\[ \Delta S = \Delta S_{tr} + \Delta S_r \]

where \( \Delta S_{tr} \), the change in translational and rotational entropy, is very similar for a series of acids and \( \Delta S_r \), the change in vibrational entropy, is due mainly to the new adduct bond.

Upon complex formation three degrees of translational and three degrees of rotational freedom are lost and \( \Delta S_r \) must be negative. It is this loss of entropy which accounts for the negative entropy changes of Table II. However, the vibrational entropy change must be positive because six new vibrational degrees of freedom result from the association. If the bonding between the acid and base is strong, the new vibrations associated with the Sn–B bond will have a higher frequency and the entropy gain will be small. If the bond is weak the entropy gain will be correspondingly large. Hence \( \Delta S^o_r \) may be a more unambiguous indicator of bond strength than \( \Delta H^o \). The linear relationship that has been shown to exist between \( \Delta H^o \) and \( \Delta S^o_r \) is a result of the fact that a tighter bond, as evidenced by a more negative \( \Delta H^o \), will produce a corresponding larger loss of entropy. The entropy decrease from (C–H3)3Sn–Cl to (C–H3)3Sn–Br to (C–H3)3Sn–I results from larger vibrational entropy loss due to increased enthalpy of bond formation. This relationship would not be expected to hold if the ligand bonds changed in less than a regular way for similar adducts or if the rehybridization enthalpy differed for each compound. This requires that the enthalpy data of Table II be interpreted as being due to a stronger bond between the tin atom and the base and not as being due to differences in the Sn–X bond energies in the complex or to rehybridization differences.

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Registry No. (CH3)3SnCl, 1066-45-1; (CH3)3SnBr, 1066-44-0; (CH3)3SnI, 811-73-4; (C6H5)3SnCl, 994-31-0; (C6H5)3SnBr, 2767-54-6; (C6H5)3SnICl, 2279-76-7; (C6H5)3SnCl, 1461-22-9; (C6H5)3SnICl, 639-58-7; (C6H5)4PO, 791-28-6.

Approaches to the Synthesis and Detection of a Transient Palladium(0) Alkylidene

Robert A. Wanat and David B. Collum*

Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

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Treatment of palladium enolate (PPh3)2BrPdCH2C(O)-t-Bu with t-BuOK in tetrahydrofuran at -63°C affords PPh3P==CH(O)C-C(t-Bu) (2) in good yield. Kinetics demonstrated the reaction to involve rate-determining dissociation of phosphate. In the presence of added phosphine, the reaction exhibited fractional direct dependence on the concentration of t-BuOK and fractional inverse dependence on the concentration of added phosphine. Isotopic labeling studies showed that the t-BuOK did not function as a Bronsted base up to the rate-determining step. Crossover experiments demonstrated that the post-rate-determining step involving phosphorus–carbon bond formation occurred by an intramolecular mechanism. Reactions of (Z)-BrCH==C(OSiMe3)-t-Bu, Br2CHC(O)-t-Bu, (Z)-BrCH==C(OLi)-t-Bu, and N,CHC(O)-t-Bu with Pd(PPh3)3 each provided phosphoran 2. The mechanism for formation of 2 and the possible intermediacy of low-valent palladium alkylidene are discussed.

Introduction

We are interested in the elucidation of the organic chemistry of highly reactive transition-metal alkylidenes. Specifically, we are intrigued by the class of alkylidenes that bear potentially destabilizing, and thus highly activating, electron-withdrawing groups. These species are frequently implicated as reactive intermediates derived from diaceto ketones and diaceto esters en route to C==C, C==C, C==N, C==O, C==S, O==H, S==H, etc.

