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Reactions of 1,3,4-Triphenyl-1,2-dihydrophosphete

Erin M. Hanawalt, Kenneth M. Doxsee,* Gregory S. Shen, and Timothy J. R. Weakley

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Carolyn B. Knobler

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Håkon Hope

Department of Chemistry, University of California, Davis, California 95616

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ABSTRACT

In contrast to previously reported reactivity of the tungsten pentacarbonyl complex of a 2-substituted 1,2-dihydrophosphete, which apparently undergoes electrocyclic ring opening to the corresponding 1-phospha-1,3-butadiene and subsequent [4 + 2] cycloaddition reactions with dienophiles, the reaction chemistry of 1,3,4-triphenyl-1,2-dihydrophosphete is dominated by its nucleophilic nature. Although low to modest yields of cycloadducts are obtained with some dienophiles, the reactions forming these products are apparently stepwise, as indicated by the loss of stereochemistry in the reaction of dimethyl maleate and in the competitive formation of a phosphorus-free dimer in the reaction of N-methylmaleimide. Dimethyl acetylenedicarboxylate affords three major products, each of which incorporates two equivalents of the acetylene, again apparently a result of initial nucleophilic addition of the dihydrophosphete to the "dienophile."

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

*To whom correspondence should be addressed.

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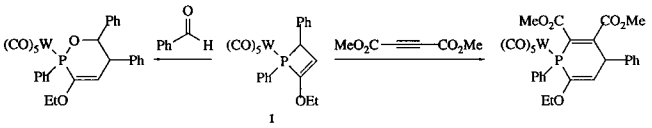
INTRODUCTION

Advances in synthetic methodology continue to afford access to new classes of small-ring phosphorus heterocycles, opening the doors to structure and reactivity studies of these often-unusual compounds [1–10]. Following Mathey's report of the preparation of a tungsten pentacarbonyl complex of a 1,2-dihydrophosphete (phosphacyclobutene) and the examination of its reactivity with several dienophiles [4], we [2] and others [3] reported the synthesis of the first example of a free 1,2-dihydrophosphete. Given our long-standing interest in hetero-Diels-Alder reactions accessed through the electrocyclic ring opening of heterocyclobutenes in the transition metal series [11], we turned our attention to the possibility of analogous ring opening and cycloaddition chemistry of the 1,2-dihydrophosphetes. In support of this conjecture, Mathey and coworkers observed the formation in good yield of formal [4 + 2]-cycloaddition products in the reactions of their tungsten-coordi-

nated 1,2-dihydrophosphete (**1**) with N-phenylmaleimide, dimethyl acetylenedicarboxylate, and benzaldehyde (equation 1) [4] and have recently reported analogous chemistry of molybdenum pentacarbonyl complexes [12].



1

In order both to shed further light on the fundamental reaction chemistry of 1,2-dihydrophosphetes and to develop synthetic access to other classes of phosphorus heterocycles derived therefrom via Diels-Alder methodology, we have examined the reactions of 1,3,4-triphenyl-1,2-dihydrophosphete (**2**) with a variety of potential dienophiles. The results of these investigations are presented herein, while in the following article [27] in this issue, we discuss the effects of metal complexation on the reaction chemistry of the 1,2-dihydrophosphete.

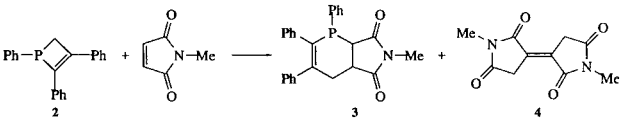
RESULTS AND DISCUSSION

Reaction of **2** *with Benzaldehyde*

In marked contrast to Mathey's reported reaction chemistry of the tungsten-coordinated 1,2-dihydrophosphete (Equation 1), **2** is inert toward benzaldehyde even after prolonged heating (several weeks) at 150°C. This extraordinary thermal stability of the dihydrophosphete was both unexpected and astonishing in light of the facile ring openings of cyclobutenes and dihydroazetes. However, consideration of the bonding preferences of phosphorus provides a qualitative rationalization for this stability, in that phosphorus is comparatively stabilizing in small rings due both to its accommodation of small intraring angles by use of high p-content orbitals in bonding to carbon and to the longer phosphorus–carbon bonds. Theoretical studies are in complete accord with this qualitative rationalization, with the ring opening of 1,2-dihydrophosphete to 1-phospha-1,3-butadiene roughly thermoneutral, in contrast to the markedly exothermic electrocyclic ring opening of cyclobutene and 1,2-dihydroazete [13–15].

Reaction of **2** *with N-Methylmaleimide*

Prolonged heating of **2** with excess N-methylmaleimide at 150°C affords copious amounts of a colorless, insoluble product together with a small quantity of a benzene-soluble compound that is identified as the formal cycloadduct (**3**) (Equation 2) on the basis of spectroscopic, mass spectral, and elemental analysis. Unfortunately, the NMR spectral data, particularly the inability to resolve longer-range phosphorus-hydrogen coupling, do not allow the determination of the relative stereochemistry of the chiral centers in **3,** but only one stereoisomer is preferentially formed. Given the propensity of the dihydrophosphete to carry out conjugate addition to Michael acceptors (vide infra), **3** is most likely formed in a step-wise manner, with the first-formed zwitterionic intermediate either collapsing directly to **3** or undergoing dihydrophosphete ring opening before final closure of the six-membered ring.

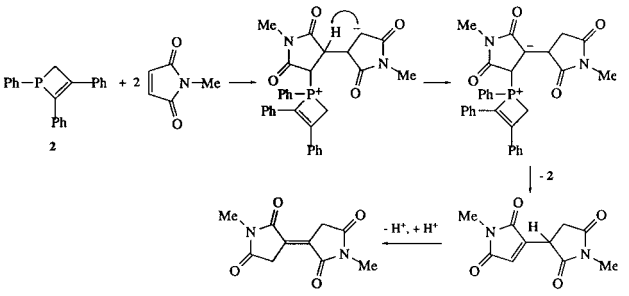


2 **3** **4**

The major product of this reaction displays two singlets in its ^{1}H NMR spectrum and typical imide-type carbonyl absorption bands in its IR spectrum. Mass spectral analysis suggested it to be a dimer of N-methylmaleimide. (Small quantities of an N-methylmaleimide trimer were suggested to be present as well.) Attempted determination of the melting point of this product in an open tube resulted in sublimation, yielding large and well-formed crystals. NMR analysis revealed no thermal chemistry had occurred during the sublimation. Single-crystal X-ray diffraction analysis [16] revealed this product to indeed be a dimer of N-methylmaleimide (**4,** Equation 2), perhaps formed via a Michael addition-initiated process, as suggested in Scheme 1. N-methylmaleimide has been reported to react analogously with amines to form the same dimer [17], and cyclodimerization of Michael acceptors has been reported as a competing reaction in their phosphinylation with trialkyl phosphites [18].

