

Articles

Destiny of Transient Phosphenium Ions Generated from the Addition of Electrophiles to Phosphaalkenes: Intramolecular C–H Activation, Donor–Acceptor Formation, and Linear Oligomerization

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The reaction of the phosphaalkenes $\text{MesP}=\text{CPh}_2$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) and $\text{Mes}^*\text{P}=\text{CH}_2$ ($\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$) with Lewis (AlCl_3 , GaCl_3 , InCl_3) and protic (HOTf) acids has been examined to evaluate the feasibility of cationic polymerization for $\text{P}=\text{C}$ bonds. Addition of GaCl_3 to $\text{Mes}^*\text{P}=\text{CH}_2$ generates the adduct $\text{Mes}^*(\text{Cl}_3\text{Ga})\text{P}=\text{CH}_2$, which can be detected spectroscopically at 193 K. At higher temperatures, GaCl_3 migrates from phosphorus to carbon to afford the fleeting phosphenium zwitterion $\text{Mes}^*\text{PCH}_2\text{GaCl}_3$. This undetected transient species immediately oxidatively adds to a C–H bond of an *o*-*t*Bu group in the *P*- Mes^* substituent, resulting in a GaCl_3 -coordinated ylide that has been characterized crystallographically. The analogous reaction of GaCl_3 with $\text{MesP}=\text{CPh}_2$ gives stable $\text{Mes}(\text{Cl}_3\text{Ga})\text{P}=\text{CPh}_2$, for which a crystal structure determination has been conducted. Significantly, treating a highly concentrated solution of $\text{Mes}^*\text{P}=\text{CH}_2$ with substoichiometric quantities of GaCl_3 leads to linear dimerization following a cationic chain growth mechanism; however, the oligomerization is terminated by intramolecular C–H activation. The novel coordinated linear dimer (C–H activated $\text{Mes}^*\text{PCH}_2\text{PH}(\text{Mes}^*)\text{CH}_2\text{GaCl}_3$) has been characterized crystallographically. Interestingly, mechanistic studies reveal that the diphosphiranium ring $\text{Mes}^*\text{PCH}_2\text{P}(\text{Mes}^*)\text{CH}_2\text{GaCl}_3$ derived from the reaction of $\text{Mes}^*\text{PCH}_2\text{GaCl}_3$ with $\text{Mes}^*\text{P}=\text{CH}_2$ is an intermediate in this transformation. The reaction of phosphaalkenes with phosphenium species appears to be a general method to prepare diphosphiranium ions. In one case, NMR spectroscopic data suggests that treating $\text{MesP}=\text{CPh}_2$ with HOTf gives both the diphosphiranium species $[\text{MesP}(\text{CPh}_2)_2\text{P}(\text{Mes})\text{CPh}_2\text{H}]\text{OTf}$ and the adduct $\text{Ph}_2\text{C}=(\text{Mes})\text{P}=\text{P}(\text{Mes})(\text{CHPh}_2)\text{OTf}$. Remarkably, treating concentrated $\text{Mes}^*\text{P}=\text{CH}_2$ solutions with HOTf results in oligomers of up to six repeat units, as determined by ESI mass spectrometry. These results suggest that it may be possible to initiate the polymerization of $\text{P}=\text{C}$ bonds using cationic initiators and that the propagating species will be a cationic phosphenium moiety.

Introduction

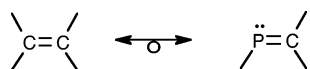
The investigation of compounds containing a multiple bond involving a heavier element of the p block often leads to unexpected results that can challenge our ideas of structure, bonding, and reactivity.¹ One of the most thoroughly studied classes of low-coordinate compounds of the main-group elements are the phosphaalkenes: compounds possessing a $(3p-2p)\pi$ bond between phosphorus and carbon.² Phosphaalkenes can formally be derived by simply replacing a carbene (R_2C) moiety in

an olefin with the isolobal and isovalent phosphinidene (RP) group. Therefore, it might be expected that there would be numerous parallels between the chemistry of $\text{P}=\text{C}$ bonds in phosphaalkenes and that of $\text{C}=\text{C}$ bonds

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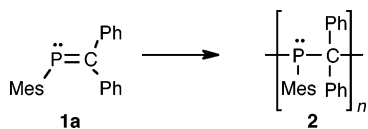
* To whom correspondence should be addressed. Tel: 604-822-9117. Fax: 604-822-2847. E-mail: dgates@chem.ubc.ca.

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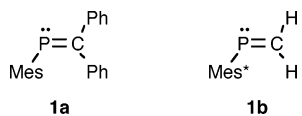
Scheme 1. Phosphorus–Carbon Isolobal Analogy

in alkenes (Scheme 1). The quest for such parallels between phosphalkenes and olefins has attracted considerable attention, and thus far, these developments have been limited primarily to molecular chemistry,^{2a,b,g} although very recently π -conjugated P=C analogues of poly(*p*-phenylenevinylene) have been developed.^{3,4}

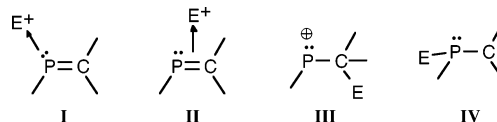
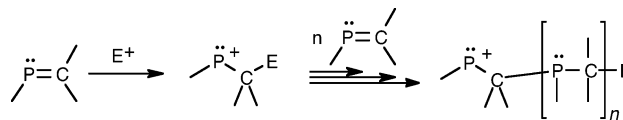
The addition polymerization of olefins is a textbook reaction for C=C double bonds; however, it remains limited primarily to C=C and in some instances C=O bonds. We have been interested in expanding addition polymerization to phosphalkenes, thereby extending the phosphorus–carbon analogy to polymer science. To this end, we have recently reported the polymerization of phosphalkene (**1a**: Mes = 2,4,6-trimethylphenyl) to afford the unprecedented poly(methylenephosphine) **2**,



an inorganic polymer composed of alternating phosphorus and carbon atoms.⁵ At present, we have successfully polymerized **1a** using either anionic or radical methods of initiation. A thorough understanding of the nature of the interaction between phosphalkenes and potential polymerization initiators at the molecular level will be essential to fully develop and optimize this new chemistry. In the case of the anionic polymerization of **1a**, we have shown that MeLi adds to the P=C bond, generating a carbanion, and preliminary investigations of the products of chain growth using MALDI-TOF mass spectroscopy suggest that backbiting may compete with linear chain growth.⁶ The work described herein will assess the potential for cationic polymerization of phosphalkenes **1a** (Mes = 2,4,6-trimethylphenyl) and **1b** (Mes* = 2,4,6-tri-*tert*-butylphenyl).



The cationic polymerization of olefins involves the addition of an electrophile across the C=C bond to generate a highly reactive carbocation which acts as the propagating species. By comparison with olefins, the reaction of a phosphalkene with an electrophile (E^+) is more complex, due to the possible interaction with the lone pair at phosphorus or the P=C π -bond. Thus, several possible products may be envisaged (Chart 1).⁷ Most studies of reactions of P=C bonds with electrophiles have focused on their use as ligands for transition metals or on the simple addition of RX across the P=C bond (R = H, alkyl; X = halide).^{2i,8,9} In phosphalkene–transition-metal complexes, the most commonly ob-

Chart 1. Possible Coordination Modes for the Reaction of a Phosphaalkene with an Electrophile (E^+)**Scheme 2. Proposed Mechanism for the Hypothetical Cationic Polymerization of a Phosphaalkene Initiated by an Electrophile (E^+)**

served coordination modes are η^1 (Chart 1, mode I), and η^2 (Chart 1, mode II) which is reminiscent of the side-on binding of olefins. Neither of these two modes would be expected to initiate cationic chain growth, although mode II is of potential interest in coordination polymerization. A possible mechanism for the putative cationic polymerization of a phosphalkene is shown in Scheme 2. Although propagation could occur through either a phosphonium ion (Chart 1, mode III) or a carbocation (Chart 1, mode IV), we hypothesized that mode III would be most likely on the basis of electronegativity differences ($\chi_P < \chi_C$).¹⁰

The cationic initiators used to polymerize alkenes tend to be either strong protic acids with relatively weakly coordinating anions (i.e. HX: X = OTf⁻, BF₄⁻) or Lewis acids (i.e. AlCl₃). Surprisingly, there are very few studies in the literature of reactions of phosphalkenes with such potential polymerization initiators, although it has been shown that ^tBuP=CH^tBu will form an η^1 complex with AlCl₃.¹¹ The generation of phosphonium ions (i.e. Chart 1; mode III) by addition of an electrophile to a P=C bond is rare; however, addition of HOTf to Cp*P=CR₂ (Cp* = C₅Me₅; R = SiMe₃) gives the phosphonium species [Cp*PCHR₂]OTf, which was characterized by NMR spectroscopy.¹² It is also possible

(7) The electronic structure of phosphalkenes has been studied extensively using photoelectron spectroscopy and molecular modeling. The two filled frontier orbitals (the lone pair on phosphorus and the (2p–3p) π bond) are closely spaced in energy, and the order is highly dependent on the nature of the substituents. (See, for example: Lacombe, S.; Gonbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J.-M.; Pfister-Guilouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964 and references therein).