N—H, and N—N bond functionalizations. Several laboratories have reported mechanistic work on the tran-
sestera4 However, acyl-substituted terminal alkylidenes
have been isolated only very rarely and never in the later
triads.13 By the very nature of the high reactivities that
vast number of possible modes of diazo activation14 that
make them spectroscopically invisible, and because of the
inferences of their intermediacy are still

describe herein an approach to the synthesis and
detection of an acyl-substituted palladium alkylidene in
which the dominant decomposition pathway involves ex-
traction of the corresponding phosphorane by a process
involving rapid intramolecular carbon-phosphorus bond
formation.16 Support for the intermediacy of an alkylidene
comes from a demonstration of common modes of re-
activity arising from independent approaches to this class
of reactive intermediate.

Results

Our strategy to prepare acyl-substituted alkylidenes is
illustrated in eq 1. Upon treatment of palladium complex
1 with 1.1 equiv of t-BuOK in tetrahydrofuran (THF) at
-78 °C with subsequent warming to room temperature, we
were able to isolate phosphorane 217 from the resulting
heterogeneous, black reaction mixture. The only other
isolable product was an incompletely characterized palladium
triphosphine complex.18 Consistent with the

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A control experiment ruled out the possibility that
bromo ketone 3 was reductively eliminated and converted
to 2 independent of the palladium: a mixture of PPh3,
t-BuOK, and ketone 3 in THF failed to give detectable
quantities of 2 even after extended reaction times at room
temperature.19 Following the course of the reaction of 1
with t-BuOK-d4 by 1H NMR in THF-d4 at -83 °C showed
that phosphorane 2 was formed along with only traces of
several tert-butyl-containing by-products. No interme-
diates could be detected. Furthermore, GC-MS analysis
of the reaction contents provided no evidence for the
formation of volatile organic by-products.

We investigated the efficacy of a variety of alkoxides to
effect dehydrohalogenation of 1. Lithium tertiary alko-
oxides and potassium phenoxides smoothly converted 1
to 2 albeit at ambient temperatures. Complex product
distributions resulted from attempted dehydrohalogenations
of 1 with alkoxides bearing hydrogens at the α-carbon
(e.g., KOCH2R). These may have arisen from facile β-
hydride eliminations20 of Pd–OCH2R intermediates (vide
infra).

One might speculate that phosphorane 2 arose from
nucleophilic attack of residual triphenylphosphine on an
intermediate alkylidene (e.g., ii) to provide an unstable

(19) In a reaction that appeared to be superficially related to the
dehydrohalogenation of 1, Stille found that reaction of Pd(PPh3)4 with
2.5 equiv of BrCH2COPh afforded Ph,P=CHCOPh and CH3COPh.
However, they postulated that the reaction simply involved formation
of the phosphonium salt from dissociated PPh3 and the excess of
BrCH2COPh independent of the palladium center, followed by depro-
tonation mediated by an equivalent of slightly basic (PPh3)2PdBrCOPh
adduct. The appropriate control experiments run in our laboratory confirmed their conclusions. Stille, J. K.; Lau, K. S.
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facile dissociation.
ylide complex. Interconversion of complexed phosphoranes (ylide complexes) and alkylidenes are well documented. However, this mechanism would require somewhat surprising electrophilicity for $\ell$ since limited experimental and theoretical evidence indicates that a low-valent alkylidene in the nickel triad containing no strongly electronegative ligands should be nucleophilic at the alkylidene carbon atom. Furthermore, a battery of experiments designed to trap the putative reactive alkylidene with large molar excesses of a variety of olefins and internal acetylenes failed to divert the formation of 2.

To gain further insight into the sequence of events leading up to formation of phosphorane 2, we conducted a kinetic study of the reaction as described below.

**Kinetics.** All kinetic runs were conducted under pseudo-first-order conditions in t-BuOK ($\geq 10.0$ molar equiv) in THF-d$_4$. Reaction rates were monitored by following loss of the tert-butyl singlet of 1 at 0.12 ppm in the 300-MHz $^1$H NMR spectra.

Conversion of complex 1 to phosphorane 2 at -63.0 °C was found to be first order in 1 and zero order in t-BuOK over more than 4 half-lives ($R^2 = 0.96-0.99$). The reaction was inhibited by the addition of 3 equiv of PPh$_3$. The phosphine inhibition was not due to an associative mechanism via a pentacoordinated palladium intermediate since following loss of the tert-butyl singlet of 1 at 0.12 ppm in THF-d$_4$, the added phosphine had no effect on the chemical shifts of PPh$_3$. Therefore, in the absence of added phosphine, dissociation of PPh$_3$ from 1 appeared to be rate limiting.