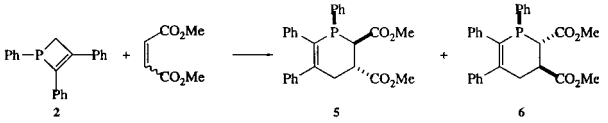
Reaction of **2** *with Dimethyl Maleate and Dimethyl Fumarate*

Michael addition chemistry also rears its head in the reactions of **2** with dimethyl maleate and dimethyl



SCHEME 1

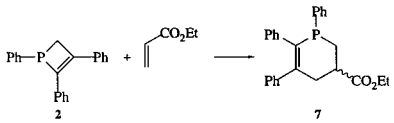
fumarate [5]. Thus, the reaction of **2** with each of these potential dienophiles affords the same mixture of two products. Analysis at short reaction times reveals that dimethyl maleate is isomerized to dimethyl fumarate prior to the formation of cycloaddition products, suggesting that a reversible Michael addition precedes, and may in fact be a first step in, the reactions of **2** with these reagents. Chromatographic isolation affords the (inseparable) mixture of products (combined yield 34%) in an ca. 3:2 ratio, as determined by ^{1}H NMR spectral analysis. Each displays well-resolved NMR spectral features, facilitating structure elucidation. Particularly informative are $^3J_{HH}$ for the protons on the ring carbons bearing the ester substituents and the two-, three-, and four-bond phosphorus-proton coupling constants, noting that protons *cis* to a lone pair on phosphorus experience a larger phosphorus-proton coupling constant than those that are *trans* to a lone pair [19]. These data, together with two-dimensional COSY and NOESY spectral analyses, permit assignment of structure **5** for the major isomer, with a *trans*-diester arrangement but a *cis* relationship of the P-phenyl substituent to the adjacent ester group, while the minor isomer is suggested by this analysis to be the all-*trans* compound, **6** (Equation 3). Subsequent successful crystallization of the major isomer (**5**) from the mixture permitted single-crystal X-ray structural analysis, confirming the structure as determined by NMR analysis (Figure 1). Both the C = C bond length (1.359 Å) and the P–CH_2 bond length (1.881 Å) are very similar to those in the 1,2-dihydrophosphete itself (1.336 and 1.886 Å, respectively).



In contrast to previously reported reactions of metal-coordinated dihydrophosphetes and phospholes [4,12,20], which appear to undergo concerted cycloaddition reactions, formation of the same mixture of **5** and **6,** each containing *trans* ester groups, from both dimethyl maleate and dimethyl fumarate points to a nonconcerted mechanism for their formation here. Also consistent with this is the acceleration of the reaction in acetone relative to that in benzene, with the former solvent better supporting the formation of zwitterionic intermediates.

Reaction of **2** *with Ethyl Acrylate*

Consistent with the stepwise mechanism for formation of cycloadducts with dimethyl fumarate and maleate, dihydrophosphete **2** reacts with ethyl acrylate to form a single regioisomer (**7**) with the carboethoxy group beta to the phosphorus, as demonstrated by two-dimensional COSY and NOESY studies. Two stereoisomers of **7** are formed, in an ca. 4:1 ratio, but unfortunately, as for the N-methylmaleimide adduct, spectral data do not allow for conclusive assignment of stereochemistry. The reaction is more sluggish than those of dimethyl maleate and fumarate, and the yield is lower (15–20%).



Reaction of **2** *with Dimethyl Acetylenedicarboxylate*

In marked contrast to the chemistry of complex **1,** which efficiently affords a simple cycloadduct with dimethyl acetylenedicarboxylate (DMAD), the reaction of **2** with DMAD affords no simple cycloadducts, but rather a mixture of products, each incorporating two equivalents of DMAD. Thus, when DMAD is added to a colorless benzene solution of **2,** a dark-brown color develops immediately. Within 1 hour, a yellow 2:1 adduct (**8**) precipitates from the stirred reaction mixture.

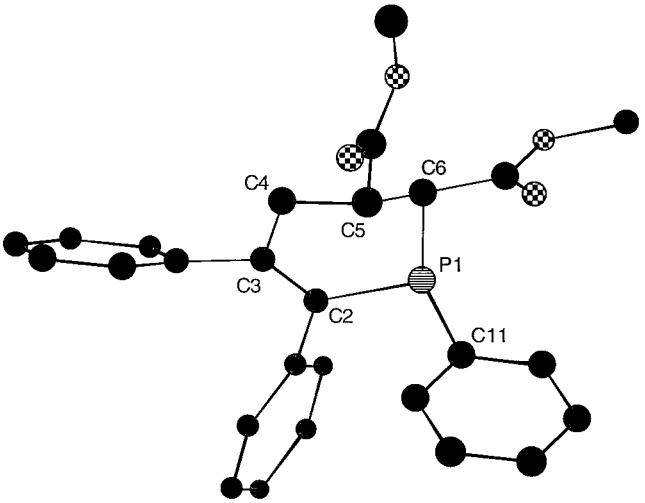
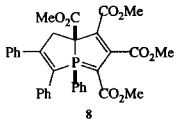


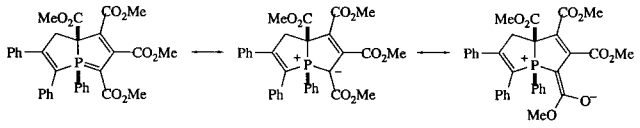
FIGURE 1 Molecular structure of dimethyl maleate cycloadduct **5,** including partial atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1–C2, 1.829(5); C2–C3, 1.359(7); C3–C4, 1.513(7); C4–C5, 1.520(7); C5–C6, 1.525(8); C6–P1, 1.881(6). Selected bond angles (deg): C6-P1-C2, 99.8(2); P1-C2-C3, 124.0(4); C2-C3-C4, 124.3(5); C3-C4-C5, 116.3(5); C4-C5-C6, 110.1(4); C5-C6-P1, 110.4(4); C2-P1-C11, 103.2(2); C6-P1-C11, 101.4(2).



8

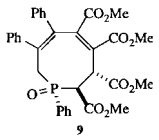
The phospholophosphole ylide structure of **8** was determined by X-ray crystallography, which reveals several noteworthy structural features (Figure 2). The *cis* geometry of the ring fusion results in a pronounced "butterfly" arrangement of the rings. The transannular bond [1.853(6) Å] is considerably longer than the other three P–C bonds, and the bond between the phosphorus and the ylide carbon [1.737(6) Å] is shorter than the P–C (phenyl) [1.781(6) Å] or P–C1 [1.789(6) Å] bonds. In the structures of other unsaturated phosphorus heterocycles, P–C bond lengths between 1.72 and 1.75 Å have been assigned a bond order of 1.5 [21]. The short P–C bond in **8** indicates some distortion of the ylide toward its phosphorane resonance structure.

Several spectroscopic features also characterize this unusual and stable ylide. In the infrared spectrum, some of the carbonyl stretches appear at unusually low frequencies (e.g., 1660, 1645, and 1524 cm^{-1}). In the ^1H NMR spectrum, one of the four methoxy resonances is severely broadened. These features have been reported in the infrared and ^1H NMR spectra of other α-ester-stabilized ylides [22–25] and were attributed to delocalization of the ylide anion onto the adjacent carbonyl group (Equation 4). Consistent with this delocalization, the X-ray analysis shows the methoxy esters on C5 and C7 to be aligned with their carbonyl bonds coplanar to the phosphole ring. The broadness of the ^{31}P NMR absorption, at δ 72.8, suggests that it is also affected by this delocalization and resulting restricted rotation.



