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Effects of Metal Coordination on the Reactivity of 1,3,4-Triphenyl-1,2-dihydrophosphete

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ABSTRACT

Nucleophilicity dominates the reaction chemistry of 1,3,4-triphenyl-1,2-dihydrophosphete even when it is coordinated to electrophilic metal centers, but coordination dramatically alters the course of its reactions. Deoxygenation of carbonyl-containing substrates is effected by both the $W(CO)_5$ complex, which reductively couples benzaldehyde, and the $HgCl_2$ complex, which converts benzaldehyde to α,α-dichlorotoluene. Metal coordination appears to decrease the tendency of the dihydrophosphete to undergo electrocyclic ring opening to the corresponding 1-phosphabutadiene, and the $HgCl_2$ complex reacts with dimethyl acetylenedicarboxylate to afford a cyclopentadienyl ylide containing an intact dihydrophosphete unit. By reducing the nucleophilicity of the dihydrophosphete and/or the availability of the highly nucleophilic uncoordinated dihydrophosphete, coordination to $HgCl_2$ and $W(CO)_5$ makes accessible new mechanistic pathways. Dihydrooxaphosphinines, although unavailable through the reactions of the dihydrophosphete, may be synthesized by exploitation of the reactivity of organotitanium metallacycles. © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9:**21–28, 1998

Dedicated to Prof. William McEwen, long-time champion of the main-group elements, on the occasion of his seventy-fifth birthday.

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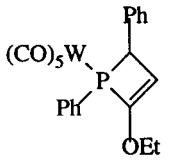
INTRODUCTION

As discussed in the preceding article [1], the chemistry of 1,3,4-triphenyl-1,2-dihydrophosphete (**2**) is dominated by its nucleophilicity. However, although nucleophilic addition is clearly the preferred mode of reactivity of dihydrophosphete **2** toward a variety of potential dienophiles, related dihydrophosphetes such as **1** have been noted to form Diels-Alder–type adducts with the same dienophiles [2,3].



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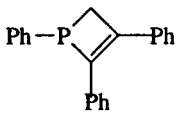


2

Since the studies of **1** were carried out with transition metal complexes rather than free dihydrophosphetes, it seemed likely that metal coordination, effectively tying up the phosphorus lone pair and thereby diminishing the possibility of nucleophilic addition chemistry, was responsible for the dramatic difference in reactivity between **1** and **2.** However, structural studies of the free dihydrophosphete **2** and its tungsten pentacarbonyl and mercuric chloride complexes suggested that, rather than enhancing the ring-opening reaction pathway, metal coordination results in structural changes consistent with a *decreased* tendency to undergo such reactions [4]. As we report herein, metal coordination does in-

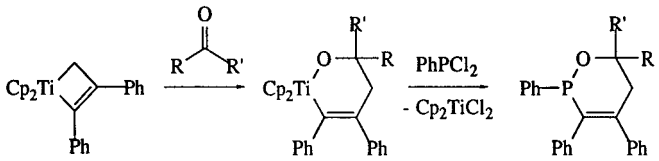
deed dramatically alter the reaction chemistry of **2,** but *not* by accessing reaction pathways involving electrocyclic ring opening of the dihydrophosphete.

RESULTS AND DISCUSSION

Reaction of 2 · W(CO)$_5$ and 2 · HgCl$_2$ with Benzaldehyde and Acetone

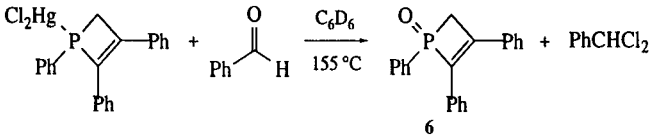
In contrast to the reported reaction chemistry of tungsten-coordinated 1,2-dihydrophosphete **1** [2], compound **2** is unreactive toward benzaldehyde even after prolonged heating at 150°C, only slowly forming small quantities of decomposition products of unknown structure but identical to those formed in the absence of benzaldehyde. A similar lack of reactivity is displayed by **2** toward acetone. Although a silacyclobutene was reported to undergo photoinduced cycloaddition with acetone [5], dihydrophosphete **2** gave no characterizable products when photolyzed in acetone.

The products expected from these unsuccessful cycloaddition reactions of **2** may be readily synthesized by exploiting the reactivity of the organotitanium complex serving as its synthetic precursor [6]. Thus, titanacyclobutene **3** undergoes facile insertion reactions with both acetone and benzaldehyde, affording the corresponding oxatitanacyclohexene complexes **4a** and **4b** in high yield [7,8]. Transmetallation to phosphorus [6] is effected by treatment of these complexes with dichlorophenylphosphine, affording dihydrooxaphosphinines **5a** and **5b.** This transmetallation is appreciably slower than that of the titanacyclobutenes, consistent with the stabilizing influence of heteroatoms in titanacyclic complexes [9].