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(10) The Pauling electronegativities (P = 2.19; C = 2.55) suggest that the polarity should be P⁺=C⁻. This is true for the σ -system; however, evidence from UV and magnetic circular dichroism of phosphinines suggests that the effective π -electronegativity of P is similar to or higher than that of C. For a useful discussion of this see: Waluk, J.; Klein, H.-P.; Ashe, A. J., III; Michl, J. *Organometallics* **1989**, *8*, 2804.

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to generate phosphonium cations from the reaction of electrophiles with the diphosphene $\text{Mes}^*\text{P}=\text{PMe}^*$.^{13,14} The synthesis of stable phosphonium ions is of considerable fundamental interest, and a fascinating chemistry for these species, which are isovalent with carbenes, has emerged.^{15–17} To date, most isolable phosphonium ions possess two adjacent π -donor substituents (i.e. NR, O, S, P), although stable systems are known with one π -donor and one bulky aryl substituent.^{18–20} A phosphonium ion generated by adding E^+ across the $\text{P}=\text{C}$ bond of either **1a** or **1b** would have no adjacent π -donors and thus will be highly reactive, which we hope will lead to polymerization.²¹

In this paper we will provide evidence that transient phosphonium ions can be generated by the addition of Lewis or protic acids to the $\text{P}=\text{C}$ bonds in **1a** and **1b**: the first step in a putative cationic polymerization. A portion of this work has appeared as a preliminary communication.²² Three different fates for these highly reactive phosphonium ions have been observed: (i) intramolecular C–H activation (in the case of **1b**), (ii) donor–acceptor coordination of phosphaalkenes to phosphonium ions, affording novel diphosphiranium (P_2C) rings (in the case of both **1a** and **1b**) and/or phosphaalkene–phosphonium adducts (in the case of **1a**), and (iii) linear oligomerization (in the case of **1b**).

Results and Discussion

Phosphaalkenes **1a** and **1b** were chosen for cationic $\text{P}=\text{C}$ bond activation studies since they are isolable yet possess minimal steric bulk and do not contain electron-rich heteroatom substituents (i.e. O, N, P) that may interfere in their reactions with electrophiles. Compound **1a** was prepared by following a modification to a literature method²³ which we have reported previously.⁵ The synthesis and characterization of phosphaalkene **1b**, a rare example of a phosphaalkene with H substituents, was first reported in 1984.²⁴ Surprisingly, the reactivity of compound **1b** has received little attention, since its initial synthesis and coordination to

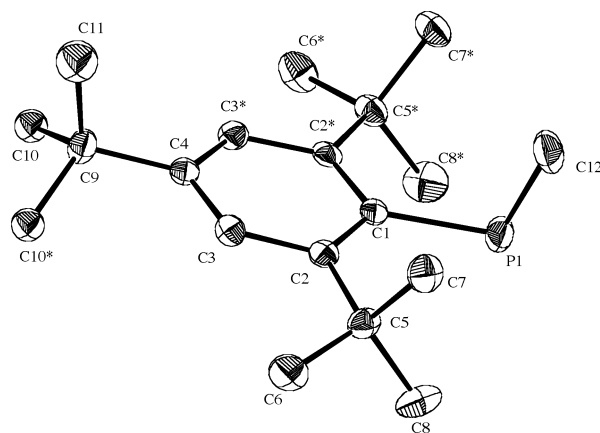


Figure 1. Molecular structure of **1b** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): $\text{P}(1)\text{--C}(12) = 1.643(3)$; $\text{C}(1)\text{--P}(1)\text{--C}(12) = 104.1(1)$.

iron.^{24,25} This is in stark contrast to the widely studied halogen-substituted systems $\text{Mes}^*\text{P}=\text{CXH}$ and $\text{Mes}^*\text{P}=\text{CX}_2$ ($\text{X} = \text{halogen}$).²⁶ Compound **1b** was prepared by the reaction of CH_2Cl_2 and Mes^*PH_2 (^{31}P NMR: $\delta -127$; $^1J_{\text{PH}} = 205$ Hz) in the presence of KOH.²⁴ Interestingly, ^{31}P NMR analysis of the initial reaction mixture revealed a previously undetected intermediate ($\delta -66$ ppm, $^1J_{\text{PH}} = 226$ Hz) that was consistent with $\text{Mes}^*\text{P}(\text{H})\text{CH}_2\text{Cl}$. After 1 week, the ^{31}P NMR spectrum of the reaction mixture revealed that phosphaalkene **1b** had been formed quantitatively. Recrystallization of the crude product afforded pale yellow crystals of **1b** suitable for X-ray diffraction (yield 59%). The molecular structure of **1b** is shown in Figure 1. The $\text{P}=\text{C}$ bond length of 1.643(3) Å is in the shorter end of the range found for the $\text{P}=\text{C}$ double bonds in phosphaalkenes (1.61–1.71 Å)^{2h} and is significantly shorter than that in **1a** (1.692(3) Å).²⁷

Reaction with Lewis Acids: Intramolecular C–H Activation. Initially, we chose to explore the possible cationic activation of the $\text{P}=\text{C}$ bond in **1b** with the Lewis acid GaCl_3 . Unexpectedly, the ^{31}P NMR spectrum of the reaction mixture revealed that **1b** ($\delta 289.0$) was completely consumed and that a new species with a doublet

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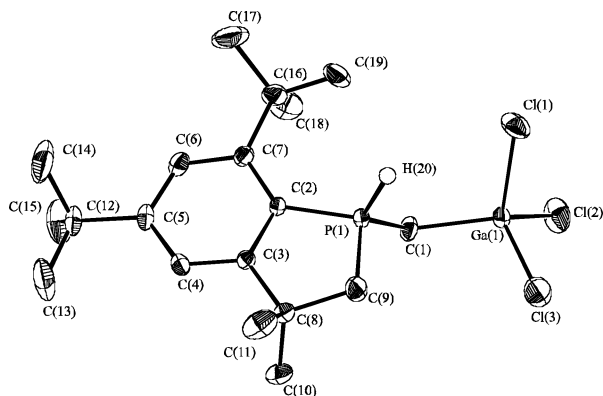
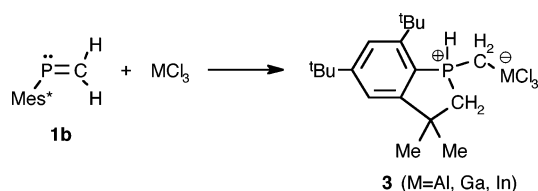


Figure 2. Molecular structure of **3** ($M = \text{Ga}$) (50% probability ellipsoids). All hydrogen atoms except H(20) are omitted for clarity. Selected bond lengths (\AA) and angles (deg): P(1)–C(1) = 1.773(3), P(1)–C(2) = 1.786(3), P(1)–C(9) = 1.793(4), Ga(1)–C(1) = 1.994(3); P(1)–C(1)–Ga(1) = 112.70(14).

resonance at 16.4 ppm and a very large P–H coupling constant of 498 Hz had been formed. The large coupling constant suggested the presence of a direct P–H bond; however, its magnitude was much greater than the P–H coupling in trivalent phosphines (i.e. Mes^*PH_2 ; $^1J_{\text{PH}} = 205$ Hz). In addition, the P–H signal in the ^1H NMR spectrum (7.4 ppm) was shifted downfield significantly with respect to a phosphine (i.e. Mes^*PH_2 ; $\delta(^1\text{H})$ 4.30 ppm), suggesting a phosphonium moiety. For comparison, $[(n\text{-Bu})_3\text{PH}]\text{BF}_4$ ($\delta(^1\text{H})$ 6.07 ppm, $\delta(^{31}\text{P})$ 14.1 ppm, $^1J_{\text{PH}} = 484$ Hz) and $[(t\text{-Bu})_3\text{PH}]\text{BF}_4$ ($\delta(^1\text{H})$ 6.07 ppm, $\delta(^{31}\text{P})$ 51.7 ppm, $^1J_{\text{PH}} = 465$ Hz) show similar spectral properties.²⁸ In addition to signals in the P–H and aryl regions, the aliphatic region of the ^1H NMR spectrum of the product showed three singlet resonances (δ 1.51, 6H; δ 1.48, 9H; δ 1.34, 9H) assigned to methyl groups and a multiplet (δ 2.26, 2H) attributed to a methylene group. This suggested that one of the $t\text{Bu}$ resonances of Mes^* had been activated, and we speculated that the product was **3** ($M = \text{Ga}$). Intramolecular C–H activation



of the Mes^* group is a reasonably common reaction in low-coordinate phosphorus chemistry.²⁹ Confirmation of our assignment of structure **3** ($M = \text{Ga}$) was obtained through X-ray crystallography, and the molecular structure is shown in Figure 2. The Ga(1)–C(1) bond length of 1.994(3) \AA is significantly longer than for GaMe_3 (Ga–C = 1.967(2) \AA)³⁰ and is comparable to most four-

