between **1–3** and **6** are due to the variation in substituents, not to any unusual effects of metal coordination.

Experimental Section

All operations were carried out under a nitrogen atmosphere in a Vacuum Atmospheres inert atmosphere box or under argon on a standard Schlenk manifold, unless otherwise indicated. Benzene, toluene, pentane, and tetrahydrofuran (THF) were dried and deoxygenated over sodium/benzophenone ketyl, vacuum transferred, and stored in the inert atmosphere box or in glass storage vessels equipped with Teflon stopcocks. 2,3-Diphenyl-1-titanacyclobut-2-ene was prepared as described¹⁷ and recrystallized from toluene/pentane at -30°C . $\text{W}(\text{CO})_5(\text{Me}_3\text{N})$ was prepared as described.¹⁸ Mercuric chloride was vacuum-sublimed before use.

Synthesis of 1,3,4-Triphenyl-1,2-dihydrophosphete (1). The diphenyltitanacyclobutene (0.200 g, 0.540 mmol) was dissolved in 5 mL of benzene. To the resulting deep red solution was added 73 μL ($d = 1.319$, 0.54 mmol) of dichlorophenylphosphine via syringe, resulting in an immediate color change to brick red and precipitation of a red solid (titanocene dichloride). The reaction mixture was stirred for 3 h at room temperature and then evaporated to dryness in vacuo. The residue was suspended in a minimum of diethyl ether and filtered through a 1 cm \times 4 cm column of basic alumina (Brockman, Activity 1, 80–200 mesh) slurred in ether, eluting with ether. Organometallic byproducts were left at the origin, while the product eluted as a colorless band that was collected in a single portion. Removal of solvent in vacuo afforded **1** as a white solid, mp 71–74 $^\circ\text{C}$, in 66% yield. Compound **1** may be recrystallized from toluene/pentane (ca. 1:10 v/v) at -30°C , affording either white crystalline clumps or colorless platelets. ^1H NMR (360 MHz, C_6D_6): δ 2.37 (dd, 1 H, $^2J_{\text{HH}} = 14.4$ Hz, $^2J_{\text{PH}} = 4.2$ Hz, CH–P), 2.71 (dd, 1 H, $^2J_{\text{HH}} = 14.4$ Hz, $^2J_{\text{PH}} = 9.6$ Hz, CH–P), 6.85–7.10 (m, 9 H, ArH), 7.40–7.46 (m, 2 H, ArH), 7.50–7.56 (m, 2 H, ArH), 7.60–7.68 (m, 2 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ 28.1 (d, $\text{CH}_2\text{–P}$, $^1J_{\text{CP}} = 7.1$ Hz), 127–130 (m), 132.4 (d, $J_{\text{CP}} = 18.8$ Hz), 136.6 (d, $J_{\text{CP}} = 10.0$ Hz), 137.2 (d, $J_{\text{CP}} = 3.8$ Hz), 138.8 (d, $J_{\text{CP}} = 34.4$ Hz), 143.0 (d, $J_{\text{CP}} = 7.5$ Hz), 144.8 (s). ^{31}P NMR (109 MHz, C_6D_6 ; relative to external H_3PO_4): δ –16.04. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{P}$: C, 83.98; H, 5.71. Found: C, 83.79; H, 5.55.

Synthesis of the HgCl_2 Complex of 1,3,4-Triphenyl-1,2-dihydrophosphete (2). Mercuric chloride (0.271 g, 0.998 mmol) was added to a benzene solution (ca. 5 mL) of **1** (prepared from 1 mmol each of diphenyltitanacyclobutene and dichlorophenylphosphine). The white suspension was stirred at room temperature for 4 h. (Formation of a new sparingly soluble white product was apparent within 5 min.) Removal of solvent in vacuo afforded **2** in quantitative yield as a white powder, mp 169–170 $^\circ\text{C}$. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a 1:1 benzene/THF solution of **2**. ^1H NMR (300 MHz, C_6D_6): δ 3.01 (dd, 1 H, $^2J_{\text{HH}} = 16.0$ Hz, $^2J_{\text{PH}} = 14.1$ Hz, CH–P), 4.68 (dd, 1 H, $^2J_{\text{HH}} = 16.0$ Hz, $^2J_{\text{PH}} = 9.7$ Hz, CH–P), 6.89–7.09 (m, 9 H, ArH), 7.45–7.52 (m, 4 H, ArH), 7.71–7.78 (m, 2 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ 33.9 (d, $^1J_{\text{CP}} = 39.2$ Hz, $\text{CH}_2\text{–P}$), 127.7–128.3 (obscured by solvent resonances), 128.5, 128.8, 129.4, 129.8, 130.0, 130.8, 133.2, 133.4. ^{31}P NMR (121 MHz, C_6D_6 ; relative to external H_3PO_4): δ 35.45 (^{199}Hg satellites not resolved). Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{Cl}_2\text{HgP}$: C, 44.11; H, 3.00. Found: C, 43.78; H, 3.06.