Also present in the ^1H NMR spectrum of **8** are two characteristic resonances (δ 4.62, dd, 1H, $^2J_{HH}$ = 19 Hz, $^3J_{PH}$ = 4 Hz; δ 3.61, 1H, obscured by OMe signal) corresponding to the CH_2 group. The ^{13}C NMR spectrum of **8** contains three sharp methoxy resonances and a fourth broad resonance that overlaps with the doublet corresponding to the methylene carbon (δ 50.0, d, $^2J_{PC}$ = 9 Hz). Assignment of the methylene carbon was confirmed by a DEPT experiment. Compound **8** survives mass spectral analysis with rather minimal fragmentation; the molecular ion (584) is the base peak, and no fragments have intensities greater than 35% of the base peak.

Following the removal of **8** from the product mixture, chromatographic separation yields tetrahydrophosphocin oxide **9.**



9

The formation of **9** presumably is due to the reaction of an initial 2:1 adduct of DMAD and **2** with one equivalent of water. X-ray crystallography demonstrates that the two added hydrogen atoms occupy *trans* positions in the eight-membered ring (Figure 3). In addition to four methyl ester singlets, the ^1H NMR spectrum of **9** contains four multiplets corresponding to the tetrahydrophosphocin ring protons (δ 5.08, dd, 1H, $^3J_{HH}$ = 12 Hz, $^2J_{PH}$ = 8.6 Hz; δ 3.98, dd, 1H, $^3J_{HH}$ = 12 Hz, $^3J_{PH}$ = 9.6 Hz; δ 3.66, dd, 1H, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 7.2 Hz; δ 3.35, dd, 1H, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 22 Hz). The *trans* relationship between the added protons is reflected in their large vicinal coupling constant (12 Hz). Resonances in the upfield region of the ^{13}C NMR spectrum correspond to the

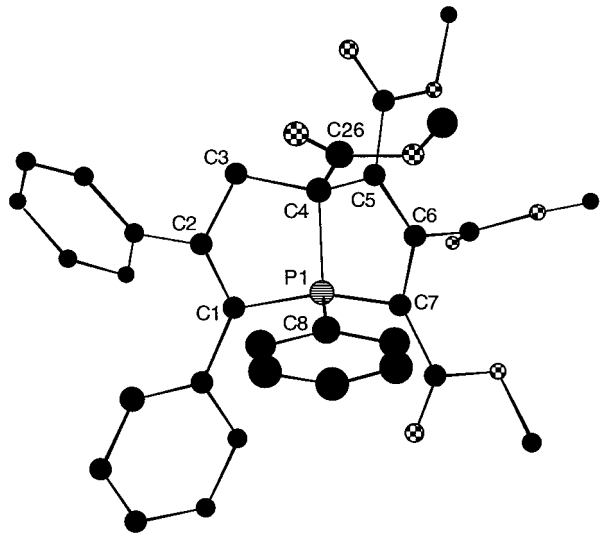


FIGURE 2 Molecular structure of phospholophosphole ylide **8,** including partial atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1–C1, 1.789(6); P1–C4, 1.853(6); P1–C7, 1.737(6); P1–C8, 1.781(6); C1–C2, 1.328(8); C2–C3, 1.533(8); C3–C4, 1.534(8); C4–C5, 1.518(8); C5–C6, 1.368(8); C6–C7, 1.414(8). Selected bond angles (deg): C1-P1-C4, 95.5(3); C1-P1-C7, 116.6(3); C4-P1-C7, 96.5(3); P1-C1-C2, 110.3(4); P1-C4-C3, 104.2(4); P1-C4-C5, 101.6(4); C1-C2-C3, 117.0(5); C2-C3-C4, 109.3(5); C3-C4-C5, 114.4(5); C4-C5-C6, 115.1(5); C5-C6-C7, 118.1(6); C6-C7-P1, 107.3(4); C1-P1-C8, 112.2(3); C7-P1-C8, 117.3(3); C3-C4-C26, 111.9(5); C5-C4-C26, 112.8(5); P1-C4-C26, 111.1(4); C4-P1-C8, 115.6(3).

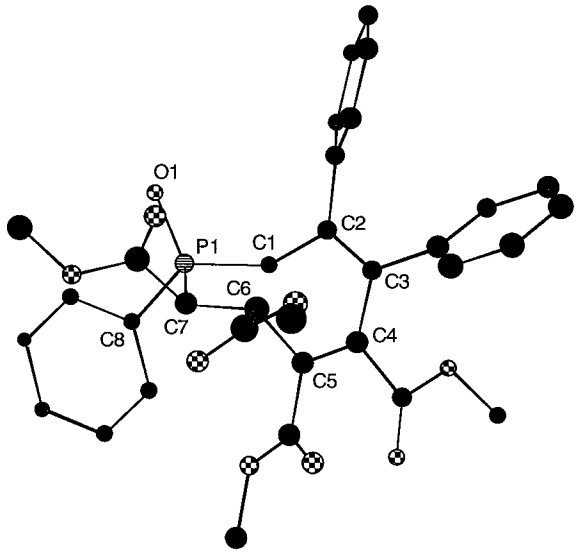
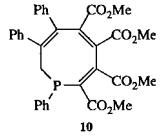


FIGURE 3 Molecular structure of dihydrophosphocin oxide **9,** including partial atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1–C1, 1.828(7); C1–C2, 1.538(12); C2–C3, 1.347(14); C3–C4, 1.476(12); C4–C5, 1.357(10); C5–C6, 1.524(10); C6–C7, 1.545; P1–C7, 1.869; P1–C8, 1.817(6); P1–O1, 1.489(5). Selected bond angles (deg): C1-P1-C7; P1-C1-C2, 117.1(6); C1-C2-C3, 119.5(7); C2-C3-C4, 121.0(7); C3-C4-C5, 122.9(7); C4-C5-C6, 120.3(7); C5-C6-C7, 112.1; C6-C7-P1, 117.2; C1-P1-C8, 105.1(3); C7-P1-C8, 103.3; C1-P1-O1, 111.8(3); C7-P1-O1, 111.1; C8-P1-O1, 113.7(3).

tetrahydrophosphocin ring carbons closest to phosphorus (δ 40.83, d, $^1J_{PC}$ = 61.8 Hz, C1; δ 44.96, s, C6; δ 48.58, d, $^1J_{PC}$ = 53.4 Hz, C7); the assignment of methine and methylene carbons was assisted by a DEPT experiment. The ^{31}P NMR spectrum displays a single absorption at δ 26.3. In the mass spectrum of **9,** the molecular ion (602) is also the base peak.

Chromatographic separation also yields a second 2:1 adduct of DMAD and **2.** The spectral characteristics of this product are consistent with the dihydrophosphocin structure (**10**).

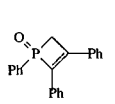


10

The mass spectrum displays a molecular ion at 584 with an intensity equal to 10% of the base peak (91). Major fragments result from the cleavage of methyl ester groups from the 2:1 adduct. Two observations suggest that **10** does not contain an α-ester-stabilized ylide: all four methoxyl groups generate sharp singlets in the ^{1}H NMR spectrum, and there are no low-frequency carbonyl stretches in the infrared spectrum.

