$$\Delta S = \Delta S_{t,r} + \Delta S_v$$

where $\Delta S_{t,r}$, the change in translational and rotational entropy, is very similar for a series of acids and ΔS_v, 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 $\Delta S_{t,r}$ 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 larger. Hence $\Delta S°$ may be a more unambiguous indicator of bond strength than $\Delta H°$. The linear relationship that has been shown to exist between $\Delta H°$ and $\Delta S°$ is a result of the fact that a tighter bond, as evidenced by a more negative $\Delta H°$, will produce a corresponding larger loss of entropy. The entropy decrease from $(CH_3)_3Sn-Cl$ to $(CH_3)_3Sn-Br$ to $(CH_3)_3Sn-I$ 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.

Acknowledgment. We are indebted to the National Science Foundation for support of this work and to Marjorie Samples and Scott Penfil for their assistance.

Registry No. $(CH_3)_3SnCl$, 1066-45-1; $(CH_3)_3SnBr$, 1066-44-0; $(CH_3)_3SnI$, 811-73-4; $(C_2H_5)_3SnCl$, 994-31-0; $(C_2H_5)_3SnBr$, 2767-54-6; $(c_3H_7)_3SnCl$, 2279-76-7; $(C_4H_9)_3SnCl$, 1461-22-9; $(C_6H_5)_3SnCl$, 639-58-7; $(C_6H_5)_3PO$, 791-28-6.

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

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Treatment of palladium enolate $(PPh_3)_2BrPdCH_2C(O)$-*t*-Bu with *t*-BuOK in tetrahydrofuran at −63 °C affords $Ph_3P{=}CHC(O)$-*t*-Bu (**2**) in good yield. Kinetics demonstrated the reaction to involve rate-determining dissociation of phosphine. 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 Brønsted 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*)-$BrCH{=}C(OSiMe_3)$-*t*-Bu, $Br_2CHC(O)$-*t*-Bu, (*Z*)-$BrCH{=}C(OLi)$-*t*-Bu, and $N_2CHC(O)$-*t*-Bu with $Pd(PPh_3)_4$ each provided phosphorane **2**. The mechanism for formation of **2** and the possible intermediacy of low-valent palladium alkylidenes are discussed.

Introduction

We are interested in the elucidation of the organic chemistry of highly reactive transition-metal alkylidenes.[1] Specifically, we are intrigued by the class of alkylidenes that bear potentially *destabilizing*, and thus highly activating, electron-withdrawing groups.[2,3] These species are frequently implicated as reactive intermediates derived from diazo ketones and diazo esters en route to C=C,[4] C≡C,[5] C≡N,[6] C—H,[7] C—O,[8a-c] C—S,[8c] O—H,[9] S—H,[10]

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(2) In those systems in which the metal carbene moieties are stabilized by electron-donating groups (Fisher carbenes), electron-withdrawing acyl substituents should be destabilizing. However, such substituent effects will be dependent upon the electronic configuration at the metal center. For recent theoretical treatments that address the question of M=C stabilities and philicities, see ref 3.

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(5) Petiniot, N.; Anciaux, A. J.; Noels, A. F.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett.* **1978**, 1239.

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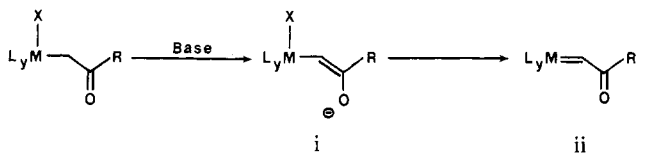
N—H,[11,12] and N—N[12] bond functionalizations. Several laboratories have reported mechanistic work on the transition-metal-catalyzed olefin cyclopropanations by α-diazo esters.[4] However, acyl-substituted terminal alkylidenes have been isolated only very rarely and never in the later triads.[13] By the very nature of the high reactivities that make them spectroscopically invisible, and because of the vast number of possible modes of diazo activation[14] that do not necessarily proceed through mononuclear terminal alkylidenes,[15] inferences of their intermediacy are still conjectural.