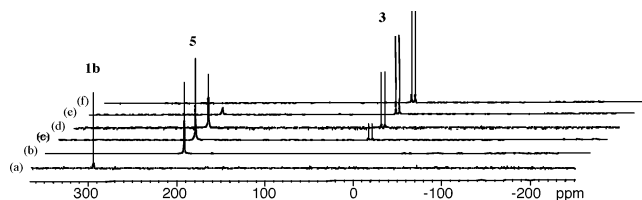


Figure 3. ^{31}P NMR spectra (CD_2Cl_2) showing reaction progress: (a) **1b** at 193 K; (b) **1b** + $\text{GaCl}_3 \rightarrow \mathbf{5}$ ($M = \text{Ga}$) at 193 K; (c) reaction in (b) with the temperature raised to 213 K; (d) reaction in (b) with the temperature raised to 233 K; (e) reaction in (b) with the temperature raised to 253 K; (f) reaction in (b) with the temperature raised to 273 K, showing quantitative formation of **3** ($M = \text{Ga}$).

coordinate gallium compounds which exhibit slightly longer Ga–C distances (i.e. $\text{Me}_3\text{GaNMe}_3$; Ga–C = 1.998(4) \AA).³¹

We have carried out a similar reaction of **1b** with AlCl_3 to afford the zwitterionic coordinated ylide **3** ($M = \text{Al}$) (^{31}P NMR: 16.9 ppm, $^1J_{\text{PH}} = 489$ Hz). In contrast to **3** ($M = \text{Ga}$), which is stable in air as a solid (≥ 1 year by NMR), compound **3** ($M = \text{Al}$) is unstable in the solid state even under inert conditions, and over several days proton migration from P to C occurs quantitatively, accompanied by AlCl_3 loss. In solution, AlCl_3 can be used to promote catalytic intramolecular C–H activation in **1b**, whereas GaCl_3 does not show turnover under ambient conditions.²² The reason for this difference in stability is not obvious; however, we speculate that this suggests a weaker Lewis acidity of AlCl_3 than GaCl_3 with respect to the ylide group in **3**. We have detected the analogous C–H activated product **3** ($M = \text{In}$) by NMR spectroscopy (^{31}P NMR: 11.5 ppm, $^1J_{\text{PH}} = 513$ Hz). Unfortunately, the reaction of **1b** with InCl_3 is very slow and there is only partial conversion of **1b** to **3** ($M = \text{In}$) even with heating.

Mechanism of C–H Activation: Is a Phosphenium Ion Involved? On the basis of the fact that the product of the reaction of **1b** with GaCl_3 contains a Ga–C bond, we reasoned that the initial step in the reaction must involve addition of GaCl_3 to the P=C bond, generating a phosphenium zwitterion (**4**; i.e.,

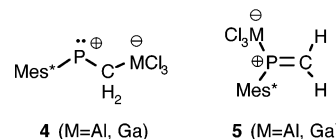


Chart 1; mode III) which subsequently inserts into the C–H bond of Mes^* . The potential involvement of **4** was encouraging from the point of view of cationic polymerization, and therefore, variable-temperature NMR studies were initiated to gain additional evidence for a phosphenium intermediate. Thus, **1b** was treated with GaCl_3 in d_2 -dichloromethane in a cooled NMR tube (163 K) and the product was immediately analyzed using ^{31}P , ^1H , and ^{13}C NMR spectroscopy. Remarkably, only a single signal is observed at 208.9 ppm in the ^{31}P NMR spectrum at 193 K (Figure 3 b). This species was stable for several days if kept at 193 K; however, upon

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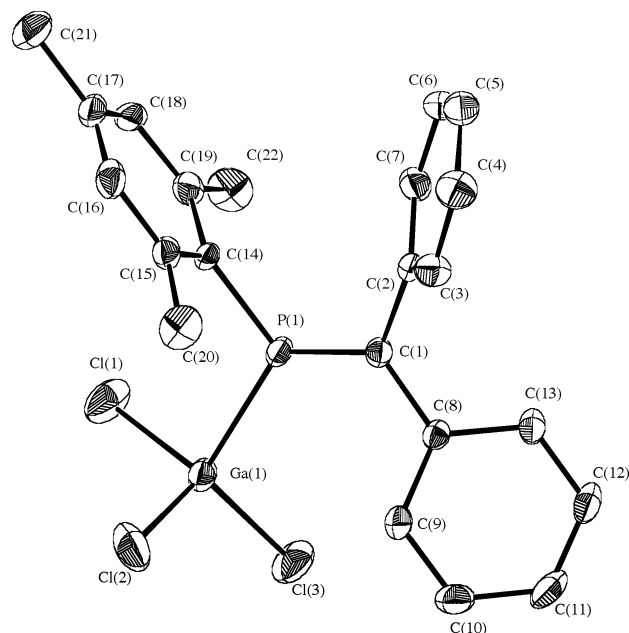
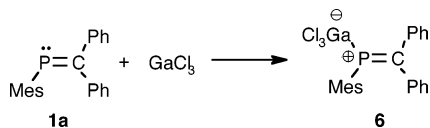


Figure 4. Molecular structure of **6** (50% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–C(1) = 1.687(3), P(1)–Ga(1) = 2.3938(7), P(1)–C(14) = 1.798(3); C(14)–P(1)–C(1) = 112.8(1), Ga(1)–P(1)–C(1) = 129.33(9), P(1)–C(1)–C(2) = 119.3(2), P(1)–C(1)–C(8) = 121.4(2).

warming to room temperature **3** (M = Ga) was formed quantitatively, confirming the intermediacy of **4** in the C–H activation reaction (Figure 3). Initially, we speculated that the intermediate might be phosphonium **4** (M = Ga); however, ^1H and ^{13}C NMR spectroscopy (including COSY) suggested that the intermediate was adduct **5** (M = Ga) (i.e. Chart 1; mode I). Convincing evidence for this assignment came from the observation of two inequivalent methylene hydrogens (δ 7.5 and 7.1; $^2J_{\text{HH}} = 8$ Hz) in the ^1H NMR spectrum and a doublet resonance at 148.7 ppm ($^1J_{\text{CP}} = 51$ Hz) in the ^{13}C NMR spectrum. This was consistent with retention of the P=CH₂ moiety in **5** (M = Ga).

The low-temperature reaction of **1b** with AlCl₃ was similarly observed to give the analogous adduct **5** (M = Al), which underwent C–H activation upon warming to room temperature. In particular, the ^{31}P NMR spectrum of **5** (M = Al) in CD₂Cl₂ (193 K) showed only a singlet resonance at 220.5 ppm. This species was also characterized using ^1H and ^{13}C NMR, and analogous to **5** (M = Ga), inequivalent methylene protons were observed and a ^{13}C signal at 152.0 assigned to the P=CH₂ moiety confirmed its identity as **5** (M = Al).

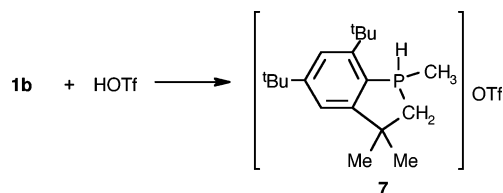
Neither species of **5** (M = Al, Ga) could be isolated to confirm their structures, since they were quantitatively converted to **3** when warmed to 213 K or above. However, when **1a** was treated with GaCl₃ (1 equiv), the only product observed was the adduct **6** (^{31}P NMR: δ 132), which was stable at room temperature and could be analyzed crystallographically. The molecular struc-



ture of **6** is shown in Figure 4. The P(1)–C(1) bond

length of 1.687(3) Å is comparable to the P=C bond length in the starting material **1a**, 1.693(3) Å,²⁷ consistent with significant multiple-bond character in **6**. To our knowledge, ^tBu(Cl₃Al)P=CH^tBu is the only related η^1 complex of a phosphaalkene to a main-group metal; however, that compound was not characterized crystallographically.^{11,32,33} In contrast, adducts with transition metals are quite common. For comparison, the P=C bond lengths found in (Ph₃P)₂PtP(Mes)=CPh₂ (1.65(1) Å)³⁴ and related Fe, Ni, and Cr phosphaalkene complexes^{34–39} are in the same range as that in **6**. Interestingly, **6** is stable under an inert atmosphere and there is no evidence for C–H activation of the *o*-Me groups. It is possible that the increased stability of **6** over **5** (M = Al, Ga) is a consequence of the steric bulk of the larger Mes* group and the absence of large C substituents in **5**, which effectively favors migration of GaCl₃ from P to C to generate the fleeting phosphonium **4**, which immediately undergoes C–H activation.