Both the ^{1}H and ^{13}C NMR spectra of **10** indicate the presence of a CH_2P moiety. The ^{1}H NMR spectrum contains four sharp methoxy singlets and two mutually coupled multiplets (δ 3.38, dd, 1H, J_{HH} = 18 Hz, J_{PH} = 2.6 Hz; δ 4.58, dd, 1H, J_{HH} = 18 Hz, J_{PH} = 12 Hz). The ^{13}C NMR spectrum of **10** contains four methoxy resonances and a doublet at δ 47.4 (J_{PC} = 11 Hz); a DEPT experiment confirms that the doublet corresponds to a CH_2 group. The magnitudes of J_{PH} and J_{PC} are in the range common for carbons directly bound to a phosphine, although the chemical shifts in both the ^{1}H and ^{13}C NMR spectra are farther downfield than those typically observed for CH_2P groups. Deshielding is also observed in the ^{31}P NMR spectrum, which displays a single resonance at δ 46.9. Delocalization of the phosphorus lone pair into the conjugated electron-withdrawing system could account for the deshielding. Quin has noted deshielding in the ^{31}P NMR spectra of phosphines conjugated with electron-withdrawing groups [21]. Unfortunately, we have been unable to crystallize **10,** and the structure proposed must remain tentative.

In addition to these three major products, the dihydrophosphete oxide (**11**) and the cyclopentadienyl ylide (**12**) are also chromatographically separated from the product mixture. The combined yield of these minor products is less than 10%.



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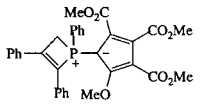


12

The three major products formed in the reaction of **2** and DMAD each contain one equivalent of **2** and two equivalents of DMAD. A possible mechanism for their formation may involve sequential Michael additions of the dihydrophosphete to DMAD to form a zwitterionic intermediate (Scheme 2). Attack of the resulting anion on the phosphonium ion would form a spirocyclic phosphole intermediate. A 1,2-shift of the methylene group would relieve the strain of the four-membered ring and yield the phospholophosphole ylide **8.** Similar rearrangement of 2:1 adducts was proposed by Trippett and coworkers in the reactions of phosphetanes with DMAD [25].

An alternative rearrangement of the spirocyclic intermediate could involve a 1,2-shift of the other dihydrophosphete ring carbon. This shift would generate an isomeric phospholophosphole ylide, which has not been observed. However, the reaction of water with this ylide, followed by cleavage of the strained transannular P–C bond, would yield the tetrahydrophosphocin oxide **9.** The relative positions of the added elements of water in the structure of **9**

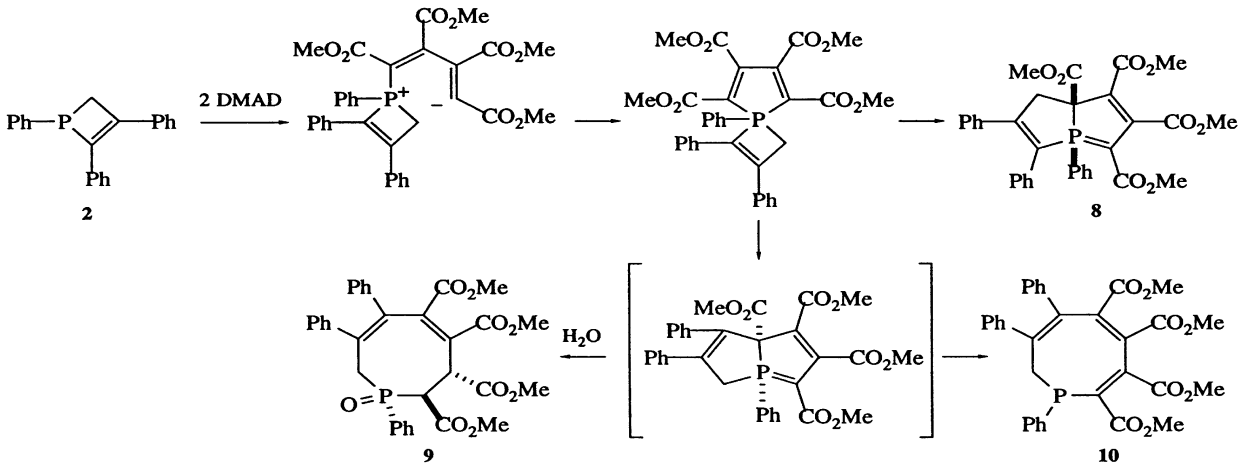
are consistent with initial protonation of the ylide anion, with addition *cis* to the P-phenyl substituent perhaps preferred due to the "butterfly" arrangement of the phospholophosphole rings (Scheme 3). Addition of the resulting hydroxide ion to the phosphonium ion may initiate cleavage of the transannular bond, and transfer of the hydroxyl proton across the ring would provide the observed stereoisomer of **9.**

A spontaneous ring opening of this isomeric phospholophosphole intermediate, without hydrolysis, would provide the dihydrophosphocin **10.** Although the unobserved phospholophosphole intermediate is structurally similar to the stable ylide **8,** conjugation of the double bond in **8** to the phosphonium ion may result in increased stability for **8** relative to the more reactive isomeric phospholophosphole intermediate.

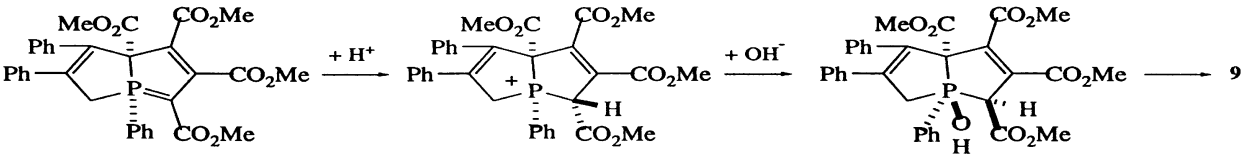
In the reactions of phosphetanes (phosphacyclobutanes) with DMAD, Trippett and coworkers also observed the formation of phospholophosphole ylides [25]. These ylides resulted from the preferential migration of quaternary vs. secondary carbons in the phosphetane ring, and it was suggested that this migratory aptitude indicates the development of positive charge in the migrating carbon. Positive charge is best stabilized upon migrating the allylic carbon of **2,** and in fact, phospholophosphole **8** results from this migration. The alternative migration, which leads to products **9** and **10,** may be promoted by the steric crowding caused by the phenyl substituent on the other phosphorus–carbon bond.

General Reactivity of the Phosphacyclobutene Ring

As the formation of 2:1 adducts is well precedented in the reactions of phosphines with DMAD, an exceptionally potent Michael acceptor, with a variety of 2:1 adducts reported from the reactions of DMAD with triphenylphosphine [22], phospholes [23], phosphindoles [24], phosphetanes [25], and phosphites [26], Mathey's reported successful formation of a cycloadduct with DMAD is particularly intriguing. The most striking difference between the Mathey system and our own, of course, is the presence of a coordinated metal in the former. The results of our studies of the impact of metal coordination on the reaction chemistry of 1,2-dihydrophosphete (**2**) are presented in the companion article [27]. As discussed therein, metal coordination does *not* appear to be responsible for the enhanced tendency of **1** to undergo ring opening and subsequent [4 + 2] cycloaddition chemistry, and the latter reactivity is most plausibly due to the presence of the phenyl substituent on the saturated carbon of



SCHEME 2



SCHEME 3

the dihydrophosphete ring, which may both sterically destabilize the key phosphorus–carbon bond and 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**) was prepared as previously described [28]. Chromatography was carried out using silica gel (Merck, grade 60). ^{1}H 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).