Synthesis of the $\text{W}(\text{CO})_5$ Complex of 1,3,4-Triphenyl-1,2-dihydrophosphete (3). Under an inert atmosphere, $\text{W}(\text{CO})_5[(\text{CH}_3)_3\text{N}]$ (0.135 g, 0.353 mmol) and **1** (0.106 g, 0.326 mmol) were dissolved in 5 mL of toluene. This solution was heated at 70 $^\circ\text{C}$ for 14 h. Solvent was removed in vacuo, affording a yellow, oily residue. In air, this residue was dissolved in CH_2Cl_2 and chromatographed through a short silica column, eluting with 1:1 pentane/ CH_2Cl_2 . Slow evaporation of a heptane solution of the resulting material afforded white crystals of the pure complex, mp 104–106 $^\circ\text{C}$, in 30% yield. ^1H NMR (300 MHz, C_6D_6): δ 2.51 (dd, 1 H, $^2J_{\text{HH}} = 15.4$ Hz, $^2J_{\text{PH}} = 9.8$ Hz, CH–P), 3.16 (dd, 1 H, $^2J_{\text{HH}} = 15.4$ Hz, $^2J_{\text{PH}} = 2.8$ Hz, CH–P), 6.80–7.10 (m, 9 H, ArH), 7.20–7.28 (m, 2 H, ArH), 7.35–7.42 (m, 2 H, ArH), 7.60–7.80 (m, 2 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ 35.5 (d, $^1J_{\text{CP}} = 38.5$ Hz, $\text{CH}_2\text{–P}$), 127.8, 128.8, 128.9–129.4 (m), 129.7, 130.8–131.3 (m), 196.7 (s, C=O), 198.5 (s, C=O). ^{31}P NMR (121 MHz, C_6D_6 ; relative to external H_3PO_4): δ 16.9 (^{183}W satellites for $J_{\text{PW}} = 231.4$ Hz). IR (pentane): ν 2074 (m), 1952 (s), 1945 (s), 1908 (w) cm^{-1} . High-resolution MS. Calcd. for $\text{C}_{26}\text{H}_{17}\text{O}_5\text{PW}$: 624.0302. Found: 624.0345. Anal. Calcd for $\text{C}_{26}\text{H}_{17}\text{O}_5\text{PW}$: C, 50.02; H, 2.74. Found: C, 49.95; H, 2.76.

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Synthesis of 1,3,4-Triphenyl-1,2-dihydrophosphate P-Oxide (4). A solution of **1** (0.0124 g, 0.0413 mmol) in 0.5 mL of C₆D₆ was exposed to oxygen and then heated in a sealed NMR tube at 150 °C for 3 h. The mixture was cooled to room temperature and then evaporated to dryness and chromatographed through a short silica column by eluting first with diethyl ether and second with acetonitrile, affording white crystals of **4** in 32% yield. Recrystallization by slow evaporation of a diethyl ether solution afforded an analytically pure sample, mp 117–120 °C. An alternative method of preparation is as follows. Under nitrogen, **1** (0.011 g, 0.037 mmol) and yellow HgO (dried in vacuo, 0.010 g, 0.046 mmol) were combined in 0.5 mL of C₆D₆ in an NMR tube. The tube was sealed under a nitrogen atmosphere and heated at 155 °C for 68 h, after which time a bead of metallic Hg (0.007 g, 0.04 mmol, 80% based on **1**) had formed and all ¹H NMR resonances for **1** had disappeared. Chromatography of the solution through silica (Merck, grade 60, 230–400 mesh), eluting with ethyl acetate, afforded white, crystalline **4** (0.010 g, 0.032 mmol, 86%). ¹H NMR (300 MHz, C₆D₆): δ 2.78 (dd, 1 H, ²J_{HH} = 15.5 Hz, ³J_{PH} = 14.1 Hz, CH-P), 3.30 (dd, 1 H, ²J_{HH} = 15.4 Hz, ³J_{PH} = 19.5 Hz, CH-P), 6.50–7.50 (m, 13 H, ArH), 7.90–8.10 (m, 2 H, ArH). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ 42.7 (d, ¹J_{CP} = 59.2 Hz, CH₂-P), 127.5–129.5 (m), 130.1, 131.5, 131.6, 131.8 (d, ¹J_{PC} = 2.1 Hz). ³¹P NMR (121 MHz, C₆D₆; relative to external H₃PO₄): δ 18.4. IR (KBr): ν 1230 (s, P=O) cm⁻¹. High-resolution MS. Calcd for C₂₁H₁₇OP: 316.1017. Found: 316.1014. Anal. Calcd for C₂₁H₁₇OP: C, 79.73; H, 5.42. Found: C, 79.67; H, 5.15.