We describe herein an approach to the synthesis and detection of an acyl-substituted palladium alkylidene in which the dominant decomposition pathway involves extrusion 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 reactivity 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)

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 **2**[17] from the resulting heterogeneous, black reaction mixture. The only other isolable product was an incompletely characterized palladium triphenylphosphine complex.[18] Consistent with the

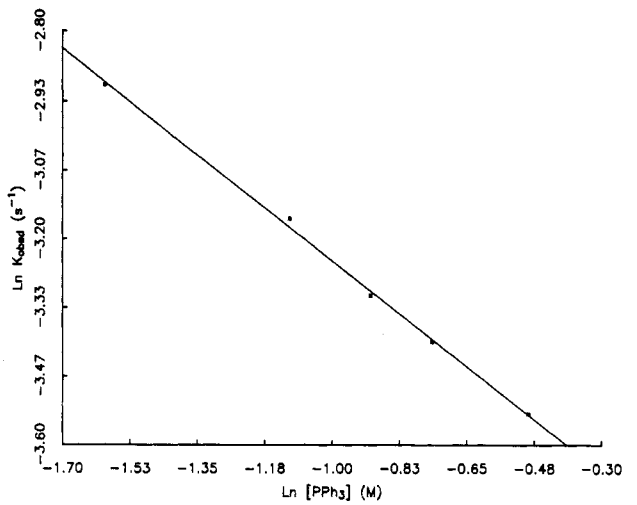
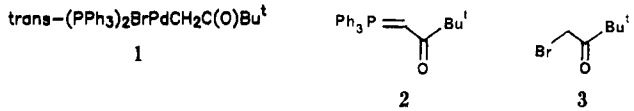


Figure 1. Dependence of ln k_{obsd} vs. ln [PPh_3]. Slope of −0.58 ± 0.02 represents reaction order in PPh_3.[20] [1] = 0.02 M; [*t*-BuOK] = 0.21 M; t = −39 °C; in THF-d_8.

black material being Pd metal arising from a deficiency of ligand, reaction in the presence of 3.0 equiv of added triphenylphosphine afforded a pale yellow, homogeneous reaction mixture from which we isolated phosphorane **2** (82% yield) and tetrakis(triphenylphosphine)palladium (84% yield).



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 PPh_3, *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-d_9 by ^{1}H NMR in THF-d_8 at −63 °C showed that phosphorane **2** was formed along with only traces of several *tert*-butyl-containing by-products. No intermediates 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 alkoxides 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., $KOCH_2R$). These may have arisen from facile β-hydride eliminations[20] of Pd–OCH_2R 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 [21]

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(16) Selected reviews of the transition-metal chemistry of phosphorus ylids: Weber, L. In "The Chemistry of the Metal-Carbon Bond", Patai, S., Hartley, F. R., Eds.; Wiley: New York, 1982; Chapter 3. Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(17) Ingham, C. F.; Massy-Westropp, R. A.; Reynolds, G. D.; Thorpe, W. D. *Aust. J. Chem.* **1975**, *28*, 2499.

(18) For reports of the formation of incompletely characterized Pd–phosphine oligomers or polymers formed under phosphine-deficient conditions see: Sisaki, A.; Ungvary, F.; Kiss, G. *J. Mol. Catal.* **1983**, *18*, 223. Onishi, M., Hiraki, K.; Itoh, T.; Ohama, Y. *J. Organomet. Chem.* **1983**, *254*, 381. Fenton, D. M. *J. Org. Chem.* **1973**, *38*, 3192.

(19) In a reaction that appeared to be superficially related to the dehydrohalogenation of **1**, Stille found that reaction of $Pd(PPh_3)_4$ with 2.5 equiv of $BrCH_2COPh$ afforded $Ph_3P{=}CHCOPh$ and CH_3COPh. However, they postulated that the reaction simply involved formation of the phosphonium salt from dissociated PPh_3 and the excess of $BrCH_2COPh$ *independent* of the palladium center, followed by deprotonation mediated by an equivalent of slightly basic $(PPh_3)_2PdBrCH_2COPh$ adduct. The appropriate control experiments run in our laboratory confirmed their conclusions. Stille, J. K.; Lau, K. S. Y. *J. Am. Chem. Soc.* **1976**, *98*, 5841.