N-Methylmaleimide. A solution of 21.0 mg of **2** (0.0699 mmol) and 7.8 mg of N-methylmaleimide (0.0699 mmol) in 0.5 mL of C_6D_6 was sealed in an NMR tube and heated at 65°C. Within 10 hours, a voluminous precipitate was observed. After a total of 24 hours, the mixture was cooled, the tube was opened, and the solution was separated from the solid by pipette. The residue obtained after removal of solvent from the solution in vacuo was eluted with diethyl ether through a short silica gel column, affording cycloadduct **3** (16%). ^{1}H NMR (C_6D_6): δ 2.57 (m, 1H, C*H*CH_2), 2.69 (dd, 1H, $^{2}J_{HH}$ = 15.7 Hz, $^{3}J_{HH}$ = 5.5 Hz, C*H*H), 2.86 (dd, 1H, $^{2}J_{HH}$ = 15.7 Hz, $^{3}J_{HH}$ = 5.5 Hz, CH*H*), 3.11 (dd, 1H, $^{3}J_{HH}$ = 9.2 Hz, $^{2}J_{PH}$ = 1.3 Hz, PCH), 6.6–7.1 (m, 11H, ArH), 7.2–7.3 (m, 2H, ArH), 7.4–7.5 (m, 2H, ArH). ^{31}P NMR (C_6D_6): δ −18.3. HRMS: calcd for $C_{26}H_{22}NO_2P$: 411. 1388; found: 411.137. Anal. calcd for $C_{26}H_{22}NO_2P$: C, 75.90; H, 5.39. Found: C, 75.83; H, 5.35.

The white solid obtained above from the preparation of **3** (crude yield ca. 50%) was sublimed at atmospheric pressure at 320°C, affording colorless crystals of **4.** The product is only sparingly soluble, but a ^{1}H NMR spectrum was obtainable in acetone-d_6. ^{1}H NMR (acetone-d_6): δ 2.99 (s, 6H, CH_3), 3.70 (s, 4H, CH_2). MS (90 eV): m/z = 222 (M^+, 100%), 191 (M-CH_3N, 12%), 163 (11%), 137 ($C_7H_7NO_2$, 24%), 52 (C_3H_2O, 25%). A peak corresponding to a trimer of N-methylmaleimide (333, 4%) is also observed.

Dimethyl Maleate. To a solution of 15.4 mg of **2** (0.051 mmol) in 0.4 mL of C_6D_6 in an NMR tube was added one equivalent of dimethyl maleate (6.41 μL, 0.051 mmol). The tube was sealed, then heated at 110°C for 14 hours, at which point ^{1}H NMR spectral analysis revealed the complete consumption of **2.** The solution was cooled to room temperature, then the tube was opened, and the solution was concentrated by evaporation of the solvent. The resulting residue was passed through a short silica gel column (8 × 0.5 cm), eluting with 65% diethyl ether/35% pentane. Removal of solvent in vacuo afforded a mixture of **5** and **6** as a white solid in 34% yield. HRMS: Calcd for $C_{27}H_{25}O_4P$: 444.149; found: 444.148. Anal. calcd for $C_{27}H_{25}O_4P$: C, 72.96; H, 5.60. Found: C, 67.59; H, 5.13. Compound **5**: ^{1}H NMR (C_6D_6): δ 2.30–2.45 (ddd, 1H, $^{2}J_{HH}$ = 19.0 Hz, $^{3}J_{HH}$ = 13.0 Hz, $^{4}J_{PH}$ = 2.6 Hz, CH*H* [*trans* to P–Ph]), 3.10–3.25 (dd, 1H, $^{2}J_{HH}$ = 19.0 Hz, $^{3}J_{HH}$ = 4.1 Hz C*H*H [*cis* to P–Ph]), 3.22 (s, 3H, CH_3), 3.36 (s, 3H, CH_3), 3.35–3.47 (dddd, 1H, $^{3}J_{HH}$ = 13.0, 11.6, 4.1 Hz, $^{3}J_{PH}$ = 2.5 Hz, CH_2CH), 3.70–3.81 (dd, 1H, $^{3}J_{HH}$ = 11.6 Hz, $^{2}J_{PH}$ = 8.9 Hz, PCH), 6.6–7.05 (m, 11H, ArH), 7.2–7.3 (m, 2H, ArH), 7.5–7.6 (m, 2H, ArH). ^{13}C NMR (C_6D_6): δ 37.9 (s), 38.2 (d, J_{PC} = 2.3 Hz), 44.4 (d, J_{PC} = 25.4 Hz), 51.4 (s), 51.7 (s), 126–130 (m), 130.6 (d, J_{PC} = 9.0 Hz), 135.0 (d, J_{PC} = 19.9 Hz), 170.9 (s), 175.5 (s). ^{31}P NMR (C_6D_6): δ −23.6. Compound **6**: ^{1}H NMR (C_6D_6): δ 2.85–2.93 (m, 1H, $^{2}J_{HH}$ = 17.4 Hz, $^{3}J_{HH}$ = 4.0 Hz, CH*H* [*cis* to P–Ph]), 3.03–3.13 (ddd, 1H, $^{2}J_{HH}$ = 17.4 Hz, $^{3}J_{HH}$ = 10.6 Hz, $^{4}J_{PH}$ = 3.9 Hz, C*H*H [*trans* to P–Ph]), 3.26 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 3.67–3.75 (m, CH_2CH), 3.90–3.95 (dd, 1H, $^{3}J_{HH}$ = 10.9 Hz, $^{2}J_{PH}$ = 2.8 Hz, PCH), 6.6–7.05 (m, 13H, ArH), 7.5–7.6 (m, 2H, ArH). ^{13}C NMR (C_6D_6): δ 36.9 (s), 41.5 (d, J_{PC} = 6.0 Hz), 45.8 (d, J_{PC} = 20.2 Hz), 126–129 (m), 129.6 (d, J_{PC} = 8.2 Hz), 130.2 (d, J_{PC} = 7.3 Hz), 134.6 (d, J_{PC} = 22.0 Hz), 142.9 (s), 145.4 (s). ^{31}P NMR (C_6D_6): δ −7.9.

Ethyl Acrylate To a solution of 47.0 mg of **2** (0.156 mmol) in 0.5 mL of C_6D_6 in an NMR tube was added 16.8 μL of ethyl acrylate (0.156 mmol). The tube was sealed, then heated at 110°C for 105 hours. Although ^{1}H NMR spectral analysis revealed the presence of unreacted **2,** continued heating did not produce any significant changes. The solution was cooled to room temperature, then the tube was opened, and the solution was concentrated by evaporation of the solvent. The resulting residue was passed through a short silica gel column, eluting with 50% CH_2Cl_2/50% pentane. Removal of solvent in vacuo afforded **7** as a colorless oil in ca. 20% yield. ^{1}H NMR (C_6D_6): δ 0.80 (t, 3H, CH_2CH_3), 2.00–2.30 (m, 2H), 2.5–2.65 (m, 1H), 2.8–3.0 (m, 1H), 3.1–3.25 (m, 1H), 3.85 (q, 2H, CH_2CH_3), 6.6–7.25 (m, 11H, ArH), 7.3–7.4 (m, 2H, ArH), 7.45–7.55 (m, 2H, ArH). ^{13}C NMR (C_6D_6): δ 14.1 (s, CH_2CH_3), 27.2 (d, $^{1}J_{PC}$ = 15.8 Hz, PCH_2), 35.2 (s), 37.4 (s), 60.5 (s, OCH_2), 125.5–

129.5 (m, Ar), 129.8 (s), 130.8 (d, J_{PC} = 10.9 Hz), 133.3 (d, J_{PC} = 18.4 Hz), 134.2 (d, J_{PC} = 20.5 Hz), 143.9 (s), 145.9 (s). ^{31}P NMR (C_6D_6): δ 30.6. HRMS: calcd for $C_{26}H_{25}O_2P$: 400.1592; found: 400.1581. Anal. calcd for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 78.18; H, 6.14.