We still had only circumstantial evidence that phosphonium ions were involved in these reactions and thought that treating **1b** with triflic acid, another potential cationic initiator, may give us additional insight into the reaction mechanism. In this case, an analogous C–H activation reaction occurred, giving phosphonium salt **7** quantitatively from **1b** by ^{31}P NMR.



The product **7** was characterized crystallographically, and the molecular structure is shown in Figure 5. Of particular interest is that there is hydrogen bonding between the cation and the anion, as evidenced by a close H1–O3A contact (2.38(2) Å), which is within the sum of the van der Waals radii ($r_{\text{vdw}} = 2.70$ Å). We were unsuccessful in detecting intermediates by using VT NMR techniques, and even at -110 °C in CDCl₂F product **7** formed cleanly from **1b**. Nevertheless, the intermediacy of a fleeting phosphonium ion in the formation of **7** was confirmed by a deuterium labeling study. Treatment of **1b** with DOTf yields **7** exclusively

(32) Ga(III) adducts of heterocycles containing low-coordinate phosphorus atoms (i.e. 1,1'-diphosphaferrocene) are known, and a GaCl₂⁺-bridged [1]diphosphaferrocenophane has been structurally characterized. See, for example: Sava, X.; Melaimi, M.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *New J. Chem.* **2002**, *26*, 1378.

(33) The adduct H₃BP(Mes*)=CH₂ has been detected spectroscopically as an intermediate in the hydroboration of **1b** with excess BH₃·THF. See: Yoshifuji, M.; Takahashi, H.; Toyota, K. *Heteroat. Chem.* **1999**, *10*, 187.

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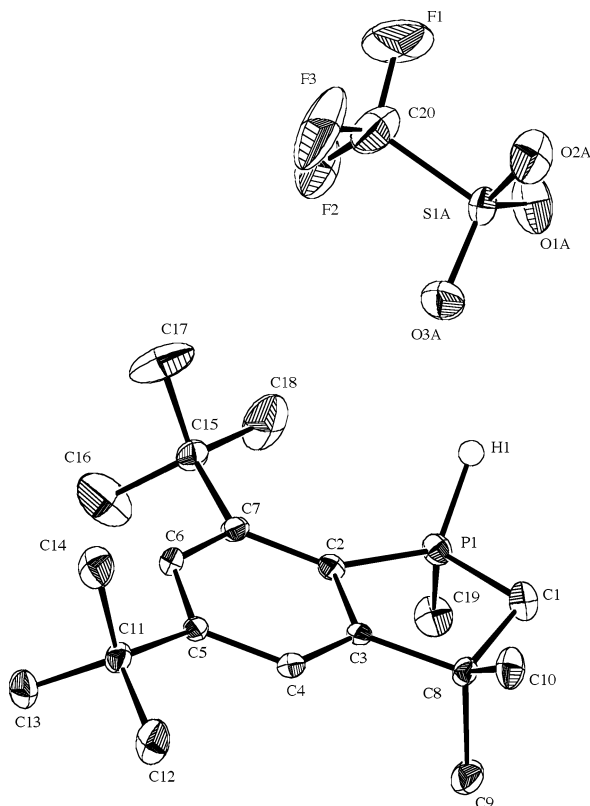


Figure 5. Molecular structure of **7** (50% probability ellipsoids). All hydrogen atoms except H1 are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–C(19) = 1.782(2), P(1)–C(1) = 1.803(3), P(1)–C(2) = 1.803(2); C(2)–P(1)–C(1) = 95.42(11), C(2)–P(1)–C(19) = 114.43(11), C(19)–P(1)–C(1) = 111.49(12).

with a $-\text{CH}_2\text{D}$ substituent and no evidence for a P–D bond in the product, as determined using NMR spectroscopy. Therefore, even if deuterium initially reacts at phosphorus to form an adduct, it must migrate to carbon, forming a phosphonium ion prior to C–H activation. Otherwise, the product **7** would possess both P–H and P–D bonds.

In this section, we have provided strong evidence that the mechanism of reaction of **2** with Lewis acids involves initial formation of adduct **5**, followed by GaCl_3 migration from P to C to form the fleeting phosphonium **4**, which rapidly undergoes C–H activation. In the case of triflic acid, a phosphonium ion must also be involved in the reaction; however, although it is unlikely, it is not clear whether $[\text{Mes}^*\text{HP}=\text{CH}_2]^+$ is also involved. With this encouraging evidence for phosphonium ion formation from **1b**, we set out to find conditions where intermolecular reaction (i.e. **4** + **1b**) could be favored over intramolecular C–H activation (i.e. **3**).

GaCl_3 -Initiated Linear Dimerization of a Phosphaalkene. We postulated that, if very concentrated solutions of monomer **1b** and substoichiometric quantities of electrophile were used, intermolecular addition of **4** to **1b** (i.e. chain growth) might be favored over intramolecular C–H activation. Thus, phosphaalkene **1b** in CH_2Cl_2 (ca. 1 M) was treated with GaCl_3 (0.5 equiv) at -40°C and warmed to room temperature. Interestingly, the ^{31}P NMR spectrum of the reaction mixture revealed a new compound that showed doublets at -72.3 and -92.6 ppm with a large coupling constant ($^1J_{\text{PP}} = 245$ Hz). These data were consistent with the

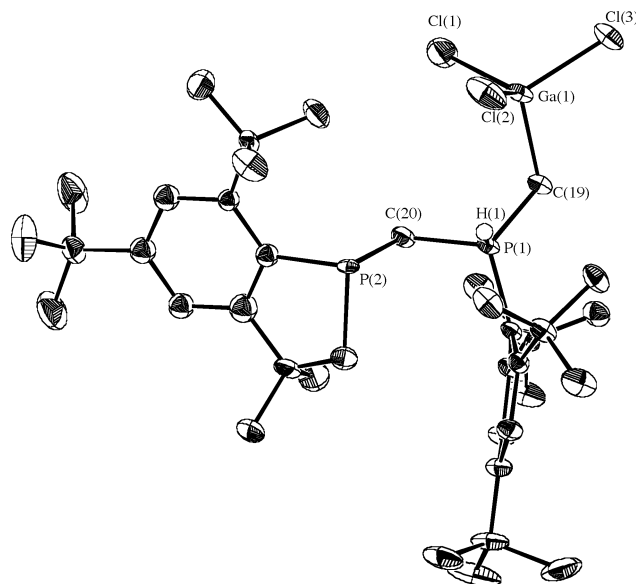
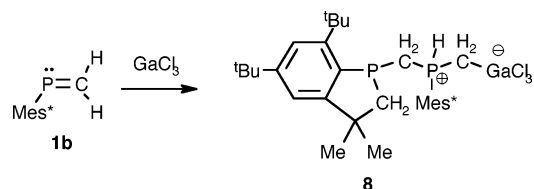


Figure 6. Molecular structure of **8** (50% probability ellipsoids). All hydrogen atoms except H(1) are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)–C(19) = 1.776(2), P(2)–C(20) = 1.919(9), P(1)–C(20) = 1.815(3), P(1)–H(1) = 1.31(2), Ga(1)–C(19) = 1.990(2); C(19)–P(1)–C(20) = 114.07(11), Ga(1)–C(19)–P(1) = 115.89(14), C(20)–P(2)–C(21) = 100.4(4), P(1)–C(20)–P(2) = 110.1(2).

formation of a dimeric species; however, the coupling constant was too large to be a P–C–P–C linkage and suggested a direct P–P bond. The only other compounds present in the crude reaction mixture were unreacted **1b** (δ 289) and zwitterionic phosphonium **3** ($M = \text{Ga}$) (δ 16.4).

Over the few hours necessary to separate **1b** and **3** ($M = \text{Ga}$) from the dimeric intermediate mentioned above, the intermediate was transformed quantitatively to a new isolable compound. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution. The molecular structure is shown in Figure 6 and confirms its identity as a linear dimer coordinated to GaCl_3 (**8**). No analogous compounds with

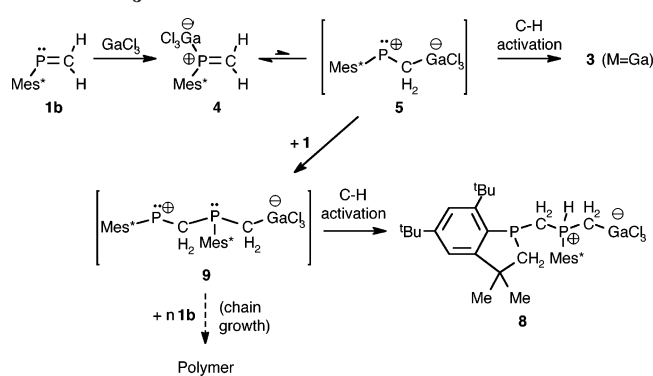


such a P–C–P–C–Ga backbone have previously been characterized. The P–C–P bond angle in **8** (P(1)–C(20)–P(2) = 110.1(2) $^\circ$) is slightly widened with respect to less sterically hindered bis(diphenylphosphino)methane (106.2(3) $^\circ$).⁴⁰ However, the P–C–P angle in **8** is significantly smaller than the very bulky $\text{Cy}_2\text{PCH}_2\text{-PCy}_2$ (120.5(1) $^\circ$),^{41,42} suggesting that the steric nature of **8** is intermediate between $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Cy}_2\text{-}$