Under pseudo-first-order conditions for PPh$_3$ and t-BuOK, the reaction proceeded smoothly at -39.0 °C, exhibiting a fractional inverse dependence on [PPh$_3$] (Figure 1; rate $\propto 1/[\text{PPh}_3]^{0.04}$) and a direct fractional order dependence on [t-BuOK] (Figure 2; rate $\propto \text{[t-BuOK]}^{0.39}$). Upon comparing the rates of reaction of 1 and 1-d$_2$ in the presence of 10 equiv of PPh$_3$ (conditions in which PPh$_3$ dissociation was not rate determining) we observed a small inverse intermolecular isotope effect ($k_{H}/k_{D} = 0.80 \pm 0.10$). Treatment of monodeuterated 1-d in THF-d$_4$ with 10 equiv of t-BuOK in the presence of 10 equiv of PPh$_3$ (monitored by $^1$H NMR at -43°C) afforded 2-d to the exclusion of 2 ($\leq 20\%$) showing the intramolecular isotope effect to be large ($k_{H}/k_{D} \approx 4$).

**Crossover Studies.** A crossover experiment was run to elucidate the extent of intramolecularity of phosphorane-carbon bond formation. The 300-MHz $^1$H NMR spectrum of triphenylphosphorane 2 in THF-d$_4$ exhibited a doublet for the ylidic proton centered at 3.64 ppm ($\nu_{p-H} = 28$ Hz) that was completely resolved from the corresponding doublet of tri-p-tolylphosphorane 4 (3.58 ppm, $\nu_{p-H} = 27$ Hz). In the absence of added phosphine at -63 °C in THF-d$_4$ (conditions in which phosphine dissociation was irreversible and proton exchange in the resulting phosphoranes was found to be slow), the reaction of a 1:1 mixture of 1 and 1-d$_2$ with t-BuOK (10 equiv) produced phosphorane 2 (and 4-d) to the exclusion of (<5%) phosphorane 4. The complimentary experiment using 5 and 1-d$_2$ provided 4 to the exclusion (<5%) of 2. Therefore, phosphorus-carbon bond formation occurred almost exclusively by an intramolecular mechanism.

**Alternative Approaches to Alkylidenes.** We investigated alternative syntheses of palladium alkylidenes to gain support for such intermediates through demonstration of common modes of reactivity. In an effort to generate an α-palladated alkali-metal enolate (cf. in eq 1) that, in some as-of-yet undefined form, was a possible reactive intermediate en route to phosphorane 2, we attempted to prepare palladated enol ether 6. When enol ether 7 (Z geometry as shown by NOE experiments) and (PPh$_3$)$_2$Pd were heated in benzene-d$_4$ at 100 °C (eq 2), we observed no sign of adduct 6. The $^1$H NMR spectrum of the reaction showed phosphorane 2 to account for over 90% of the product distribution.

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27. The postulated predissociation of phosphine from 1 was further supported by the observation that the relatively nondissociating bis(diphenylphosphino)ethane (dppe) and bis(trimethylphosphino) complexes corresponding to 1 required higher temperatures (-50 °C) for reaction to occur. Although we observed smooth formation of Me$_2$P=CH(OC)=C=C(COOH)-t-Bu from the latter, the dppe derivative afforded a complex product distribution.

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29. The reaction orders in PPh$_3$ and t-BuOK were obtained from the general rate equations $k_{H}/k_{D} = k_{H}^{[3]}$ and $k_{H}/k_{D} = k_{H} + Z$ in [V]. Plots of $k_{H}$ vs. [V] ($\nu_{p-H}$ and t-BuOK in Figures 1 and 2, respectively) afforded lines with slopes (Z) representing the calculated reaction orders in component Y. Frost, A.; Pearson, R. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; Chapter 3.

tert-butyl-containing material. Although superficially this result implicated a rate-determining oxidative addition followed by alkylidene formation via rapid (halide ion assisted?) decomposition of 6, the mechanistic implications outlined in the Discussion are more complex.