Dimethyl Acetylenedicarboxylate. A solution of dimethyl acetylenedicarboxylate (ca. 4.0 mmol) in 5 mL of benzene was added to a solution of **2** (ca. 1.7 mmol) in 5 mL of benzene. The initially colorless solutions immediately turned dark brown, and within 1 hour, a yellow solid precipitated from solution. After stirring for at least 4 hours, the reaction mixture was exposed to air, and the benzene was removed on a rotary evaporator. The resulting brown residue was stirred with diethyl ether (ca. 20 mL). The resulting brown solution was decanted from an insoluble yellow solid and saved for workup as described below. The yellow solid was heated with 10 mL of diethyl ether, then the suspension was cooled at −30°C for several hours, and the ether solution was decanted from the yellow solid. The ether washing procedure was repeated, affording the phospholophosphole ylide **3** (0.25 g, 25%) as a yellow solid, mp 195–200°C, in analytically pure form. ^{1}H NMR: δ 3.05 (s, 3H, CH_3O), 3.31 (br s, 3H, CH_3O), 3.57 [m, 1H, HC(3)], 3.64 (s, 3H, CH_3O), 4.03 (s, 3H, CH_3O), 4.63 [dd, $^2J_{HH}$ = 19 Hz, $^3J_{PH}$ = 3.8 Hz, 1H, HC(3)], 7.1–7.8 (m, 15H, ArH). ^{13}C NMR: δ 50.0 (br, CH_3O), 50.0 [d, $^2J_{PC}$ = 11 Hz, C(3)], 51.1 (s, CH_3O), 52.1 [d, $^1J_{PC}$ = 25 Hz, C(4)], 52.5 (s, CH_3O), 52.5 (s, CH_3O), 57.3 [d, $^1J_{PC}$ = 51 Hz, C(7)], 107.9 [d, $^2J_{PC}$ = 11 Hz, C(5)], 120.5 (d, $^1J_{PC}$ = 82 Hz), 124.1 [d, $^1J_{PC}$ = 81 Hz, C(1) and P-phenyl], 127–136 (m, aromatic and olefinic), 156.5 (d, J_{PC} = 27 Hz), 163.4 (s), 163.8 (s), 164.40 (s), 164.42 (d, J_{PC} = 24 Hz), 167.0 (d, J_{PC} = 20 Hz), 169.2 (d, J_{PC} = 2 Hz). IR: ν(C=O) = 1730, 1724, 1660 (shoulder), 1645, 1525 cm^{-1}. MS: 586 (M+2, 10%), 585 (M+1, 40%), 584 (M^+, 100%), 553 (M–OCH_2, 15%), 525 (M–CO_2CH_3, 25%). HRMS: calcd for $C_{33}H_{29}O_8P$: 584.1592. Found: 584.1632. Anal: calcd for $C_{33}H_{29}O_8P$: C, 67.80; H, 5.00; P, 5.30. Found: C, 67.76; H, 5.08; P, 5.32.

Solvent was removed from the brown ether solution on a rotary evaporator, and the resulting brown residue was dissolved in CH_2Cl_2 (ca. 5 mL). The solution was filtered through a short column of silica gel (0.5 × 3 cm), eluting with ethyl acetate (ca. 15 mL). The volume of the filtrate was reduced to 2 mL on a rotary evaporator. Chromatographic separation was performed on a Shimadzu LC-69 HPLC equipped with an IB-Sil5 silica column (250 × 10 mm). Injections of 40 μL were eluted at a constant flow rate of 4 mL/min using a 60/40 mixture of ethyl acetate in hexane. A UV detector was employed at 330 nm with an absorbance of 2.56. The products eluted in the following order under these conditions: **12,** 13.1 minutes; **10,** 14.8 minutes, **9,** 18.3 minutes; **11,** 25.3 minutes.

Tetrahydrophosphocin oxide **9** was obtained in 19% yield as a colorless crystalline solid, mp 240°C (partial dec at 235°C). ^{1}H NMR: δ 3.35 [dd, 1H, $^2J_{HH}$ = 14.4 Hz, $^2J_{PH}$ = 21.8 Hz, HC(1)], 3.57 (s, 3H, MeO), 3.59 (s, 3H, MeO), 3.66 [dd, 1H, $^2J_{HH}$ = 14.3 Hz, $^2J_{PH}$ = 7.2 Hz, HC(1)], 3.84 (s, 3H, MeO), 3.88 (s, 3H, MeO), 3.98 [dd, 1H, $^3J_{HH}$ = 12.1 Hz, $^3J_{PH}$ = 9.6 Hz, HC(6)], 5.08 [dd, 1H, $^3J_{HH}$ = 12.2 Hz, $^2J_{PH}$ = 8.6 Hz, HC(7)], 7.0–7.8 (m, 15H, ArH). ^{13}C NMR: δ 40.8 [d, $^1J_{PC}$ = 62 Hz, C(1)], 45.0 [s, C(6)], 48.6 [d, $^1J_{PC}$ = 53 Hz, C(7)], 52.4 (OMe), 52.5 (OMe), 52.8 (OMe), 53.0 (OMe), 127.4–140.1 (m, aromatic and olefinic), 165.0 (d, J_{PC} = 2.9 Hz, CO_2Me), 167.2 (s, CO_2Me), 167.5 (d, J_{PC} = 6.5 Hz, CO_2Me), 170.4 (d, J_{PC} = 12 Hz, CO_2Me). IR: ν(C=O) = 1745 (br) and 1727 cm^{-1}. MS: 603 (M+1, 35%), 602 (M^+, 100%), 571 (M–OMe, 20%), 542 (M–CO_2Me+H, 85%), 510 (M–CO_2Me+OMe+2H, 65%), 334 (M–[PhP(O)CH(CO_2Me)CH(CO_2Me)], 32%). HRMS: calcd. for $C_{33}H_{31}O_9P$: 602.1705. Found: 602.1670. Anal. calcd. for $C_{33}H_{31}O_9P$: C, 65.78; H, 5.19; P, 5.14. Found: C, 65.41; H, 5.16; P, 5.21.