3 **4a** R = R' = Me; **4b** R = Ph, R' = H **5a** R = R' = Me; **5b** R = Ph, R' = H

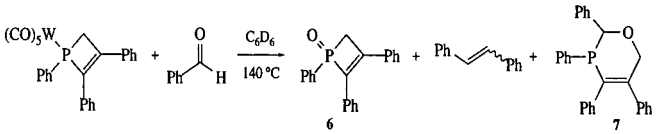
In contrast to the inertness of **2** toward benzaldehyde, **2** · HgCl$_2$ is completely consumed when heated with benzaldehyde in benzene solution at 155°C for 8 hours. The dihydrophosphete is converted to the corresponding P-oxide (**6**) (vide infra for characterization), isolated in 74% yield after chromatography, while benzaldehyde is converted to α,α-dichlorotoluene (56%), identified by comparison with an authentic sample on the basis of ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. The fate of the mercury has not been unambiguously determined, but an insoluble mercury-containing solid forms during the course of the reaction. Similar deoxygenation chemistry is observed in the reaction of **2** · HgCl$_2$ with dimethyl acetylenedicarboxylate (vide infra); possible mechanisms for this reactivity are discussed in that context below.



6

The HgCl$_2$ complexes of triphenylphosphine, triphenyl phosphite, and triethyl phosphite do not appear to convert benzaldehyde to α,α-dichlorotoluene even after prolonged heating at elevated temperatures. However, the tributylphosphine complex does effect this reaction, albeit more sluggishly than the reaction of **2** · HgCl$_2$, forming α,α-dichlorotoluene in 46% yield. When the tributylphosphine complex is heated in the absence of benzaldehyde, metallic mercury is formed, apparently due to a redox reaction also forming Bu_3PCl_2(Bu_3PCl^+ Cl^-), analogous to the redox chemistry between phosphines and mercuric fluoride observed previously [10]. Given both the geometric constraints of the dihydrophosphete ring, which are expected to destabilize such a phosphorane intermediate, and the fact that the tributylphosphine complex affords elemental mercury whereas the dihydrophosphete complex does not, it is possible that the two complexes follow different mechanisms for the chlorination of benzaldehyde.

Benzaldehyde also reacts with **2** · W(CO)$_5$, although appreciably more sluggishly than with the mercuric chloride complex, again affording the dihydrophosphete P-oxide (**6**). The major organic product of this reaction is stilbene, isolated as a mixture of the *cis* and *trans* isomers, representing the product of reductive coupling of two equivalents of benzaldehyde. A third product is also formed, displaying a ^{1}H NMR spectrum with a characteristic singlet at δ 6.35 ppm and an AB quartet at δ 4.9. Although this product has thus far resisted all attempts at unambiguous structure determination, it may tentatively be assigned structure **7,** representing a regioisomer of **4b.**



6 **7**

Formation of regioisomer **7,** seemingly contrathermodynamic given the strength of P–O bonds,

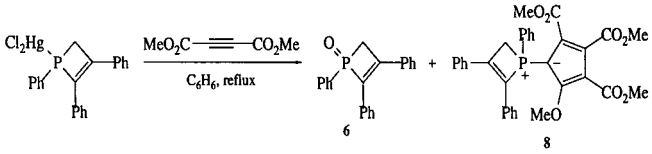
may be due to nucleophilic addition of the dihydrophosphete to the carbonyl group of benzaldehyde, perhaps assisted by the $W(CO)_5$ group, or may be the result of orbital overlap control of a [4 + 2] cycloaddition between the ring-opened dihydrophosphete and benzaldehyde. This matter, although clearly deserving of attention, is beyond the scope of this report.

Reaction of **2** · *$W(CO)_5$ with Dimethyl Acetylenedicarboxylate*

In contrast to the rapid thermal reactions of dihydrophosphete **2** with dimethyl acetylenedicarboxylate (DMAD) [1], only a very sluggish reaction is observed for the tungsten pentacarbonyl complex. Treatment of **2** · $W(CO)_5$ with a large excess of DMAD in benzene solution at 100°C for 20 days gave no identifiable phosphorus-containing products, and although some decomposition of the dihydrophosphete was apparent, significant amounts of **2** · $W(CO)_5$ remained. New methoxy peaks were apparent in the ^{1}H NMR spectrum of the reaction mixture, suggesting possible oligomerization of DMAD [11].

Reaction of **2** · *$HgCl_2$ with Dimethyl Acetylenedicarboxylate*

Refluxing a suspension of **2** · $HgCl_2$ in benzene with DMAD produces a dark-brown solution and a light-colored insoluble solid. Chromatographic separation of the soluble fraction yields the colorless crystalline dihydrophosphete P-oxide **6** [4].