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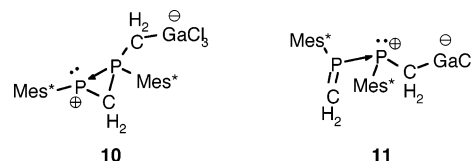
Scheme 3. Proposed Mechanism for the GaCl₃-Initiated Linear Dimerization of **1b**


PCH₂PCy₂. The Ga(1)–C(19) bond length of 1.990(2) Å is comparable to that of compound **3** (M = Ga) (1.994(3) Å). The P–C bond lengths in **8** (average 1.836(9) Å) are typical of P–C single bonds and are close to those in dppm (1.848(5) Å)⁴⁰ and differ only slightly from that in Cy₂PCH₂PCy₂ (1.858 Å).^{41,42}

Presumably, this product results from the termination of growing chain **9** by C–H activation of the *o*-^tBu group (Scheme 3). Interestingly, the phosphonium hydrogen atom in **8** was found bound to P(1) rather than P(2). Compound **8** was fully characterized by ³¹P and ¹H NMR spectroscopy (¹J_{PH} = 490 Hz; ²J_{PP} = 90 Hz). Although [2 + 2] cycloaddition reactions of phosphaalkenes forming diphosphetaines are quite common,^{2a,b} to our knowledge, the linear dimerization of a phosphaalkene has not been observed previously.⁴³ Furthermore, the formation of **8** from **1b** and GaCl₃ represents a proof of concept for the potential use of cationic species to initiate the polymerization of phosphaalkenes.

Mechanism of Linear Dimerization: Evidence for Diphosphiranium Ions and Phosphaalkene–Phosphenium Adducts. On the basis of our studies of the mechanism of formation for **3** described above, and the mechanism of cationic polymerization for olefins,⁴⁴ we propose that this reaction follows the addition mechanism outlined in Scheme 3. However, the ³¹P NMR data for the intermediate species mentioned above (δ –72.3, –92.6; ¹J_{PP} = 245 Hz) are not consistent with any of the species in Scheme 3 and suggest that the mechanism of formation for **8** is slightly more complicated. It is well known that phosphenium ions can behave as Lewis acid acceptors toward phosphorus donors, forming phosphanyl–phosphenium ions.^{16,45–47} Since intermediate **9** contains both a phosphenium moiety and a phosphine, we postulate that the spectroscopically detected intermediate could be the intramolecular donor–acceptor complex **10**, although the phos-

phaalkene–phosphenium complex **11** is also a possibility.



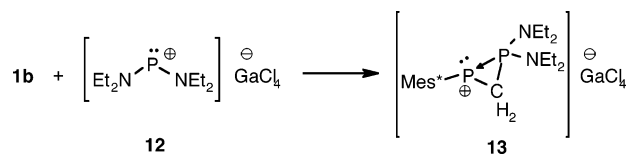
We favored structure **10** on the basis of the observed ³¹P chemical shifts (–72.3 and –92.6 ppm), which were shifted upfield from that predicted for the P=C moiety in **11** (>100 ppm). Moreover, recently the analogous diphosphiranium heterocycle [Mes*(Me)PCH₂PMes*]–

OTf was prepared from the reaction of Mes*PCH₂PMes* with excess MeOTf and has been characterized in solution at low temperature (³¹P NMR: δ –80.5 and –95.4; ¹J_{PP} = 261 Hz).⁴⁸

Diphosphiranium zwitterion **10** may be viewed as an intramolecularly stabilized phosphenium ion that ring opens to **9** and, subsequently, rapidly undergoes C–H activation, forming **8** (Scheme 3). From the perspective of a cationic polymerization, this type of reversible stabilization at the phosphenium end of a growing chain may slow propagation and, in the absence of C–H activation, lead to a novel controlled polymerization.⁴⁹ The preparation of diphosphiranium (P₂CR₅)⁺ rings is an area of growing interest,^{50–52} and compound **10** is a

rare example of a (R₂PCR₂PR)⁺ heterocycle.⁴⁸ Furthermore, we are not aware of any previous report of the formation of a diphosphiranium ring from the reaction of phosphenium cations with P=C bonds. It has been reported that one of the products of the reaction of a phosphenium ion and an iminophosphine was a three-membered (P₂N)⁺ ring similar to **10**.^{53,54} Moreover, it is well-known that alkynes react with RPCl₂–AlCl₃ complexes to yield phosphirenium salts.⁵⁰ Significantly, recent work on the reversible exchange of free alkynes with coordinated alkyne in MePhPCRCR' ions has implicated a transient phosphenium ion (MePPh)⁺ as an intermediate after dissociation of RC≡CR'.⁵⁵

We have explored the potential synthetic utility of this novel method to prepare diphosphiranium rings. Treatment of **1b** with **12**⁵⁶ in CD₂Cl₂ at –80 °C successfully formed diphosphiranium **13** (³¹P NMR: δ 17.7, –81.6; ¹J_{PP} = 225 Hz). The results of ³¹P–¹H HSQC NMR



experiments allowed for the estimation of the ¹H chemical shift of the ring-CH₂ moiety at 2.2–2.3 ppm and a ²J_{PH} value of ca. 40–50 Hz. Although diphosphiranium

(43) Recently, the ambient-temperature oligomerization of iminophosphines (RN=PX; R = Dipp, X = Cl) using GaCl₃ has been reported to give cyclic dimeric and trimeric species. See: Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylshen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012.

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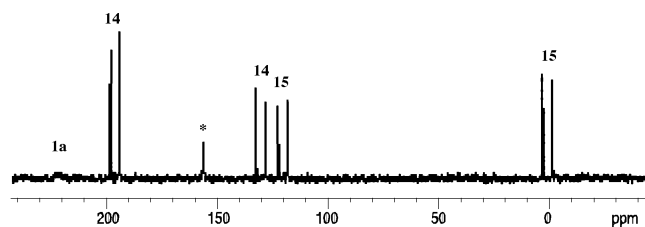
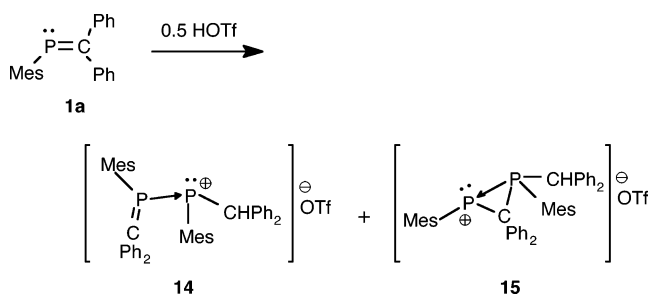


Figure 7. ^{31}P NMR spectrum (CD_2Cl_2 ; 298 K) of the reaction mixture after phosphalkene **1a** was treated with HOTf (0.5 equiv). The peak marked with an asterisk is tentatively assigned to $\text{MesP}(\text{OTf})\text{CHPh}_2$.

13 was formed reasonably cleanly from **1b** and **12** at -80°C , it was not formed quantitatively and is unstable at room temperature.

Due to the fascinating linear dimerization of **1b** initiated by a cationic initiator (i.e. GaCl_3), it seemed that the logical next step would be to investigate the reaction of **1a** and HOTf to see if a similar linear oligomerization would occur (recall that **1a** + GaCl_3 gives stable **6**). We rationalized that the *o*- CH_3 groups of the Mes substituent in **1a** would not undergo C–H activation, which effectively terminates chain growth with **1b**. The ^{31}P NMR spectrum of the reaction mixture when phosphalkene **1b** was treated with HOTf (0.5 equiv) is shown in Figure 7. Significantly, two sets of doublets with coupling constants greater than 500 Hz in an approximate 1:1 ratio are observed. Confirmation that this was P–P coupling rather than P–H coupling was obtained from $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P – ^{31}P COSY experiments. We speculate that these signals result from the unprecedented donor–acceptor adduct **14** (δ 196.4 and 130.5; $^1J_{\text{PP}} = 509$ Hz) and diphosphiranium cation **15** (δ 120.3 and 0.2; $^1J_{\text{PP}} = 516$ Hz). We speculate that the signals at 196.4 and 0.2 ppm are due to the P=C in **14** and the phosphine moiety in **15**, respectively. $^1\text{H}\{^{31}\text{P}\}$



NMR selective decoupling experiments on the proton signal from the CHPh_2 moieties in **14** and **15** are also consistent with this assignment. An additional minor singlet resonance at 155 ppm in the ^{31}P NMR spectrum was observed, which we tentatively assign to the phosphonium triflate $[\text{MesP}(\text{OTf})\text{CHPh}_2]^+$. These species are stable in solution for several days at room temperature, and after solvent removal a red oil is obtained. Thus far, we have been unsuccessful in obtaining crystals suitable for X-ray diffraction from this mixture. Until

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such a time, the proposal of compounds **14** and **15**, although consistent with NMR observations, remains tentative.