Dihydrophosphocin **10** was obtained in 20% yield as a colorless oil. ^{1}H NMR: δ 3.09 (s, 3H, OMe), 3.38 (dd, 1H, $^2J_{HH}$ = 18 Hz, $^2J_{PH}$ = 2.6 Hz, HCHP), 3.72 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.96 (s, 3H, OMe), 4.58 (dd, 1H, $^2J_{HH}$ = 18 Hz, $^2J_{PH}$ = 12 Hz, HCHP), 7.1–7.6 (m, 15H, ArH). ^{13}C NMR: δ 47.4 (d, $^1J_{PC}$ = 11 Hz, CH_2P), 52.6 (s, OMe), 52.7 (s, OMe), 53.1 (s, OMe), 56.4, 57.0 [d?, (C=C−C=C–P?)], 58.1 (s, OMe), 75.8, 90.0, 127–140 (aromatic and olefinic), 152.7, 156.3, 156.6, 166.0, 170.1. IR: ν(C=O) = 1739 (br) and 1718 cm^{-1}. MS: 585 (M+1, 3%), 584 (M^+, 10%), 569 (M–Me, 18%), 553 (M–OMe, 75%), 525 (M–CO_2Me, 50%), 507 (M–Ph, 10%), 493 (M–CO_2Me+MeOH, 100%). HRMS: calcd. for $C_{33}H_{29}O_8P$: 584.1592. Found: 584.1579.

Dihydrophosphete oxide **11** was obtained in 4% yield as a white solid; characterization of this compound has been presented elsewhere [28]. Cyclopentadienyl ylide **12** was also obtained in ca. 4% yield as a white crystalline solid; its characterization is presented in the following article in this issue [27].

Crystallographic Analysis of 5. Vapor diffusion of heptane into a toluene solution of a mixture of stereoisomers **5** and **6** afforded crystals of **5.** A colorless plate of approximate dimensions 0.1 × 0.38 × 0.4 mm was mounted on a fiber on a Huber diffractometer constructed by C. E. Strause of the UCLA Department of Chemistry and Biochemistry.

TABLE 1 Crystallographic Data for **5, 8,** and **9**

	Compound		
	5	**8**	**9**
Composition	$C_{27}H_{25}O_4P$	$C_{33}H_{29}O_8P \cdot 0.5C_7H_8$	$C_{33}H_{31}O_9P$
Formula weight	444.5	630.6	602.5
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a(Å)	10.142(1)	11.076(5)	12.140(4)
b(Å)	10.799(2)	11.967(6)	16.999(5)
c(Å)	11.560(2)	12.505(5)	14.594(3)
α(deg)	67.752(4)	90.34(4)	90
β(deg)	82.163(5)	101.86(4)	98.620
λ(deg)	85.705(5)	100.92(4)	90
V(Å^3)	1160	1591(3)	2977.7(15)
Z	2	2	4
d_{calcd} (g cm^{-3})	1.27	1.32	1.344
λ(Å)	0.71069	0.71069	1.54184
No. obs reflns	2225	3115	1955
$R(F_0)$	0.074	0.069	0.0788
$wR(F_0)$	0.085	0.094	0.0915

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement coefficeints (Å^2) for Cycloadduct **5**

Atom	*x*	*y*	*z*	U_{equiv}
P1	3323(2)	2454(1)	4278(1)	0.049
C2	2617(5)	3848(5)	3027(5)	0.042
C3	2399(5)	5102(5)	3036(5)	0.045
C4	2440(6)	5458(5)	4176(5)	0.055
C5	2480(6)	4290(5)	5428(5)	0.055
C6	3639(6)	3335(5)	5336(5)	0.051
C11	1869(4)	1479(3)	5161(3)	0.053
C12	561(4)	1971(3)	5056(3)	0.055
C13	−491(4)	1182(3)	5812(3)	0.070
C14	−235(4)	−100(3)	6672(3)	0.084
C15	1073(4)	−592(3)	6776(3)	0.091
C16	2125(4)	198(3)	6021(3)	0.076
C21	2386(3)	3482(3)	1936(3)	0.040
C22	1142(3)	3760(3)	1495(3)	0.048
C23	884(3)	3374(3)	526(3)	0.057
C24	1872(3)	2711(3)	−3(3)	0.060
C25	3117(3)	2434(3)	438(3)	0.063
C26	3374(3)	2819(3)	1407(3)	0.056
C31	2176(3)	6315(3)	1872(3)	0.043
C32	3086(3)	6584(3)	792(3)	0.057
C33	2989(3)	7789(3)	−230(3)	0.066
C34	1981(3)	8724(3)	−172(3)	0.062
C35	1072(3)	8454(3)	908(3)	0.063
C36	1169(3)	7250(3)	1930(3)	0.054
C51	2429(9)	4907(7)	6423(6)	0.075
C52	3473(11)	5719(9)	7615(8)	0.128
C61	3924(7)	2324(6)	6585(6)	0.054
C62	5590(8)	838(8)	7660(7)	0.108
O51	1452(6)	5304(6)	6851(5)	0.119
O52	3634(5)	4977(5)	6707(4)	0.084
O61	3141(5)	1931(4)	7514(4)	0.074
O62	5183(5)	1866(4)	6522(4)	0.079

TABLE 3 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) for Phospholophosphole Ylide **8** ($B_{equiv} = 8\pi^2/3)\Sigma_i \Sigma_j U_{ij}\, a_i\, a^*_j\, a_i \cdot a_j$)

Atom	*x*	*y*	*z*	B_{equiv}
P1	2291.9(15)	3732.2(14)	6735.8(13)	2.89(6)
O1	−501(5)	3285(4)	4640(4)	5.3(2)
O2	310(5)	1737(4)	5108(3)	4.6(2)
O3	−1620(4)	1692(4)	6840(4)	5.4(2)
O4	−604(4)	619(4)	8018(4)	4.6(2)
O5	2033(4)	1212(4)	9518(4)	4.5(2)
O6	1821(5)	0(4)	8092(4)	4.5(2)
O7	4969(5)	3277(5)	7619(5)	5.8(3)
O8	4288(4)	1609(4)	8335(4)	5.3(2)
C1	2231(5)	4973(5)	7511(4)	2.7(2)
C2	1056(6)	4977(5)	7596(5)	2.8(2)
C3	16(5)	4100(5)	6873(5)	3.1(2)
C4	587(5)	3126(5)	6513(4)	2.7(2)
C5	573(5)	2137(5)	7267(4)	2.8(2)
C6	1731(6)	1916(5)	7726(5)	3.0(2)
C7	2802(6)	2622(5)	7473(5)	3.2(2)
C8	2879(6)	4081(5)	5532(5)	3.3(3)
C9	3321(7)	3285(6)	4992(6)	4.5(3)
C10	3721(7)	3545(8)	4038(6)	5.5(4)
C11	3728(7)	4613(8)	3638(6)	5.5(4)
C12	3293(7)	5404(7)	4164(6)	5.0(3)
C13	2873(6)	5159(6)	5106(5)	4.0(3)
C14	3340(6)	5861(6)	7940(5)	3.4(3)
C15	4402(7)	5643(7)	8624(6)	5.0(3)
C16	5427(7)	6513(9)	9021(7)	6.3(4)
C17	5393(9)	7614(10)	8715(8)	7.1(5)
C18	4372(10)	7849(7)	8029(7)	6.8(4)
C19	3341(7)	6974(6)	7628(6)	4.9(3)
C20	636(6)	5740(5)	8326(5)	3.3(3)
C21	1328(6)	5999(6)	9391(5)	4.0(3)
C22	8.57(8)	6619(6)	10115(6)	5.1(3)
C23	−271(9)	6957(7)	9778(8)	5.9(4)
C24	−941(7)	6706(7)	8727(7)	5.5(4)
C25	−498(7)	6106(6)	8011(6)	4.4(3)
C26	39(6)	2743(5)	5308(5)	3.5(3)
C27	−136(10)	1259(7)	3987(6)	7.9(5)
C28	−639(6)	1491(5)	7336(5)	3.3(3)
C29	−1768(8)	−99(7)	8077(7)	6.2(4)
C30	1888(6)	1019(6)	8550(5)	3.5(3)
C31	1876(10)	−903(7)	8860(7)	7.5(4)
C32	4108(7)	2567(7)	7799(6)	4.4(3)
C33	5595(10)	1554(10)	8704(9)	9.8(6)