The cyclopentadienyl ylide **8** is also isolated from this product mixture. The structure of this colorless crystalline product was confirmed by X-ray crystallography (Figure 1). The mass spectrum of **8** contains a molecular ion (568) that has an intensity equal to 17% of the base peak (316); the molecular weight of 568 corresponds to a 2:1 adduct of DMAD and **2**, minus one oxygen atom. The infrared spectrum displays two carbonyl stretches at frequencies (1700 and 1640 cm^{-1}) lower than those typical for esters, suggesting some conjugation with the cyclopentadienyl ring. Hughes and coworkers reported similar stretches in the infrared spectrum of a related cyclopentadienyl ylide [12]. The ^{1}H NMR spectrum of **8** contains four sharp singlets for the methoxy groups and two characteristic multiplets for the dihydrophosphete ring protons (δ 3.64, dd, 1H, $^2J_{HH}$ = $^2J_{PH}$ = 16.5 Hz; δ 3.95, dd, 1H, $^2J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 17.8 Hz). In the ^{13}C NMR spectrum of **8**, a doublet at δ 35.1 ($^1J_{PC}$ = 65 Hz) corresponds to the dihydrophosphete methylene carbon. The ^{31}P NMR spectrum of **8** contains a single absorption at δ 15.2.

The cyclopentadienyl ylide (**8**) formed in the reaction of **2** · $HgCl_2$ with DMAD resembles that observed in the reaction of a phosphindole with DMAD [12]. By analogy with the mechanism proposed for the latter reaction, the mechanism depicted in Scheme 1 is suggested to account for the formation of **6** and **8**. Nucleophilic addition of the dihydro-

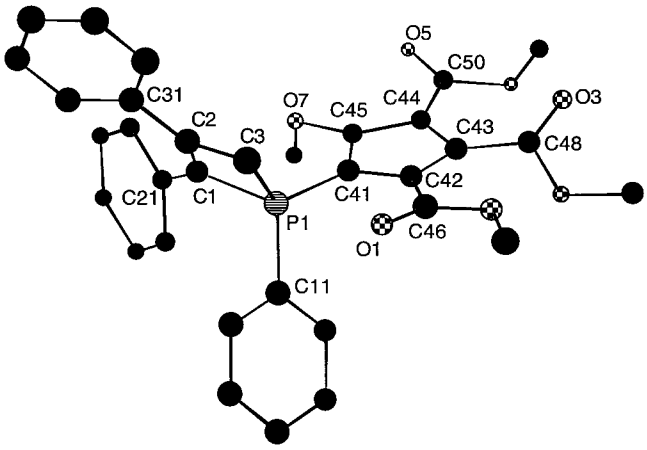
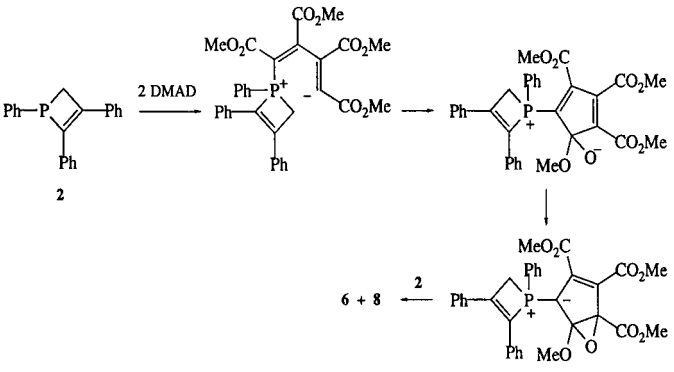


FIGURE 1 Molecular structure of cyclopentadienyl ylide **8,** including partial atom numbering scheme. Hydrogen atoms and diethyl ether solvate molecule are omitted for clarity. Selected bond lengths (Å): P1–C1, 1.797(18); P1–C3, 1.796(15); P1–C11, 1.802(13); P1–C41, 1.801(22); C1–C2, 1.354(22); C2–C3, 1.518(24); C41–C42, 1.396(31); C42–C43, 1.377(29); C43–C44, 1.418(28); C44–C45, 1.397(35); C45–C41, 1.397(31). Selected bond angles (deg): C1-P1-C3, 78.7(8); P1-C1-C2, 90.7(12); C1-C2-C3, 104.8(13); P1-C3-C2, 85.7(9); C1-P1-C11, 112.9(6); C1-P1-C41, 114.0(9); C11-P1-C41, 113.1(7).