X-ray Analysis of 1,3,4-Triphenyl-1,2-dihydrophosphate (1). Crystallographic Summary. 1,3,4-Triphenyl-1,2-dihydrophosphate crystallized in the monoclinic space group *P*2₁/*n* with *a* = 9.265 (4) Å, *b* = 6.863 (3) Å, and *c* = 26.082 (11) Å, β = 93.826 (11)°, *V* = 1655 Å³, and *Z* = 4. Data were collected on a Syntex P1 diffractometer modified by Professor C. E. Strouse of the UCLA Department of Chemistry and Biochemistry, using Cu Kα radiation, to a maximum of 2θ = 100°, giving 1707 unique reflections, and the structure was solved by direct methods. The final discrepancy index was *R* = 0.050, *R*_w = 0.073 for 1471 independent reflections with *I* > 3σ(*I*).

A colorless platelet, obtained from a pentane/toluene solution was coated with epoxy and mounted on a thin glass fiber. Unit cell parameters were determined from a least-squares fit of 15 accurately centered reflections (20.0° < 2θ < 37.5°). These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections (0 1 – 6, 1 – 2 – 3, 2 1 7) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay and fluctuated less than 1.5% during the course of the experiment (24.1 h of exposure). Of the 1707 unique reflections measured, 1471 were considered observed [*I* > 3σ(*I*)] and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction. Programs used in this work included locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; MULTAN80, direct methods; and SHELX76 (Sheldrick), a crystallographic package.

Atoms were located by direct methods. All calculations were performed on the VAX 11/750 crystallographic computer. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located on difference electron density maps and were then kept in calculated positions, with C–H = 1.0 Å. Phenyl groups were constrained to be regular hexagons, with C–C = 1.395 Å and angles of 120°. An isotropic *B* value of 6.32 was assigned for the CH₂ hydrogens; a *B* value of 7.90 was assigned for all other hydrogens. Scattering factors for hydrogens were obtained from Stewart et al.,⁴³ and for other atoms from ref 44. The maximum and minimum peaks on a final difference electron density map were 0.25 e/Å³. Final positions and thermal parameters for all atoms are given in Table II. Bond lengths, angles, and torsion angles are provided in Tables III–V. Observed and calculated structure factors are provided in the supplementary material.

X-ray Analysis of the HgCl₂ Complex of 1,3,4-Triphenyl-1,2-dihydrophosphate (2). Crystallographic Summary. The HgCl₂ complex of 1,3,4-triphenyl-1,2-dihydrophosphate crystallized in the monoclinic space group *P*2₁/*c* with *a* = 18.465 (5) Å, *b* = 10.624 (4) Å, and *c* = 23.507 (4) Å, β = 94.62 (2)°, *V* = 4597 Å³, and *Z* = 4. Data were collected on a Rigaku AFC6R diffractometer, using Mo Kα radiation, to a maximum of 2θ = 50°, giving 8862 unique reflections. The final discrepancy

index was *R* = 0.044, *R*_w = 0.051 for 4498 independent reflections with *I* > 3σ(*I*).

Colorless laths were obtained from benzene–tetrahydrofuran solution. A crystal of dimensions 0.30 × 0.15 × 0.10 mm was mounted on a glass fiber and protected with a thin coat of diluted polystyrene cement. Initial values of cell dimensions were obtained by use of a Rigaku AFC6R diffractometer from the setting angles of 18 centered reflections in the range 11° ≤ 2θ ≤ 14° and refined values from 25 strong reflections identified from a rapid scan of the shell 28° ≤ 2θ ≤ 30°. Data were collected by use of ω–2θ scans between 2° and 50° in 2θ, over the index ranges 0 ≤ *h* ≤ 21, 0 ≤ *k* ≤ 12, –27 ≤ *l* ≤ 27 [speed 16° min⁻¹ in ω, up to three scans per reflections, width (deg) = 1.00 + 0.30 tan θ]; 8862 reflections were scanned, with *R*_{int} = 0.060 for the 0,*k*,±1 pairs. Crystal data are summarized in Table I.