We prepared the α-brominated palladium derivative 8 in order to investigate reductive dehalogenation routes to acyl-substituted alkylidenes (eq 2). Reaction of Pd(PPh₃)₄ and dibrominated ketone 9 in benzene-d₆ at 25 °C for 0.5 h afforded an approximate 3:2 mixture of stereoisomers. The major isomer was shown to be trans-8 by the symmetric methine triplet (J_p-H = 8.0 Hz) centered at 4.81 ppm and a singlet corresponding to the tert-butyl group at 1.02 ppm. The minor isomer (cis-8) exhibited a doublet of doublets (J_α,p-H = 9.5 Hz, J_α,trans-p-H = 14.3 Hz) centered at 4.55 ppm and a tert-butyl resonance at 1.42 ppm. When the mixture in benzene-d₆ was left at room temperature and monitored by ¹H NMR spectroscopy, the resonances corresponding to cis-8 and trans-8 disappeared with concomitant appearance of the resonances corresponding to phosphorane 2 and precipitation of a highly insoluble phosphine-containing material (presumably [(PPh₃)₂PdBr]). Conversions of M-C-X (X = halogen) to phosphorane 2 and precipitation of a new compound that exhibited a tert-butyl resonance at 1.30 ppm. Over a period of 48 h, both tert-butyl resonances were replaced by a tert-butyl resonance at 1.51 ppm that was shown to belong to phosphorane 2. We assigned the intermediate resonance to phosphazine 12 based on well-documented phosphazine-diazoalkane equilibria. When 11 and PPh₃ in benzene-d₆ were warmed to 60 °C for 3 days in the absence of palladium, the resulting mixture of 11 and 12 was not converted to 2.

**Discussion**

We were able to observe kinetically only a portion of the pathway in the t-BuOK-mediated conversion of complex 1 to phosphorane 2 (eq 6–8). In the absence of added phosphine, the dehydrohalogenation of 1 with palladium-mediated diazo ketone chemistry, diazo ketone 1134 and 0.25 equiv of Pd(PPh₃)₄ were heated in benzene-d₆ at 55 °C (eq 5). Within 0.5 h there appeared a static 12:1 mixture of diazo ketone 11 and a new compound that exhibited a tert-butyl resonance at 1.30 ppm. Over a period of 48 h, both tert-butyl resonances were replaced by a tert-butyl resonance at 1.51 ppm that was shown to belong to phosphorane 2. We assigned the intermediate resonance to phosphazine 12 based on well-documented phosphazine-diazoalkane equilibria. When 11 and PPh₃ in benzene-d₆ were warmed to 60 °C for 3 days in the absence of palladium, the resulting mixture of 11 and 12 was not converted to 2.


reaction of three-coordinate intermediate iii with t-BuOK (eq 7). The observed fractional value for the reaction order in t-BuOK (0.35 order) undoubtedly derived, at least in part, from concentration-dependent alkoxide aggregation phenomena.26 However, an inverse first-order dependence on added phosphine would have been anticipated rather than the measured inverse fractional order dependence.28 From crossover experiments we know that during the course of the reaction in the absence of added phosphine, the dissociated phosphine does not return to any of the intermediates along the reaction pathway to 2. In the presence of added phosphine the reaction may be more complex.40 (One possibility is that the added phosphine played a role in the presumed desaggregation of t-BuOK oligomers.39) In any event, although we were unable to obtain useful quantitative information from the rate data, the qualitative dependencies proved valuable for the interpretation of the observed isotope effects (see below).