Cationic Linear Oligomerization of 1b Initiated by HOTf. On the basis of the results described thus far, triflic acid appears to be a more effective activator of the P=C bond than Lewis acids, since the latter tend to form η^1 complexes through phosphorus. Therefore, we attempted to prepare higher oligomers by treating a concentrated CH_2Cl_2 solution of **1b** with triflic acid (0.39 equiv). A complex ^{31}P NMR spectrum was observed, displaying many multiplets due to P–P coupling (range -50 to 50 ppm) in addition to dominant signals for **1b** and **7**. Although we were unsuccessful in separating these products, we observed ions consistent with the phosphonium cation $(\text{Mes}^*\text{PCH}_2)_n\text{H}^+$ in the oligomers $(\text{Mes}^*\text{PCH}_2)_n\text{H}^+\text{OTf}^-$ ($n = 2$ – 6) using electrospray mass spectrometry. These ES-MS results, although preliminary, are important, since they suggest that it may be possible to polymerize phosphalkenes using cationic initiators if the right initiator and monomer are chosen.

Summary

We have conducted a thorough investigation of the reactions of electrophiles and phosphalkenes in order to demonstrate the feasibility of cationic polymerization for phosphalkenes. In particular, we have demonstrated that Lewis or protic acids can add across the P=C bond, generating highly reactive phosphonium ions: the first step in a putative cationic polymerization. In the case of the reaction of Lewis acids (MCl_3 ; M = Al, Ga) with **1b**, the transient phosphonium (**4**) undergoes intramolecular C–H activation to give **3**. Significantly, we have shown that, at high concentrations of monomer **1b** in CH_2Cl_2 , GaCl_3 initiates a linear dimerization to afford **8** following a cationic chain growth mechanism. We have identified the diphosphiranium zwitterion **10** spectroscopically as an intermediate in this reaction. Interestingly, the addition of phosphonium ions to phosphalkenes appears to be a general route to $(\text{P}_2\text{C})^+$ cycles, and we have prepared several novel rings using this method (i.e. **10**, **13**, and **15**). Finally, we provide MS evidence that oligomers containing up to six repeat units can be generated from the addition of HOTf to **1b**. We hope that these studies will form the basis for the future development of cationic polymerization for P=C bonds.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive compounds were performed under prepurified nitrogen (Praxair, 99.998%) using standard high-vacuum or Schlenk techniques or in an Innovative Technology Inc. glovebox. ^1H , ^{31}P , and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported relative to the following: CHCl_3 or HC_6D_5 (δ 7.24 and 7.15 for ^1H); 85% H_3PO_4 as an external standard (δ 0.0 for ^{31}P); CDCl_3 or C_6D_6 (δ 77.0 and 128.0 for ^{13}C). NMR assignments were made with the aid of multidimensional NMR techniques.

Materials. Hexanes, dichloromethane, and toluene were dried by passing through activated alumina columns.⁵⁷ Tet-

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rahydrofuran was distilled from sodium/benzophenone immediately prior to use; CDCl_3 (CIL) was distilled from P_2O_5 and degassed. CD_2Cl_2 (CIL) was purchased in ampules and used as received. GaCl_3 and AlCl_3 were purchased from Aldrich and sublimed prior to use. HOTf was freshly distilled prior to use, while DOTf was used as received. $\text{Mes}^*\text{PH}_2^{58}$ and **1a**⁵⁹ were prepared by following the literature procedures. The KOH used in the preparation of **1a** was made anhydrous by recrystallization from EtOH.⁶⁰

Preparation of 1b. This compound was prepared by following a modification to the original literature procedure.^{24,61} A solution of Mes^*PH_2 (10.0 g, 0.0359 mol) and finely ground undried 85% KOH (15 g, ≥ 0.23 mol) was stirred at room temperature in CH_2Cl_2 (200 mL). When the reaction was complete as determined by ³¹P NMR spectroscopy (ca. 7 days), the solvent was removed in vacuo, the solid was dissolved in hexanes (300 mL), and this solution was filtered through a Celite to remove KOH. The solvent was removed from the filtrate in vacuo, affording a pale yellow powder. The crude product was recrystallized from a minimal amount of toluene/ CH_3CN (9:1) to give light yellow crystals. Yield: 6.20 g (59%).

³¹P NMR (CDCl_3 , 300 K): δ 289.5 (t, $^2J_{\text{PH}} = 31$ Hz). ¹H NMR (CDCl_3 , 300 K): δ 7.60 (s, 2H, *m-H*), 7.02 (dd, $^2J_{\text{PH}} = 33$ Hz, $^2J_{\text{HH}} = 5$ Hz, 1H, *P=CH*), 6.73 (dd, $^2J_{\text{PH}} = 28$, $^2J_{\text{HH}} = 5$ Hz, 1H, *P=CH*), 1.60 (s, 18H, *o-C(CH_3)_3*), 1.30 (s, 9H, *p-C(CH_3)_3*). MS (EI): *m/z* [%] 290 [9, M^+], 275 [13, $\text{M}^+ - \text{CH}_3$]. Anal. Calcd for $\text{C}_{19}\text{H}_{31}\text{P}$: C, 78.58; H, 10.75. Found: C, 78.68; H, 10.77.

Preparation of C–H Activation Product 3 (M = Ga). A solution of GaCl_3 (0.303 g, 1.72 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of **1b** (0.500 g, 1.72 mmol) in CH_2Cl_2 (40 mL) at 20 °C. ³¹P NMR analysis showed quantitative conversion of **1b** to a new product. The reaction mixture was stirred for several hours, and the solvent was removed in vacuo to give a colorless powder. The product was recrystallized by slow evaporation of a concentrated CH_3CN solution to yield crystals suitable for X-ray diffraction. Yield: 0.650 g (81%).

³¹P NMR (CDCl_3 , 300 K): δ 16.4 ppm (d, $^1J_{\text{PH}} = 498$ Hz). ¹H NMR (CDCl_3 , 300 K): δ 7.60 (d, $^4J_{\text{HP}} = 6$ Hz, 1H, *m-H*), 7.4 (dm, $^1J_{\text{HP}} = 498$ Hz, 1H, *PH*), 7.28 (s, 1H, *m-H*), 2.84 (dd, $^2J_{\text{HP}} = 11$ Hz, $^3J_{\text{HH}} = 5$ Hz, 2H, *PCH_2C(CH_3)_2*), 1.93 (m, 2H, *PCH_2Ga*), 1.51 (s, 6H, *C(CH_3)_2*), 1.48 (s, 9H, *o-C(CH_3)_3*), 1.34 (s, 9H, *p-C(CH_3)_3*). Anal. Calcd for $\text{C}_{19}\text{H}_{31}\text{Cl}_3\text{GaP}$: C, 48.92; H, 6.70; Cl, 22.80. Found: C, 49.09; H, 6.90; Cl, 22.83.

Preparation of C–H Activation Product 2 (M = Al). Under an inert atmosphere, AlCl_3 (0.046 g, 0.34 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of **1b** (0.100 g, 0.34 mmol) in CH_2Cl_2 (10 mL) at 25 °C. After the mixture was stirred for 1/2 h, the solvent was removed in vacuo, yielding a pale yellow powder. The product was recrystallized from CH_3CN to obtain colorless crystals. The crystals were further washed with hexanes. Yield: 0.110 g (76%). This compound is not stable and decomposes after ca. 1 week in the solid state under N_2 (see text for a discussion of the decomposition product).

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(60) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, U.K., 1996. To dry KOH we follow the procedure for drying NaOH on p 429.

(61) Appel's procedure for **1b** uses dry, powdered KOH; however, a drying procedure was not provided. We have found that anhydrous, powdered KOH (recrystallization from EtOH and subsequent heating) contains a trace of KOEt impurity. The presence of this impurity led to the formation of $\text{Mes}^*\text{P}(\text{OEt})\text{CH}_3$, which was difficult to separate from **1b**. We have found that finely ground "wet" KOH pellets yield **1b** free from impurities, although longer reaction times are necessary (several days rather than several hours). Characterization data for $\text{Mes}^*\text{P}(\text{OEt})\text{CH}_3$ are as follows. ³¹P{¹H} NMR: δ 110 (s). ¹H NMR: δ 7.58 (d, $^4J_{\text{PH}} = 4$ Hz, 2H, *m-Ar*), 3.70 (mult, 2H, POCH_2CH_3), 1.68 (s, 18H, *o*-^tBu), 1.40 (d, $^2J_{\text{PH}} = 9$ Hz, 3H, PCH_3), 1.35 (s, 9H, *p*-^tBu), 1.10 (t, POCH_2CH_3).