The systematic absences unambiguously showed the space group to be *P*2₁/*c*. The positions of the two independent Hg atoms were found by direct methods (MITHRIL⁴⁵) at positions in agreement with the strongest Patterson vectors. The remaining non-hydrogen atoms were located by means of difference syntheses. An empirical absorption correction (DIFABS⁴⁶) was applied after isotropic refinement (relative correction factors 0.67–1.49). Seven weak (ca. 1.5 e Å⁻³), roughly coplanar peaks in an intermolecular void were apparently due to a disordered molecule of the solvent; as no clear model for rigid-group refinement of these peaks suggested itself, they were treated as half-atoms of carbon and included in the later stages of refinement with fixed coordinates and with *B*_{iso} arbitrarily set at 10 Å². Full-matrix least-squares refinement (on *F*) converged at *R*_w = 0.044, *R*_w = 0.051, and *S* = 1.53: function minimized, Σw(|*F*_o – *F*_c|)²; w = 1/σ²(*F*); 4498 independent reflections with *I* ≥ 3σ(*I*); 451 parameters; all Hg, Cl, P, C atoms (except solvent) anisotropic; H atoms riding with *B*(H) = 1.2*B*_{eq}(C). The TEXSAN program suite⁴⁷ was used in all calculations. Final positions and thermal parameters for all atoms are given in Table VI. Bond lengths and angles and dihedral angles are provided in Tables III–V, VII, and VIII. Dihedral angles for the HgCl₂ core of **2** are provided in the supplementary material, as are observed and calculated structure factors.

X-ray Analysis of the W(CO)₃ Complex of 1,3,4-Triphenyl-1,2-dihydrophosphate (3). Crystallographic Summary. The W(CO)₃ complex of 1,3,4-triphenyl-1,2-dihydrophosphate crystallized in the triclinic space group *P*1 with *a* = 9.373 (5) Å, *b* = 11.464 (9) Å, and *c* = 12.976 (7) Å, α = 114.29 (5)°, β = 96.60 (4)°, γ = 109.03 (5)°, *V* = 1150.1 (13) Å³, and *Z* = 2. Data were collected on a Siemens P3mR rotating anode diffractometer, using Cu Kα radiation and anode power 50 kV and 300 mA, to a maximum of 2θ = 108.0°, giving 2762 unique reflections. The final discrepancy index was *R* = 0.0818, *R*_w = 0.1086 for 2155 independent reflections with *I* > 3σ(*I*).

Colorless slivers were obtained by breaking up a deposit formed by evaporation of a heptane solution of **3**. An irregular crystal of dimensions 0.03 × 0.12 × 0.16 mm was mounted on a glass fiber and cooled to 140 K in a stream of cold nitrogen. Data were collected by use of ω scans between 0 and 108° in 2θ, over the index ranges –9 ≤ *h* ≤ 9, –12 ≤ *k* ≤ 10, 0 ≤ *l* ≤ 13 (speed 58.6° min⁻¹ in ω); 2762 reflections were scanned. Crystal data are summarized in Table I.

Symmetry and intensity statistics pointed to space group *P*1; successful refinement confirmed this choice. The structure was solved by using the PATT function of the Siemens SHELXTL PLUS (Sheldrick) system. An empirical absorption correction⁴⁸ (obtained from Δ*F*) was applied after isotropic refinement. Phenyl groups were refined with idealized geometry. CO ligands were constrained to near-equal W–C and C–O distances. Full-matrix least-squares refinement (on *F*) converged at *R*_w = 0.0818, *R*_w = 0.1086; weighting scheme w⁻¹ = σ²(*F*) + 0.0146*F*²; 2155 independent reflections with *I* ≥ 3σ(*I*); 264 parameters; P and all C atoms anisotropic; H atoms riding with fixed isotropic *U*. The largest peaks in the final difference map, +2.1 and –1.5 e Å⁻³, were both close to the tungsten atom. Final positions and thermal parameters for all atoms are given in Table IX. Bond lengths and angles and dihedral angles are provided in Tables III–V, X, and XI. Dihedral angles for the W(CO)₃ unit are provided in the supplementary material, as are observed and calculated structure factors.

Supplementary Material Available: Tables of anisotropic thermal parameters and coordinates of atoms introduced at calculated positions for 1–3 and selected dihedral angles for **2** and **3** (8 pages); listings of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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