The t-BuOK and PPh3 rate dependencies were qualitatively consistent with a mechanism involving rapid phosphine predissociation followed by a slower t-BuOK-mediated deprotonation step. Nevertheless, the small inverse isotope effect measured at −39 °C in the presence of added PPh3 ($k_{H}/k_{D} = 0.80$) was contrary to that normally observed for a primary kinetic isotope effect.41 If, on the other hand, the deprotonation step was rapid and reversible, the resulting equilibrium isotope effect would be small and either normal or inverse.42 However, the observed isotope effect was shown not to be an equilibrium isotope effect from several observations. A plot of ln $k_{H}/k_{D}$ vs. time was linear over greater than 4 half-lives showing no autoinhibition from the presumed increase in $[t$-BuOH] over the course of the reaction. Furthermore, conversion of 1-d2 to phosphorane 2-d in the presence of excess PPh3 and an additional 1.0 equiv of t-BuOH showed no proton incorporation in the methylene position of 1-d2 at partial conversion.43 Most importantly, the large discrepancy between the small intramolecular and the large intramolecular isotope effects indicated that kinetic deprotonation had occurred, in a kinetically invisible, post-rate-determining step.28 Therefore, there must have occurred an interaction between t-BuOK and a palladium intermediate during (or prior to) the rate-determining step that did not involve deprotonation; palladate iv would be the logical intermediate (eq 9).44 An additional step involving extrusion of bromide from palladate iv followed by a second reaction with t-BuOK to provide palladate v clearly cannot be dismissed at this time.

![Chemical equation](image)

Important aspects of the mechanism, including a putative deprotonation step and the crucial carbon–phosphorus bond-forming step, remained obscure in a kinetically invisible section of the pathway. We are able to account for many of our experimental observations by invoking either of two mechanistic rationales. Although a distinction between the two pathways cannot be made at this time, close inspection shows that the two seemingly disparate mechanisms may actually be variants of the same theme. In the following mechanistic discussions only some of the details of the metal coordination spheres can be surmised from kinetic and crossover data. Additionally, the structures may vary for conditions that provide Pd metal (no added PPh3) vs. those that provide Pd(PPh3)2. Accordingly, only the portions of the coordination spheres that are relevant to the discussion are depicted; implicit additional ligands of undefined structure are designated as “Ly". Furthermore, with the exception of eq 10 and 11, the diagrams are not intended to imply stereochemistry at trigonal palladium centers.45

**Alkylidene Mechanism.** To argue for the intermediacy of an alkylidene in the dehydrohalogenation of 1, we are forced to keep within several constraints. Deprotonation of the methylene group of iv or v, whether via a biomolecular or possibly a more facile unimolecular pathway (eq 10), must have occurred subsequent to the

![Chemical equation](image)
Support for the intermediacy of an alkylidene during the dehydrohalogenation of 1 comes from the common modes of reactivity observed in the reactions of Pd[P(Ph)3]2 with enol ether 7, dibromo ketone 8, enolate 10, or diazoalkane 11. Reactions intimately related to eq 3-4 have been postulated to provide or proceed through alkylidene intermediates. The common product (phosphonate 2) obtained from each of the five different approaches to alkylidenes argues in support of related reactive intermediates.

**Phosphonium Salt Reductive Elimination Mechanism.** We must also consider an alternative mechanism for phosphonate formation involving a rate-determining reductive elimination of a phosphonium salt (e.g., Ph3PCH2CO-t-Bu'X-) with subsequent deprotonation by t-BuOK. Product distributions that appear to arise from similar aryl and vinyl phosphonium salt reductive eliminations at elevated temperatures have been reported. Although such a reductive elimination mechanism is consistent with the experimental results, we are troubled by a number of points. Since the reported examples of phosphonium salt reductive eliminations require elevated temperatures (75-100 °C) for extended reaction times, by crudest estimates the t-BuOK-mediated reaction of 1 occurred at least 106 times faster. It might be tempting to invoke a scenario in which formation of a t-BuOK ate complex (e.g., iv or v) facilitated a phosphonium salt reductive elimination. However, reductive eliminations typically proceed more slowly from electron-rich metal centers. Furthermore, Kampmeier provided evidence that the carbon-phosphorus bond-forming step in the corresponding alkyl phosphonium reductive eliminations proceed independent of the metal centers subsequent to reductive elimination of the alkyl halide moiety, such a mechanism was unambiguously ruled out in the t-BuOK-mediated conversion of 1 to 2.