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(21) Zerovalent metal complexes of stabilized ylides typically undergo facile dissociation.[16]

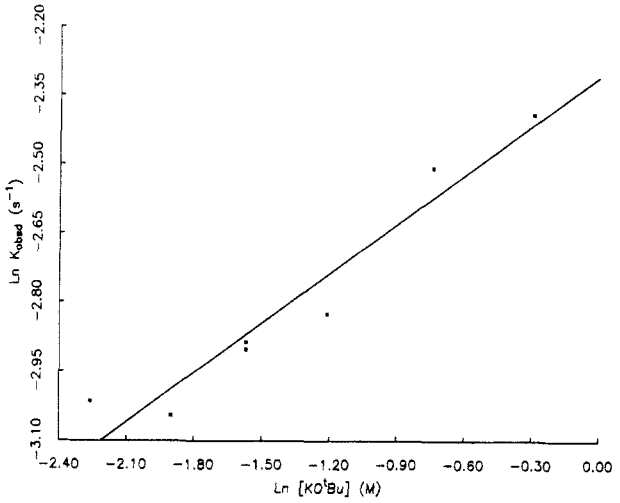


Figure 2. Dependence of ln k_{obsd} vs. ln [*t*-BuOK]. Slope of 0.35 ± 0.04 represents reaction order in *t*-BuOK.[20] [1] = 0.02 M; [PPh_3] = 0.21 M; t = −39 °C; in THF-d_8.

ylide complex. Interconversion of complexed phosphoranes (ylide complexes) and alkylidenes are well documented.[22] However, this mechanism would require somewhat surprising electrophilicity for ii since limited experimental[29] and theoretical[3,24] evidence indicates that a low-valent alkylidene in the nickel triad containing no strongly π-acidic 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 (≥10.0 molar equiv) in THF-d_8. 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 the added phosphine had no effect on the chemical shifts or multiplicities of the proton resonances of the low-temperature (−63 °C), slow-exchange spectrum of starting complex **1**. Upon comparison of the reaction rates for dehydrohalogenation of **1** and **1**-d_2, no appreciable kinetic isotope effect was detected (k_H/k_D = 1.06 ± 0.04). Therefore, in the absence of added phosphine, dissociation of PPh_3 from **1** appeared to be rate limiting.[25,26]

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 ∝ $1/[PPh_3]^{0.58\pm0.02}$) and a direct fractional order dependence on [*t*-BuOK] (Figure 2; rate ∝ [*t*-BuOK]$^{0.35\pm0.04}$).[27] 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 ± 0.10). Treatment of monodeuterated **1**-*d* in THF-d_8 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** (≤20%) showing the intramolecular isotope effect[28] to be large ($k_H/k_D \geq 4$).

trans-$(Ar_3P)_2BrPd$-R

1-d_2;	R = $CD_2C(O)Bu^t$,	Ar = Ph
1-*d*;	R = $CHDC(O)Bu^t$,	Ar = Ph
5;	R = $CH_2C(O)Bu^t$,	Ar = p-tolyl
5-d_2;	R = $CD_2C(O)Bu^t$,	Ar = p-tolyl

Ar_3P=R

2-*d*;	R = $CDC(O)Bu_t$,	Ar = Ph
4;	R = $CHC(O)Bu^t$,	Ar = p-tolyl
4-*d*;	R = $CDC(O)Bu^t$,	Ar = p-tolyl

Crossover Studies. A crossover experiment was run to elucidate the extent of intramolecularity of phosphorus–carbon bond formation. The 300-MHz ^{1}H NMR spectrum of triphenylphosphorane **2** in THF-d_8 exhibited a doublet for the ylidic proton centered at 3.64 ppm ($^2J_{P-H}$ = 28 Hz) that was completely resolved from the corresponding doublet of tri-*p*-tolylphosphorane **4** (3.58 ppm, $^2J_{P-H}$ = 27 Hz). In the absence of added phosphine at −63 °C in THF-d_8 (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 **5**-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 generate an α-palladated alkali-metal enolate (cf. i 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 $(PPh_3)_4Pd$ were heated in benzene-d_6 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

(22) Leading references: (a) Canestrari, M.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1789. (b) Nakazawa, H.; Johnson, D. L.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846. (c) Choi, H. S.; Sweigart, D. A. *J. Organomet. Chem.* **1982**, *228*, 249. (d) See ref 16.