Unit cell parameters were determined by a least-squares fit of 42 accurately centered reflections ($8.2° < 2\theta < 18.3°$). These dimensions and other parameters are summarized in Table 1. Data were collected at 25°C in the θ-2θ scan mode. Three intense reflections (2 1 0, 1 0 −2, 0 3 −1) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of data acquisition (51.8 h). Of the 4079 unique reflections measured, 2225 were considered observed [$I > 3\sigma(I)$] and were used in the subsequent structure analysis. Data were corrected for Lorentz and polariza-

TABLE 4 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Dihydrophosphocin Oxide **9**

Atom	*x*	*y*	*z*	U_{equiv}
P	2663(2)	4901(1)	6354(2)	58(1)
C1	1191(5)	4824(4)	5863(7)	60(4)
C2	505(6)	4184(5)	6264(7)	58(4)
C3	−149(6)	4381(5)	6896(7)	56(4)
C4	−45(5)	5156(5)	7358(6)	52(3)
C5	883(5)	5384(4)	7933(7)	55(4)
C6	1872(5)	4827(5)	8145(6)	53(3)
C7	2847(5)	5066(4)	7634(6)	57(3)
C8	3129	5822	5910	55(4)
C9	2655(4)	6549(3)	6058(4)	58(4)
C10	3116	7238	5760	66(4)
C11	4053	7198	5312	65(4)
C12	4528	6471	5164	68(4)
C13	4066	5782	5462	60(4)
C14	556	3370	5888	52(4)
C15	396(4)	3217(3)	4938(4)	60(4)
C16	312	2442	4620	65(4)
C17	387	1821	5251	66(4)
C18	546	1975	6200	66(4)
C19	631	2749	6519	57(4)
C20	−976	3854	7279	59(4)
C21	−1752(4)	3424(3)	6676(3)	63(4)
C22	−2532	2954	7028	63(4)
C23	−2537	2913	7982	58(4)
C24	−1761	3342	8585	61(4)
C25	−980	3812	8233	63(4)
C26	−1001(6)	5732(5)	7174(7)	56(4)
C27	−2800(6)	5915(5)	6299(7)	72(4)
C28	963(7)	6145(6)	8442(10)	62(5)
C29	1406(7)	7488(5)	8354(7)	75(4)
C30	2288(7)	4824(5)	9204(7)	56(4)
C31	1997(7)	4247(5)	10636(7)	69(4)
C32	3883(6)	4581(6)	7982(6)	50(4)
C33	5816(6)	4497(5)	7952(7)	77(4)
O1	3309(4)	4204(3)	6120(4)	58(2)
O2	−1038(4)	6364(3)	7516(4)	62(3)
O3	−1804(4)	5431(3)	6525(4)	65(2)
O4	727(5)	6227(4)	9221(6)	69(3)
O5	1357(4)	6715(3)	7950(4)	61(2)
O6	3013(4)	5234(3)	9589(4)	68(3)
O7	1702(4)	4299(3)	9630(5)	58(3)
O8	3864(4)	3952(3)	8350(5)	66(3)
O9	4795(4)	4965(3)	7807(4)	64(2)

tion effects. Programs used included locally modified versions of CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections, SHELX86 (Sheldrick), structure solution package, SHELX76 (Sheldrick), structure calculation and full matrix least-squares refinement, and ORTEP (Johnson). Atoms were located by statistical methods. All calculations were performed on a VAX 3100 crystallographic computer. All nonhydrogen atoms were refined with anisotropic parameters. Hydrogen atoms were included in calculated positions as members of rigid groups with C–H = 1.0 Å and angles of either 109.5° or 120° as appropriate and were assigned U values based on those of the attached atoms. Scattering factors for hydrogen were obtained from Stewart et al. [29] and for other atoms from the International Tables for X-ray Crystallography [30]. Anomalous dispersion terms were applied to the scattering by phosphorus. The largest peak on the final difference electron density map was 0.6 $e/Å^3$. Final positional and thermal parameters for nonhydrogen atoms are provided in Table 2; full data tables are provided in the supplementary materials.

Crystallographic Analysis of **8**. Compound **8** was recrystallized from toluene/heptane, affording light-yellow tablets. Data were collected from a crystal of dimensions 0.10 × 0.15 × 0.25 mm after determination of the cell dimensions and orientation matrix from the setting angles of a Rigaku AFC6R diffractometer for 20 centered reflections in the range $11° \leq 2\theta \leq \theta$ 17°. Crystal data are provided in Table 1. The crystal diffracted sharply but weakly, and near the limit of data collection (2θ = 50°) only ca. one-third of the reflections were observed by the criterion $I \geq 3\sigma(I)$. The standard reflections showed no systematic change in intensity during data collection. All nonhydrogen atoms of the molecule were apparent in an E-map generated by use of SHELXS [31]. They were allowed anisotropic thermal parameters in the later stages of refinement, and hydrogen atoms were included at riding positions with U(H) equal to $1.2U_{equiv}$(C). A difference synthesis showed peaks apparently due to atoms of disordered solvent molecules in the region of an inversion center in an intermolecular void. Attempts to refine these peaks as carbon atoms resulted in site occupancy factors greater than unity and large thermal parameters. As no basis for rigid-body refinement suggested itself, the solvent peaks were included in the final refinement as fractional carbon atoms with fixed coordinates and thermal parameters. The TEXSAN 5.0 program suite [32] was used in all calculations. Final positional and thermal parameters for nonhydrogen atoms are provided in Table 3; full data tables are provided in the supplementary materials.

Crystallographic Analysis of **9**. Crystallographic data were collected from a colorless plate of dimensions 0.10 × 0.16 × 0.20 mm on a Siemens R3m/V diffractometer in the range $0° \leq 2\theta \leq 107.3°$ at a scan speed of 30.0° 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 1955 reflections were collected, and all were considered observed by the criterion $F > 6\sigma(F)$. Structure solution was carried out using the Siemens SHELXTL PLUS direct methods program. Riding hydrogen atoms with fixed isotropic U were used. Full-matrix least-squares refinement converged to a final R factor of 0.0788, with the largest features in the final-difference electron density map $+0.50$ and -0.58 $e/Å^3$. Final positional and thermal parameters for nonhydrogen atoms are provided in Table 4; full data tables are provided in the supplementary materials.

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SUPPLEMENTARY MATERIAL AVAILABLE

Complete crystallographic details and data tables for compounds **5, 8,** and **9** (86 pp).

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