SCHEME 1

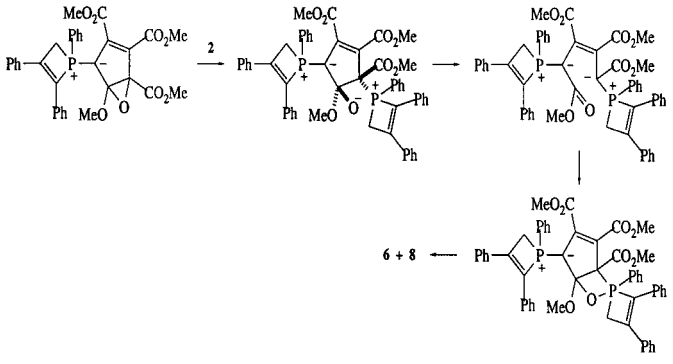
phosphete to DMAD, presumably following decomplexation from mercuric chloride, is followed by addition to a second equivalent of DMAD. The resulting zwitterionic intermediate then undergoes intramolecular cyclization via attack of the carbanion at an ester carbonyl group, producing a five-membered ring, and the product of this attack collapses via closure of the epoxide ring through conjugate addition of the alkoxide.

Hughes and coworkers suggest that deoxygenation of the epoxide intermediate may involve a direct attack of phosphorus on the epoxide oxygen, yielding the phosphine oxide and cyclopentadienyl ylide, since attack of phosphorus on an epoxide carbon would generate a *trans* betaine unable to eliminate phosphine oxide. We suggest that attack by phosphorus on an epoxide carbon may in fact be a plausible first step in the deoxygenation. Thus, although the direct elimination of phosphine from the betaine is precluded by the *trans* relationship between the oxide and phosphonium ions, ring opening of this betaine would generate a new ylide and ester (Scheme 2). (Alternate attack at the other carbon of the epoxide would proceed similarly.) Analogous decomposition of phosphine-epoxide adducts to form ylides and carbonyl compounds was observed by Bissing and Speziale [13]. A Wittig reaction between the so-generated ylide and ester would provide an oxaphosphetane intermediate. Esters, which do not generally react with phosphorus ylides, will do so intramolecularly [14]. The resulting oxaphosphetane intermediate would be expected to eliminate phosphine oxide to provide the cyclopentadienyl ylide.

In the absence of $HgCl_2$, **6** and **8** are only minor products in the reaction of the dihydrophosphete with DMAD [1]. However, when the reaction is performed using the mercuric chloride complex of the dihydrophosphete, **6** and **8** are the only products observed, and no traces of the products formed in the absence of mercuric chloride are obtained. We believe there are several ways in which mercury complexation may lead to such a dramatic shift in product distribution.

The proposed mechanisms leading to the observed products of both reactions begin with two successive Michael additions to DMAD. In the reaction of the $HgCl_2$ complex, this requires the decomplexation of **2** from $HgCl_2$. From the common intermediate resulting from these sequential additions to DMAD, formation of **6** and **8** requires attack of the carbanion at an ester carbonyl group, while formation of the products observed in the absence of $HgCl_2$ is best rationalized on the basis of attack by the carbanion at phosphorus [1]. This change in attack site may perhaps be rationalized on the basis of formation of a mercury derivative of the intermediate carbanion, which would be expected to undergo more significant steric interference in the addition to phosphorus than would the metal-free carbanion. Alternatively, the ester may be activated toward nucleophilic attack by coordination of $HgCl_2$. Deoxygenation of the intermediate epoxide might also be influenced by the presence of free $HgCl_2$, with coordination of $HgCl_2$ to the epoxide enhancing the requisite nucleophilic attack by the dihydrophosphete.

The relative courses of the reactions of **2** with and without $HgCl_2$ present may also be directed by a somewhat more subtle effect. Clearly, formation of **6** and **8** requires a second equivalent of the dihydrophosphete to effect the deoxygenation. With free dihydrophosphete **2,** addition to DMAD, a potent Michael acceptor, is presumably rapid, and it is unlikely that significant amounts of unreacted **2** are present following the initial addition of DMAD. In contrast, the $HgCl_2$ complex can serve as a controlled source of **2,** essentially providing for the slow addition of **2** to the reaction mixture through equilibrium-driven decomplexation as the reaction proceeds and thereby preserving some **2** to effect the deoxygenation in the later stages of the reaction.



SCHEME 2

General Effects of Metal Coordination on the Reactivity of the Dihydrophosphete Ring

The 1,2-dihydrophosphete ring can potentially undergo electrocyclic ring opening to form the corresponding 1-phosphabutadiene, although theoretical studies suggest that, in contrast to the exothermic ring opening of cyclobutenes and dihydroazetes, the ring opening of dihydrophosphetes is very nearly thermoneutral [15–17]. Indeed, in the reactions of tungsten-coordinated dihydrophosphete **1,** Mathey and coworkers observe the formation of products resulting from formal [4 + 2]-cycloaddition of the ring-opened 1-phosphabutadiene to dienophiles [2,3],

and we have reported that **2** reacts with Michael acceptors to provide products that appear to result from stepwise cycloadditions [1,18].