The dilemma of differentiating two seemingly disparate mechanisms might be partially resolved by considering the possible mechanisms by which carbon-phosphorus bond formation occurs at transition-metal centers. Many cationic and Fischer carbene complexes and cationic olefin complexes are sufficiently electrophilic to react with nucleophilic phosphines. However, there also exist examples of σ-vinyl complexes and π-complexed acetylenes that undergo facile P-C bond-forming reactions via mechanisms that are not necessarily so transparent. One of the common threads connecting all such reactions is that the starting materials or logical reactive intermediates can be depicted in alkylidene-like resonance structures (Chart I).

Thus, metal-centered phosphorus-carbon bond formation may prove facile only when the transition state is stabilized by alkylidene character. The reaction of bromoacetal ether 7 with Pd[P(Ph)3]2 to give phosphonate 2 can be represented as either a phosphonium salt reductive elimination or phosphine–alkylidene coupling, depending on whether the putative intermediate is drawn as a σ-vinyl derivative (e.g., 6) or as the alternative alkylidene resonance structure x or xi. By depicting the intermediate palladium-bound enolate of type vi as the alternative alkylidene resonance structures xii or xiii, we find that it too may be represented as an alkylidene–phosphine coupling or a vinyl phosphonium salt reductive elimination analogous to those studied by Kampmeier. Nevertheless, the P-C coupling reaction from the dehydrohalogenation of 1 is extraordinarily facile given that the putative alkylidene intermediates along the pathway are unlikely to exhibit any positive character at the alkylidene carbon atom. We attribute the facility of the coupling step to the intramolecular that was demonstrated by the crossover ex-
experiments. We have begun to question whether the role of intramolecularity in alkylidene-to-phosphorane
consversions has been underestimated and, in turn, whether this has resulted in the importance of the alkylidene charge
polarizations to be overestimated. In this connection, the calculations of Nakataju et al. suggest that alkylidene
philicities are determined by frontier orbital control rather than charge distribution.13

**Experimental Section**

**General Data.** 1H and 31P NMR spectra were recorded on a JEOL FX-90Q spectrometer. Routine 1H NMR spectra were
recorded on a Varian CPT-20 (80 MHz) spectrometer. The low-temperature reaction kinetics were monitored on a Bruker
WP 300 spectrometer with temperature correction to within 0.1 °C. The phosphines were obtained from Strem and recrystallized
prior to use. The t-BuOK obtained from Aldrich was purified by sublimation. The t-BuOK-d5 was prepared from commercially
available tert-butyl alcohol (Aldrich) with oil-free potassium hydrde in THF and was sublimed before use. Tetrakis(tri-
phenylphosphine) palladium and tetrakis(tri-p-tolylphosphine) palladium were prepared by standard literature procedures.56
Both complexes benzene and tetrahydrofuran-d5 were distilled in vacuo from sodium benzophenone ketyl by using
standard vacuum line techniques. All other reagents were handled by using standard protocols, and all air-sensitive compounds
were manipulated by using standard vacuum line and glovebox techniques.

1. Bromo-3,3-dimethyl-2-butane none (3). Bromo ketone 3 was prepared by using a nonstandard literature procedure as follows.25
(Note: the reaction evolves large volumes of gaseous HBr and should be performed in a well-ventilated hood.) A 500-mL
round-bottom flask was charged with 1,3-C6H4Cl2 (0.12 g, 1.0 mmol) and 4 mL of 0.5 M HBr in anhydrous hexane under argon at
25 °C, and after 1.0 h, the colorless solution was concentrated in vacuo. The resulting yellow solid was washed with
hexane to afford a pale yellow solid. The yellow solid was extracted twice with diethyl ether and once with THF. The
extracted twice with diethyl ether and once with THF. The