³¹P NMR (CDCl_3 , 300 K): δ 16.9 ppm (d, $^1J_{\text{PH}} = 488$ Hz). ¹H NMR (CDCl_3 , 300 K): δ 7.62 (d, 1H), 7.20 (dm, $^1J_{\text{HP}} = 488$ Hz, 1H, *PH*), 7.27 (s, 1H, *m-H*), 2.77 (dd, $^2J_{\text{HP}} = 11$ Hz, $^3J_{\text{HH}} = 5$ Hz, 2H, *PCH_2C(CH_3)_2*), 2.37 (m, 2H, *PCH_2Al*), 1.52 (s, 6H, *C(CH_3)_2*), 1.49 (s, 9H, *o-C(CH_3)_3*), 1.35 (s, 9H, *p-C(CH_3)_3*).

NMR-Scale Preparation of Intermediate 5 (M = Ga). To an NMR tube charged with $\text{Mes}^*\text{P}=\text{CH}_2$ (**1b**; 25.0 mg, 0.09 mmol) in CD_2Cl_2 (0.5 mL) and cooled to 163 K was added a solution of GaCl_3 (15 mg, 0.09 mmol) in CD_2Cl_2 (0.5 mL) by syringe. The contents of the NMR tube were carefully shaken at 193 K until the solids dissolved. The NMR tube was introduced into the NMR spectrometer that had been precooled to 193 K.

³¹P NMR (CD_2Cl_2 , 193 K): δ 208.9. ¹H NMR (CD_2Cl_2 , 193 K): δ 7.5 (s, 2H, *m-H*), 7.5 (d, $^2J_{\text{HH}} = 8$ Hz, 1H, *P=CH*), 7.1 (dd, $^2J_{\text{HH}} = 8$ Hz, $^2J_{\text{PH}} = 33$ Hz, 1H, *P=CH*), 1.5 (s, 18H, *o-C(CH_3)_3*), 1.3 (s, 9H, *p-C(CH_3)_3*). ¹³C NMR (CD_2Cl_2 , 193 K): δ 156.4 (s, *o-Ar*), 155.0 (s, *p-Ar*), 148.7 (d, $^1J_{\text{CP}} = 51$ Hz, *P=CH_2*), 123.3 (d, $^3J_{\text{CP}} = 8$ Hz, *m-Ar*), 117.5 (d, $^1J_{\text{CP}} = 14$ Hz, *i-Ar*), 37.5 (s, *o-CMe_3*), 34.9 (s, *p-CMe_3*), 33.0 (s, *o-C(CH_3)_3*), 30.1 (s, *p-C(CH_3)_3*).

NMR-Scale Preparation of Intermediate 5 (M = Al). To an NMR tube charged with $\text{Mes}^*\text{P}=\text{CH}_2$ (**1b**; 25.0 mg, 0.09 mmol) in CD_2Cl_2 (0.5 mL) and cooled to 163 K, a solution of AlCl_3 (12 mg, 0.09 mmol) in CD_2Cl_2 (0.5 mL) was added by syringe. The contents of the NMR tube were carefully shaken to ensure rapid mixing and were kept at 193 K. Then the NMR tube was introduced into the NMR instrument equipped with a low-temperature unit, and the experiments were run at 193 K.

³¹P NMR (CD_2Cl_2 , 193 K): δ 220.5. ¹H NMR (CD_2Cl_2 , 193 K): δ 7.5 (d, $^4J_{\text{PH}} = 3$ Hz, 2H, *m-H*), 7.4 (dd, $^2J_{\text{HH}} = 7$ Hz, $^2J_{\text{PH}} = 13$ Hz, 1H, *P=CH*), 7.0 (dd, $^2J_{\text{HH}} = 8$ Hz, $^2J_{\text{PH}} = 32$ Hz, 1H, *P=CH*), 1.5 (s, 18H, *o-C(CH_3)_3*), 1.3 (s, 9H, *p-C(CH_3)_3*). ¹³C NMR (CD_2Cl_2 , 193 K): δ 155.6 (s, *o-Ar*), 153.6 (s, *p-Ar*), 152.0 (br, *P=CH_2*), 124.1 (s, *m-Ar*) (*i-Ar* not observed), 37.7 (s, *o-CMe_3*), 34.9 (s, *p-CMe_3*), 33.4 (s, *o-C(CH_3)_3*), 30.5 (s, *p-C(CH_3)_3*).

Preparation of Adduct 6. To a stirred solution of **1a** (0.490 g, 1.55 mmol) in 20 mL of CH_2Cl_2 at room temperature was added dropwise GaCl_3 (0.290 g, 1.7 mmol) in 10 mL of CH_2Cl_2 . The mixture was checked by NMR (³¹P: 132 ppm). The product is stable in CH_2Cl_2 at room temperature indefinitely. The product was recrystallized from CH_2Cl_2 /pentane solution to obtain single crystals suitable for X-ray diffraction. Yield: 0.65 g (85%).

³¹P NMR (CDCl_3 , 300 K): δ 132 (s). ¹H NMR (CDCl_3 , 300 K): δ 7.03–7.64 (m, 10H, aryl *H*), 6.96 (d, $^4J_{\text{PH}} = 3$ Hz, 2H, *Mes H*), 2.53 (d, $^4J_{\text{PH}} = 2$ Hz, 6H, *o-CH_3*), 2.28 (s, 3H, *p-CH_3*). ¹³C NMR (CDCl_3 , 300 K): δ 193.0 (d, $^1J_{\text{PC}} = 36$ Hz, *P=C*), 143.5–121.9 (m, aryl *C*), 23.4 (s, *o-CH_3*), 21.5 (s, *p-CH_3*).

Preparation of C–H Activation Product 7. Freshly distilled HOTf (0.284 g, 1.89 mmol) was added to a stirred solution of **1b** (0.500 g, 1.72 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for ca. 30 min, and the solvent was removed in vacuo. The white solid obtained was recrystallized from a minimum amount of CH_3CN /toluene (3:1) at –40 °C. Yield: 0.45 g (59%).

³¹P NMR (CDCl_3 , 300 K): δ 13.6 ppm (d, $^1J_{\text{PH}} = 539$ Hz). ¹H NMR (CDCl_3 , 300 K): δ 7.84 (dqdd, $^1J_{\text{HP}} = 538$ Hz, $^3J_{\text{HH}} = 5$ Hz (to CH_3), $^3J_{\text{HH}} = 5$ and 2 Hz (to CH_2), 1H, *P-H*), 7.55 (d, $^4J_{\text{HP}} = 6$ Hz, 1H, *m-H*), 7.20 (s, 1H, *m-H*), 2.95 (dm, $^2J_{\text{HP}} = 16$ Hz, 1H, 1H in *PCH_2*), 2.68 (dm, $^2J_{\text{HP}} = 14$ Hz, 1H, 1H in *PCH_2*), 2.30 (dd, $^2J_{\text{HP}} = 15$ Hz, $^3J_{\text{HH}} = 5$ Hz, 3H, CH_3), 1.49 (s, 6H, *C(CH_3)_2*), 1.42 (s, 9H, *o*-^tBu), 1.29 (s, 9H, *p*-^tBu). ¹⁹F NMR (CDCl_3 , 300 K): δ –78.9 ppm (s, OTf).

Preparation of Linear Dimer 8. To a stirred solution of **1b** (1.50 g, 5.16 mmol) in a minimal amount of CH_2Cl_2 (5 mL) at –40 °C was added a saturated solution of GaCl_3 (0.45 g, 2.58 mmol) in CH_2Cl_2 (ca. 2 mL), and the mixture was warmed to room temperature over ca. 1 h. ³¹P NMR analysis of the

Table 1. Details of Crystal Structure Determinations of **1b**, **3** (M = Ga), **6**, **7**, and **8**