However, the nucleophilicity of the phosphorus lone pair of electrons dominates the reactivity of **2.** Some differences in the reactivity of **2** and Mathey's tungsten-coordinated dihydrophosphete can clearly be attributed to the relative availability of the lone pair in these two systems. However, a comparison of the structures of **2, 2** · $HgCl_2$, and **2** · $W(CO)_5$ revealed no distortion toward a ring-opened 1-phosphabutadiene in the metal-coordinated dihydrophosphete [4]. In fact, the P–CH_2 bond, which might be anticipated to be lengthened, is in fact appreciably *shortened* in the metal complexes relative to the free dihydrophosphete. While readily understandable in terms of rehybridization at phosphorus to introduce p-character into the phosphorus-metal bond [4], this effect is of course inconsistent with facilitation of the electrocyclic ring opening of the 1,2-dihydrophosphete ring. Indeed, in the reaction of the $HgCl_2$ complex of the dihydrophosphete with DMAD, the dihydrophosphete ring never does open; only products retaining the four-membered ring are obtained. In contrast, Mathey's tungsten-coordinated dihydrophosphete contains an elongated intraring P–C bond, suggesting some distortion toward the 1-phosphabutadiene [19]. Since metal coordination does not induce ring opening in **2,** we conclude that another structural difference, most likely the presence of the phenyl substituent on the sp^3 carbon, may sterically weaken the P–CHPh bond in **1** and/or electronically stabilize the corresponding 1-phosphabutadiene.

EXPERIMENTAL

Unless otherwise noted, all operations were carried out under an atmosphere of dry nitrogen or argon using standard inert atmosphere techniques. Solvents were dried over sodium/benzophenone ketyl and stored in an inert atmosphere dry box or in sealed storage vessels under argon. 1,3,4-Triphenyl-1,2-dihydrophosphete (**2**) and its $W(CO)_5$ and $HgCl_2$ complexes were prepared as previously described [4]. 1,1-Bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclobut-2-ene (**3**) was prepared as described [20] and recrystallized from toluene/pentane at −30°C. Chromatography was carried out using silica gel (Merck, grade 60). ^1H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane; ^{31}P chemical shifts are reported relative to external H_3PO_4. Elemental analyses were performed by Desert Analytics (Tucson, Arizona).

Dihydrooxaphosphinine **5a**. To a solution of titanacyclobutene **3** (0.0517 g, 0.140 mmol) in ca. 0.5 mL of C_6D_6 in an NMR tube was added 10.3 μL of acetone (0.140 mmol). The deep-red solution was heated at 65°C overnight, affording an orange solution, ^1H NMR analysis of which indicated complete conversion to the oxatitanacyclohexene (**4a**) [7]. Dichlorophenylphosphine (19.0 μL, 0.140 mmol) was added by syringe, resulting in an immediate change in color to a very pale orange. The mixture was heated at 65°C for 48 hours, resulting in the precipitation of a white amorphous solid and red titanocene dichloride. After cooling to room temperature, the solution was concentrated by evaporation, then chromatographed on a short silica column, eluting with diethyl ether, affording **5a** as a colorless oil (7%). ^1H NMR (C_6D_6): δ 1.36 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.75–3.00 (AB quartet, 2H, $^2J_{HH}$ = 13.5 Hz, CH_2), 6.80–7.10 (m, 13H, ArH), 7.55–7.65 (m, 2H, ArH). ^{31}P NMR (C_6D_6): δ 14.3. HRMS: calcd for $C_{24}H_{23}OP$: 358.1486. Found: 358.1478.

Dihydrooxaphosphinine **5b**. This compound was prepared analogously, using benzaldehyde in place of acetone. The transmetallation with dichlorophenylphosphine required 3–4 days at 65°C. Chromatographic purification was effected using 1:1 diethyl ether/pentane, affording **5b** as a yellow oil. ^1H NMR (C_6D_6): δ 3.00–3.10 (dd, 1H, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 6.2 Hz, C*H*H), 3.14–3.25 (dd, 1H, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 8.7 Hz, CH*H*), 4.65–4.85 (dd, 1H, $^3J_{HH}$ = 8.7, 6.2 Hz, CH), 6.5–7.5 (m, 20H, ArH).

Reaction of **2** · *$HgCl_2$ with Benzaldehyde.* To a suspension of **2** · $HgCl_2$ in C_6D_6 containing approximately one equivalent of toluene as an internal standard was added an excess of benzaldehyde. The mixture was heated in a sealed NMR tube at 155°C for at least 8 hours, with monitoring of the progress of the reaction by ^1H NMR spectroscopy. Integration relative to the internal standard revealed dihydrophosphete P-oxide (**6**) to be formed in 74% yield and α,α-dichlorotoluene in 56% yield. (The same products are obtained in the absence of the internal standard, ruling out toluene as the source of α,α-dichlorotoluene.) Chromatography through a short silica column afforded pure α,α-dichlorotoluene upon elution with 15% diethyl ether in pentane and **6** upon elution with ethyl acetate. The off-white solid that forms in the course of this reaction is insoluble in benzene, chloroform, acetone, and water. It appears slightly soluble in dimethylsulfoxide, and a copper wire placed in contact with a solution/suspension of the solid in this solvent quickly amalgamates, confirming the presence of either Hg(I) or Hg(II). The solid does not melt below 400°C but does darken and