3.2-Dimethyl-1,1,1-trideuterio-2-butane. A two-phase mixture of picoline (25 mL, 200 mmol), anhydrous potassium
carbonate (500 mg, 3.62 mmol), and D2O (99.8% d, 50 mL) was held at reflux for 48 h under N2. The aqueous phase was removed,
and the picoline was carried through two additional cycles using fresh potassium carbonate and fresh D2O each time. After
the third cycle, the organic layer was dried over anhydrous Na2SO4 and distilled (105 °C, 760 mmHg) to afford 14 g of
3,3-dimethyl-1,1,1-trideuterio-2-butane (68% yield) with >99% deuteration at the methyl group as shown by 300-MHz 1H NMR.

1-Benzyl-1,1-dideuterio-3,3-dimethyl-2-butanone (3-d5). Doubly deuterated 3-d5 was prepared in 68% yield from the
tetradeuterated picoline (vide supra) by the procedure used to prepare 3 with substitution of CCL3 for CHCl3 as reaction solvent.

300-MHz 1H NMR (CDCl3) showed 96% deuteration of the bromomethyl moiety of 3-d5.

**Authentic Ph,P=CHC(O)-t-Bu (2).** Authentic Ph,P=CHC(O)-t-Bu (2) was prepared by sublimation. The t-BuOK obtained from Aldrich was purified
by sublimation. The t-BuOK-d5 was prepared analogously to 1 by starting with (p-tolyl)3P,Pd.56

Recrystallization from hexane/ether afforded the product as colorless oil (bp 78-80 °C at 11 mm): 1H NMR (CDCl3) δ 4.15 (s, 2 H), 1.21
13 C (CDCl3) δ 28.0 (CH3), 21.1 (aryl-CH3), 40.9 (d, Jp..C 15 Hz, CH), 39.3 (CH3), 133.6 (d, Jp..C 110 Hz, CH3), 126.9 (CH3), 27.4 (CH3), 36.2 (d, Jp..C 28 Hz, 1 H), 0.12
3P (CDCl3) δ 27.60 (quaternary C); 31P(1H) NMR (CDCl3) δ 27.60 (quaternary C); 31P(1H) NMR (CDCl3) δ 27.60 (quaternary C).

GC-MS analysis of the reaction contents afforded no evidence of volatile organic products.

**Authentic Ph,P=CHC(O)-t-Bu (2).** Phosphorane 2 was prepared by standard literature procedure.20 The resulting yellow solid
was washed with ethereal ether to afford a yellow solid, afforded 19% of phosphorane 2 that was identical with an authentic sample prepared by a literature procedure.27 When the reaction was run in THF-d8 with t-BuOK-d5 on an NMR scale (for the experimental procedure, see the Kinetics section), phosphorane 2 (tert-butyl resonance; 1.14 ppm) was formed in ≥90% purity along with minor impurities exhibiting tert-butyl resonances at 1.10, 1.07, and 0.88 ppm. GC–MS analysis of the reaction contents afforded no evidence of volatile organic products.
Crossover Experiment. To an argon-flushed NMR tube at −95 °C were added 1 (5 mg) and 5-1d5 (6 mg) each in 175 μL of THF-d8, followed by t-BuOK-dg (14 mg) in 200 μL of THF-d8. The tube was sealed under vacuum, warmed to −78 °C, agitated vigorously, and inserted in a probe of a 300-MHz NMR spectrometer held at −63 °C. Proton NMR analysis showed the growth of the doublet centered at 5.6 ppm to phosphorane 2 to the exclusion (<5%) of the doublet centered at 3.58 ppm corresponding to phosphorane 4. When the experiment was repeated by using 5 and 1-d5, phosphorane 4 formed to the exclusion (<5%) of phosphorane 2.