	1b	3 (M = Ga)	6	7	8
formula	C ₁₉ H ₃₁ P	C ₁₉ H ₃₁ PCl ₃ Ga	C ₂₂ H ₂₁ PCl ₃ Ga	C ₂₀ H ₃₂ O ₃ F ₃ PS	C ₃₈ H ₆₂ P ₂ GaCl ₃
fw	290.43	466.51	492.46	440.50	756.93
cryst syst	orthorhombic	triclinic	triclinic	monoclinic	triclinic
space group	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P2</i> ₁ / <i>n</i>	<i>P</i> $\bar{1}$
color	colorless	colorless	yellow	colorless	colorless
<i>a</i> (Å)	18.865(3)	10.0454(6)	9.882(1)	15.515(1)	9.8363(4)
<i>b</i> (Å)	15.809(1)	11.0240(7)	10.263(2)	9.5822(5)	11.1839(5)
<i>c</i> (Å)	6.1010(4)	11.1410(9)	12.204(2)	15.143(1)	18.9750(8)
α (deg)	90	94.935(4)	108.054(5)	90	87.698(6)
β (deg)	90	112.222(3)	94.760(3)	92.118(4)	81.603(5)
γ (deg)	90	94.093(2)	103.022(4)	90	85.666(5)
<i>V</i> (Å ³)	1820(1)	1130.6(1)	1130.8(2)	2249.8(2)	2058.2(2)
<i>Z</i>	4	2	2	4	2
<i>T</i> (K)	173(1)	173(1)	173(1)	173(1)	173(1)
μ (Mo K α) (cm ⁻¹)	1.42	16.41	16.46	2.57	9.64
cryst size (mm)	0.50 × 0.30 × 0.20	0.25 × 0.10 × 0.05	0.23 × 0.12 × 0.08	0.40 × 0.25 × 0.10	0.20 × 0.20 × 0.10
calcd density (Mg m ⁻³)	1.060	1.370	1.446	1.300	1.22
2 θ (max) (deg)	50.1	55.8	55.8	55.8	55.8
no. of rflns	13 855	10 364	9381	20 436	19 332
no. of unique data	1894	4599	4618	5130	8464
<i>R</i> (int)	0.062	0.043	0.039	0.062	0.044
rfln/param ratio	16.06	19.32	18.92	17.20	16.50
<i>R</i> 1 ^a	0.043; <i>I</i> > 3 σ (<i>I</i>)	0.037; <i>I</i> > 2 σ (<i>I</i>)	0.037; <i>I</i> > 3 σ (<i>I</i>)	0.050; <i>I</i> > 2 σ (<i>I</i>)	0.039; <i>I</i> > 2 σ (<i>I</i>)
wR2 (all data) ^b	0.110	0.092	0.093	0.136	0.098
GOF	1.20	1.07	1.25	0.95	0.95

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum (F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

reaction mixture showed signals for **1b**, **3** (M = Ga), and a new product with doublets at -72.3 ($^1J_{PP} = 245$ Hz) and -92.6 ($^1J_{PP} = 245$ Hz) ppm (a $^{31}P-^{31}P$ COSY experiment confirmed the coupling). GaCl₃ (ca. 0.6 mmol total in several steps) in CH₂Cl₂ was added, and the reaction was monitored by ^{31}P NMR, until **1b** was entirely converted to **3** (M = Ga). The solvent was removed in vacuo, and the colorless solid residue was extracted with hexanes (ca. 2 × 30 mL) to remove **3** (M = Ga). During this process the signals at -72.3 and -92.6 ppm slowly converted to compound **8**. Yield: 0.30 g (15%).

^{31}P NMR (CDCl₃, 300 K): isomer 1, δ 3.5 (dd, $^1J_{HP} = 490$, $^2J_{PP} = 95$ Hz, P(1)), -9.4 (d, $^2J_{PP} = 95$ Hz, P(2)); isomer 2, 1.6 (dd, $^1J_{HP} = 490$ Hz, $^2J_{PP} = 90$ Hz, P(1)), -8.9 (d, $^2J_{PP} = 90$ Hz, P(2)). 1H NMR (CDCl₃, 300 K): δ 7.59, 7.45 (isomer 1/2, dm, $^1J_{PH} = 490$ Hz, 1H, *PH*), 7.63–7.52 (br, 1H, *m-H*), 7.26 (d, $^4J_{PH} = 5$ Hz, 1H, *m-H*), 6.97 (d, $^4J_{PH} = 5$ Hz, 2H, *m-H*), 2.66 (dm, $^2J_{PH} = 13$ Hz, 2H, PCH₂(CH₃)₂), 2.37 (dd, $^2J_{PH} = 37$ Hz, $^2J_{PH} = 15$ Hz, 2H, PCH₂P), 1.98 (m, 2H, PCH₂GaCl₃), 1.65, 1.63 (isomer 1/2, s, 6H, C(CH₃)₂), 1.48 (s, 9H, *o*-C(CH₃)₃), 1.45 (s, 9H, *o*-C(CH₃)₃), 1.35 (s, 9H, *p*-C(CH₃)₃), 1.34 (s, 9H, *p*-C(CH₃)₃), 1.27 (s, 18H, *p*-C(CH₃)₃).

Synthesis of [(Et₂N)₂P]GaCl₄ (12**).**⁵⁶ To neat (Et₂N)₂PCl (20 mg, 0.095 mmol) at -78 °C was slowly added GaCl₃ (17 mg, 0.096 mmol) in CD₂Cl₂ (0.2 mL). The compound was not isolated, but the ^{31}P NMR spectrum showed that the (Et₂N)₂-PCl was consumed and **12** was formed quantitatively.

^{31}P NMR (CD₂Cl₂, 300 K): δ 245 ppm (s). 1H NMR (CD₂Cl₂, 300 K): δ 3.67 (m, 8H, (CH₃CH₂)₂N₂P⁺), 1.36 (t, $^3J_{HH} = 7$ Hz, 12H, (CH₃CH₂)₂N₂P⁺). ^{13}C NMR (CD₂Cl₂, 300 K): δ 46.5 (d, $^2J_{PC} = 58$ Hz, (CH₃CH₂)₂N₂P⁺), 14.8 (d, $^3J_{PC} = 13$ Hz, (CH₃-CH₂)₂N₂P⁺).

Preparation of the Diphosphiranium **13.** To the freshly prepared solution of **12** (see above) in CD₂Cl₂ at -78 °C in an NMR tube was slowly added a solution of **1a** (0.028 g, 0.096 mmol) in CD₂Cl₂ (0.3 mL). NMR analysis of the reaction mixture showed partial, but clean, conversion (ca. 30%) to **13**.

^{31}P NMR (CD₂Cl₂, 293 K): δ 17.7 (d, $^1J_{PP} = 225$ Hz), -81.6 (d, $^1J_{PP} = 225$ Hz). $^{31}P-^1H$ HSQC experiments show strong cross signals between both the ^{31}P NMR signals and a broad signal at 2.2–2.3 ppm in the 1H NMR spectrum. This was assigned to the ring CH₂ moiety.

Preparation of the Adduct **14 and the Diphosphiranium Ring **15**.** To a solution of **1a** (0.25 g, 0.79 mmol) in CH₂-Cl₂ (5 mL) was added dropwise HOTf (0.059 g, 0.39 mmol) in CH₂Cl₂ (5 mL) over ca. 10 min at room temperature. ^{31}P NMR (CDCl₃, 300 K) showed the clean formation of two major products from this reaction in an approximate 1:1 ratio. The solvent was removed in vacuo, and attempts to obtain crystals from the oily red residue using CH₂Cl₂/hexanes, CH₃CN, and 1,2-Cl₂C₂H₄ have thus far proven unsuccessful.

Assignments are tentative. ^{31}P NMR: **14**, δ 196.4 (d, $^1J_{PP} = 509$ Hz), 130.5 (d, $^1J_{PP} = 509$ Hz); **15**, δ 120.3 (d, $^1J_{PP} = 516$ Hz), 0.2 (d, $^1J_{PP} = 516$ Hz). 1H NMR (CDCl₃, 300 K): two types of CH moiety corresponding to **14**, δ 5.35 ppm (d, $^2J_{PH} = 16.8$ Hz, $^3J_{PH}$ was not observed); **15**, δ 5.50 ppm (dd, $^2J_{PH} = 14.6$ Hz, $^3J_{PH} = 4.1$ Hz). $^1H\{^{31}P\}$ selective decoupling experiments suggest that in **14** the 16.8 Hz coupling is to the ^{31}P signal at 130.5 ppm, while the same experiment shows that in **15** the 14.6 Hz coupling is to the ^{31}P signal at 0.2 ppm.

Oligomerization of Mes*P=CH₂ Initiated by HOTf. To a stirred solution of **1b** (1.0 g, 3.44 mmol) in a minimal amount of CH₂Cl₂ (3 mL) was added HOTf (0.20 g, 1.33 mmol) in CH₂-Cl₂ (ca. 1 mL) at room temperature. The ^{31}P NMR spectrum of the reaction mixture showed signals for **1b**, **7**, and several complex multiplets in the range of -50 to 50 ppm with P–P coupling (from $^{31}P-^{31}P$ COSY). Analysis of this mixture using electrospray mass spectrometry revealed that the product mixture contains oligomers (Mes*PCH₂)_{*n*}H⁺OTf⁻ (*n* = 2–6). ES MS (*m/z*): 581.7 [C₃₈H₆₃P₂]⁺, 871.8 [C₅₇H₉₄P₃]⁺, 1161.9 [C₇₆H₁₂₅P₄]⁺, 1451.9 [C₉₅H₁₅₆P₅]⁺, 1741.9 [C₁₁₄H₁₈₇P₆]⁺. The ions listed are the data for the all ^{12}C oligomer. Ions that we have not been able to account for were observed 46 *m/z* units below each ion.

X-ray Crystallography. All single crystals were immersed in Paratone-N oil and were mounted on a glass fiber. Data were collected at 293 K on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo K α radiation. Data were collected and processed using the d*TREK program. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on *F*² using the Siemens SHELXTL97 version. Crystal data and details of the data collection and structure

refinement are given in Table 1. Further details are included in the Supporting Information.

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Supporting Information Available: Full details of the crystal structure investigations are available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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