TABLE 1 Crystallographic Data for **8** · Et_2O

Composition	$C_{33}H_{29}O_7P \cdot C_4H_{10}O$
Formula weight	642.7
Space group	$P2_1/c$
a (Å)	9.126 (7)
b (Å)	13.075 (13)
c (Å)	27.74 (2)
α (deg)	90
β (deg)	97.57 (6)
γ (deg)	90
V (Å^3)	3281 (5)
Z	4
d_{calcd} (g cm^3)	1.281
λ (Å)	1.54178
No. obs reflns	1248
$R(F_0)$	0.0822
$wR(F_0)$	0.1082

TABLE 2 Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^2) for Cyclopentadienyl Ylide **8**

Atom	*x*	*y*	*z*	U_{equiv}
P1	880(5)	4865(4)	4073(2)	0.067(2)
C1	1763(16)	6025(13)	3916(6)	0.065(7)
C2	2386(16)	6146(13)	4383(6)	0.062(7)
C3	1815(15)	5254(14)	4655(5)	0.065(7)
C11	−1106	4964	4001	0.061(7)
C12	−1985(13)	4290(8)	3699(3)	0.066(7)
C13	−3519	4392	3639	0.065(8)
C14	−4176	5168	3881	0.072(7)
C15	−3297	5842	4184	0.061(7)
C16	−1762	5740	4244	0.075(9)
C21	1706	6573	3442	0.061(7)
C22	2971(11)	6988(9)	3285(4)	0.068(8)
C23	2886	7447	2828	0.075(8)
C24	1536	7491	2528	0.077(8)
C25	271	7077	2684	0.073(8)
C26	356	6618	3141	0.069(8)
C31	3390	6926	4626	0.060(7)
C32	4180(12)	6665(8)	5075(4)	0.066(7)
C33	5141	7371	5326	0.072(8)
C34	5311	8339	5129	0.076(8)
C35	4521	8601	4681	0.076(8)
C36	3560	7894	4430	0.075(8)
C41	1525(21)	3734(15)	3796(9)	0.072(9)
C42	1235(17)	2790(19)	3999(6)	0.065(9)
C43	1821(21)	2068(13)	3718(8)	0.066(9)
C44	2573(18)	2562(16)	3367(6)	0.061(8)
C45	2393(19)	3615(21)	3421(7)	0.068(10)
C46	487(20)	2601(13)	4425(7)	0.075(10)
O1	128(13)	3299(11)	4665(4)	0.076(5)
O2	294(13)	1612(11)	4534(5)	0.074(5)
C47	−510(21)	1454(15)	4942(6)	0.102(10)
C48	1830(16)	951(13)	3745(5)	0.065(8)
O3	2696(12)	398(9)	3981(4)	0.068(5)
O4	625(12)	550(9)	3481(4)	0.071(5)
C49	508(18)	−548(12)	3479(6)	0.093(10)
C50	3475(19)	2174(14)	3009(6)	0.075(11)
O5	4254(16)	2657(11)	2776(5)	0.092(7)
O6	3243(13)	1164(11)	2947(4)	0.078(5)
C51	4060(20)	679(16)	2600(7)	0.113(11)
O7	2815(11)	4462(10)	3203(4)	0.065(5)
C52	2092(17)	4525(14)	2706(5)	0.082(8)
O60[a]	6809(15)	−103(13)	3485(7)	0.132(8)
C61[a]	6085(38)	−1038(21)	3565(14)	0.241(23)
C62[a]	6894(25)	−1957(21)	3473(10)	0.150(13)
C63[a]	6660(21)	648(20)	3846(6)	0.101(10)
C64[a]	7200(19)	1630(16)	3696(6)	0.085(8)

[a]Heavy atoms of diethyl ether solvate molecule.

shrink above 300°C. α,α-Dichlorotoluene: ^{1}H NMR ($CDCl_3$): δ 6.75 (s, 1H, $CHCl_2$), 7.4 (m, 3H, ArH), 7.6 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 72.2, 126.3, 128.7, 129.8. MS: 160 (M^+, 17%), 125 (M–Cl, 100%). Compound **6,** after recrystallization from diethyl ether, displays identical properties to those previously reported [4].