Kinetics: Representative Procedure. With standard glovebox and vacuum line procedures, a 5-mm NMR tube was charged with a solution containing 1.0 mg (0.012 mmol) of complex 1-(CH2Cl)2 and PPh3 (32 mg, 0.12 mmol) in THF-d8 (250 μL) and capped with a septum. After cooling the tube to −78 °C under argon, a solution of freshly sublimed t-BuOK-dg (14 mg, 0.12 mmol) in THF-d8 (200 μL) was syringed down the cold walls of the NMR tube. Following sealing of the tube with a torch, it was immediately placed without warming into the 300-MHz NMR probe held at −39.3 °C. (The probe temperature was checked between each run, and the temperature equilibration upon insertion of the tube occurred in ≤5 min.) The reaction was monitored for loss of the tert-butyl resonance of 1 at 0.12 ppm relative to a CHCl3 internal standard. All reported errors represent one standard deviation from linear, nonweighted least-squares analyses. Reaction orders were calculated as described elsewhere.27 (Z)-BrCH=CO(SiMe3)Bu (7). To a solution of lithium disopropylamide (1.0 mmol) in THF (3 mL) at −78 °C under nitrogen was added neat bromo ketone 1 (135 μL, 1.00 mmol). The reaction was warmed to room temperature and partitioned between ethyl acetate and aqueous NaHCO3. The organic layer was dried (Na2SO4), stripped to an HCl diethylether solution of phosphorane 12 appeared: 6 1.31 ppm (s, 1 H), 0.91 ppm (s, 9 H); 13C{1H} NMR (CDCl3) δ 199.5 (s, CO), 142-124 (envelope of aryl carbons), 46.8 (d, Jp-P = 110 Hz, 1 H), 1.42 ppm (s, 9 H). (trans-8) (major isomer): 6 5.24 ppm (s, 1 H), 0.91 ppm (s, 9 H), 1.42 ppm (s, 9 H). (cis-8) (minor isomer): 6 5.10 ppm (s, 1 H), 0.91 ppm (s, 9 H), 1.42 ppm (s, 9 H). trans-8 (major isomer): 6 5.24 (s, 1 H), 0.91 (s, 9 H), 1.42 (s, 9 H). trans-8 (minor isomer): 6 5.10 ppm (s, 1 H), 0.91 ppm (s, 9 H), 1.42 ppm (s, 9 H). 

Addition of 10 to Pd(PPh3)4: Stoichiometric. An argon-flushed NMR tube was charged with PPh3 (46 mg, 0.176 mmol), enolate 10 (30 mg, 0.16 mmol), PPh3-Pd (9 mg, 0.008 mmol), and C6Ds (2.0 mL) and sealed under vacuum with a flame. After 9 days at 25 °C 1H NMR analysis showed the yellow, homogeneous solution to contain almost exclusively phosphorane 2 with approximately 5% of enolate 10 remaining. Workup as described above for the stoichiometric transformation afforded 30 mg of phosphorane 2 (52% yield; 55% yield based on 10 conversion). 

Diazoketone 11. Diazoketone 11 was prepared by a non-descript literature procedure as follows. To a solution of pivaloyl chloride (500 mg, 4.90 mmol) in 20 mL of anhydrous diethyl ether at 0 °C under N2 was added an excess of ethereal diazomethane. After stirring for 12 h at 25 °C, the solution was concentrated, and the resulting pale yellow oil was flash chromatographed (20% ethyl acetate in hexane) to afford diazo ketone 11 (480 mg, 78% yield) as a yellow oil: 1H NMR (CD2Cl2) δ 4.35 (s, 1 H), 0.91 (s, 9 H); 13C{1H} NMR (CDCl3) δ 200.4 (CO), 51.0 (br s, CHN), 41.7 (CHBr), 38.0 (C(CH3)2), 28.1 (CH3 of t-Bu), 1.3 (SiCH3); IR (film) 3120 (w), 1623 (m), 1595 (m), 1480 (s), 1100 (s) cm−1; exact mass calcd for C9H10CL0P 250.0389, found 250.0382. 

Addition of 10 to Pd(PPh3)4: Catalytic. A representative experiment is made to the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643) for support of the Cornell Nuclear Magnetic Resonance Facility. 

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