Reaction of $Bu_3P \cdot HgCl_2$ with Benzaldehyde. To a stirred suspension of $HgCl_2$ in benzene was added one equivalent of tributylphosphine. The solution became homogenous within 10 minutes, but stirring was continued overnight. Removal of solvent in vacuo afforded $Bu_3P \cdot HgCl_2$ as a white powder, mp 70–71°C. ^{1}H NMR (C_6D_6): δ 0.80 (m, 3H, CH_3), 1.24 (m, 4H, CH_2CH_2), 1.70 (m, 2H, CH_2P). ^{13}C NMR (C_6D_6): δ 13.7 (s), 22.6 (d, J_{PC} = 28 Hz), 24.1 (d, J_{PC} = 15 Hz), 26.3 (s). Addition of excess benzaldehyde and ca. one equivalent of toluene as an internal standard, followed by heating at 155°C for ca. 48 hours, monitoring by ^{1}H NMR, resulted in complete disappearance of the phosphine complex and the formation of elemental mercury and α,α-dichlorotoluene (46%). Heating of the complex in C_6D_6 solution in the absence of benzaldehyde resulted in the formation of elemental mercury and the appearance of a new resonance (δ 3.2, quartet) in the ^{1}H NMR spectrum.

*Reaction of **2** · $W(CO)_5$ with Benzaldehyde.* To a solution of **2** · $W(CO)_5$ in C_6D_6 was added an excess of benzaldehyde. The mixture was heated in a sealed NMR tube at 140°C for 138 hours, with monitoring of the progress of the reaction by ^{1}H NMR spectroscopy. The resulting reaction mixture was chromatographed on a short silica column. A mixture of *cis* and *trans* stilbene, identified by comparison with authentic samples, was obtained by elution with dichloromethane (rf ca. 1.0) and recrystallization from pentane. Ethyl acetate eluted P-oxide **6.** The mother liquor from recrystallization of the stilbene fraction gave putative compound **7** (16%). ^{1}H NMR (C_6D_6): δ 4.88 (AB quartet, 2H, CH_2), 6.35 (s, 1H, PhCH), 6.85–

7.30 (m, 17H, ArH), 7.35–7.45 (m, 1H, ArH), 7.7–7.8 (m, 2H, ArH). ^{13}C NMR (C_6D_6): δ 85.3 (s), 87.3 (s), 104.6 (s), 126–129 (m, Ar). ^{31}P NMR (C_6D_6): δ 18.5.

Reaction of **2**·$HgCl_2$ *with Dimethyl Acetylenedicarboxylate.* The complex was prepared in situ by stirring **2** (0.196 g, 0.653 mmol) and $HgCl_2$ (0.191 g, 0.703 mmol) in ca. 6 mL of benzene for 24 hours at room temperature, affording a white suspension [4]. A solution of dimethyl acetylenedicarboxylate (0.232 g, 1.63 mmol) in benzene (ca. 1 mL) was added to the suspension. The flask was equipped with a reflux condenser, and the mixture was heated to reflux. Within 5 minutes, the reaction mixture developed a brown color, and a yellow solid was visible on the walls of the flask. After having been heated at reflux for 1.5 hours, the mixture was cooled to room temperature, and the benzene was removed in vacuo. The resulting brown residue was extracted into methylene chloride (1 mL). The brown solution was decanted away from a finely divided, light-colored precipitate and chromatographed on a silica column (1 × 13 cm), eluting first with a 20/80 mixture of ethyl acetate in methylene chloride, then with pure ethyl acetate. Cyclopentadienyl ylide **8** (rf = 0.5) was obtained in 23% yield (80 mg, 0.15 mmol) as a white solid, and dihydrophosphete P-oxide **6** (rf = 0.2), displaying properties identical to those previously reported [4], was obtained in 34% yield (70 mg, 0.22 mmol). Cyclopentadienyl ylide **8**, mp 169–172°C. ^{1}H NMR: δ 3.18 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.64 (dd, 1H, $^2J_{HH}$ = $^2J_{PH}$ = 16.5 Hz, C*H*H), 3.74 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.95 (m, partially obscured by OCH_3, 1H, CH*H*), 7.2–7.8 (m, 15H, ArH). ^{13}C NMR: δ 35.1 (d, $^1J_{PC}$ = 65 Hz, C3), 50.7 (s, OCH_3) 51.2 (s, OCH_3), 52.1 (s, OCH_3), 62.7 (s, OCH_3), 80.3 (d, $^1J_{PC}$ = 100 Hz, C41), 107.2 (d, J_{PC} = 14.4 Hz), 108.8 (d, J_{PC} = 8.0 Hz), 126.0 (d, J_{PC} = 11.8 Hz) (C42, C43, C44), 125.8 (d, $^1J_{PC}$ = 82.9 Hz), 135.2 (d, $^1J_{PC}$ = 71.9 Hz) (C1, C21), 127.9–133.4 (m, aromatic and olefinic), 152.7 (d, J_{PC} = 9.7 Hz), 159.3 (d, J_{PC} = 7.9 Hz) (C2, C22), 163.8 (d, J_{PC} = 2.8 Hz, *C*O_2Me), 165.4 (*C*O_2Me), 169.5 (d, J_{PC} = 2.7 Hz, *C*O_2Me). IR: ν(C=O) = 1730, 1700, 1640 cm^{-1}. MS: 569 (M+1, 7%), 568 (M^+, 18%), 553 (M–CH_3, 11%), 537 (M–OCH_3, 4%), 509 (M–CO_2CH_3, 5%), 444 (10%), 385 (15%), 316 (100%). Anal. calcd for $C_{33}H_{29}O_7P$: C, 69.71; H, 5.14; P, 5.45. Found: C, 69.76; H, 5.12; P, 5.39.

Crystallographic Analysis of Cyclopentadienyl Ylide **8.** Crystallographic data were collected from a colorless needle of dimensions 0.04 × 0.04 × 0.10 mm on a Siemens R3m/V diffractometer in the range $0° \leq 2\theta \leq 105.0°$ at a scan speed of 5.0° min^{-1} in ω. Crystal data are provided in Table 1. Background measurements were made with a stationary crystal and counter at the beginning and end of each scan, each for a total of 50% of the total scan time, and two standard reflections were checked every 200 reflections to monitor possible crystal degradation. A total of 4478 reflections were collected, 3966 of which were independent and 1248 of which were considered observed by the criterion $F > 6\sigma(F)$. Structure solution was carried out using the Siemens SHELXTL PLUS direct methods program. A molecule of diethyl ether was present as an ordered solvate. Riding hydrogen atoms with fixed isotropic U were used. Full-matrix least-squares refinement converged to a final R factor of 0.0822, with the largest features in the final difference electron density map +0.46 and −0.29 e/Å^3. Final positional and thermal parameters for nonhydrogen atoms are provided in Table 2; full data tables are provided in the supplementary materials.

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SUPPLEMENTARY MATERIAL AVAILABLE

Complete crystallographic details and data tables for compound **8** (26 pp).

REFERENCES

[1] E. M. Hanawalt, K. M. Doxsee, G. S. Shen, T. J. R. Weakley, C. B. Knobler, H. Hope, *Heteroatom Chemistry, 8,* 1997, 000–0000.
[2] N. H. Tran Huy, F. Mathey, *Tetrahedron Lett., 29,* 1988, 3077.
[3] H. Trauner, E. Delacuestra, A. Marinetti, F. Mathey, *Bull. Soc. Chim. Fr., 132,* 1995, 384.
[4] K. M. Doxsee, E. M. Hanawalt, G. S. Shen, T. J. R. Weakley, H. Hope, C. B. Knobler, *Inorg. Chem., 30,* 1991, 3381.
[5] D. Tzeng, R. H. Fong, H. S. D. Spysa, W. P. Weber, *J. Organomet. Chem., 219,* 1981, 153.
[6] K. M. Doxsee, G. S. Shen, C. B. Knobler, *J. Am. Chem. Soc., 111,* 1989, 9129.
[7] K. M. Doxsee, J. K. M. Mouser, *Tetrahedron Lett., 32,* 1991, 1687.
[8] J. D. Meinhart, R. H. Grubbs, *Bull. Chem. Soc. Jpn., 61,* 1988, 171.
[9] K. M. Doxsee, unpublished observations.
[10] K. M. Doxsee, E. M. Hanawalt, T. J. R. Weakley, *Inorg. Chem., 31,* 1992, 4420; K. M. Doxsee, E. M. Hanawalt, T. J. R. Weakley, *Acta Crystallogr., C48,* 1992, 1288.
[11] R. M. Acheson, N. F. Elmore, *Adv. Heterocycl. Chem., 23,* 1978, 263.

[12] A. N. Hughes, K. Amornraksa, S. Phisithkul, V. Reutrakul, *J. Heterocycl. Chem., 13,* 1976, 65.
[13] D. E. Bissing, A. J. Speziale, *J. Am. Chem. Soc., 87,* 1965, 2683.
[14] H. O. House: *Modern Synthetic Reactions,* Benjamin/Cummings, Menlo Park, CA, p. 693 (1972).
[15] S. M. Bachrach, M. Liu, *J. Org. Chem., 57,* 1992, 209; S. M. Bachrach, U. Salzner, *Theochem.–J. Mol. Struct., 337,* 1995, 201.
[16] B. S. Jursic, Z. Zdravkovski, *Int. J. Quantum Chem., 56,* 1995, 115.
[17] K. N. Houk, K. M. Doxsee, unpublished results.
[18] K. M. Doxsee, G. S. Shen, C. B. Knobler, *J. Chem. Soc. Chem. Commun.,* 1990, 1649.
[19] N. H. Tran Huy, L. Ricard, F. Mathey, *Organometallics, 7,* 1988, 1791.
[20] F. N. Tebbe, R. L. Harlow, *J. Am. Chem. Soc., 102,* 1980, 6149.