(23) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, *22*, 1255. Noyori, R. *Tetrahedron Lett.* **1973**, 1691. Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108.

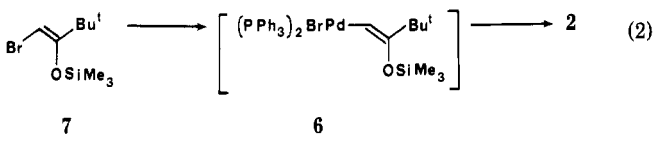
(24) Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 3966; **1982**, *104*, 448. Spangler, D.; Wendoloski, J. J.; Dupuis, M.; Chen, M. M. L.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1981**, *103*, 3985.

(25) The postulated predissociation of phosphine from **1** was further supported by the observation that the relatively nondissociationg bis(diphenylphosphino)ethane (dppe) and bis(trimethylphosphine) complexes corresponding to **1** required higher temperatures (−50 °C) for reaction to occur. Although we observed smooth formation of Me_3P=CHC(O)-*t*-Bu from the latter, the dppe derivative afforded a complex product distribution.

(26) For leading references to kinetic analyses for reactions of d^8 square-planar $(PR_3)_2MX_2$ species, see: (a) Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (c) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, 185.

(27) The reaction orders in PPh_3 and *t*-BuOK were obtained from the general rate equations[20b] $k_{obsd} = k'[Y]^Z$ and $\ln k_{obsd} = \ln k' + Z \ln [Y]$. Plots of ln k_{obsd} vs. ln [Y] (Y = PPh_3 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. In "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; Chapter 3.

(28) Dai, S.-H.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3946. Chipman, D. M.; Yaniv, R.; van Eikeren, P. *J. Am. Chem. Soc.* **1980**, *102*, 3244.



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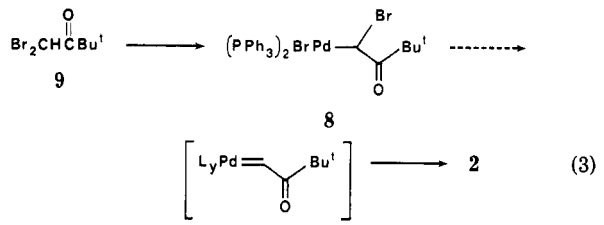
tert-butyl-containing material. Although superficially this result implicated a rate-determining oxidative addition followed by alkylidene formation via rapid (halide ion assisted?) decomposition of **6**, the mechanistic implications outlined in the Discussion are more complex.

We prepared the α-brominated palladium derivative **8** in order to investigate reductive dehalogenation routes to acyl-substituted alkylidenes (eq 2). Reaction of $Pd(PPh_3)_4$ and dibrominated ketone **9**[29] in benzene-d_6 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 ($J_{cis\text{-}P\text{-}H}$ = 9.5 Hz, $J_{trans\text{-}P\text{-}H}$ = 14.3 Hz) centered at 4.55 ppm and a *tert*-butyl resonance at 1.42 ppm.[30] When the mixture in benzene-d_6 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 $[(PPh_3)_2PdBr]_2$). Conversions of M–C–X (X = halogen) species to the corresponding alkylidenes[31] (as well as the reverse reaction involving insertion of alkylidenes into metal–halogen bonds[32]) have been implicated previously.



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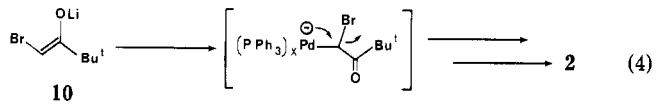
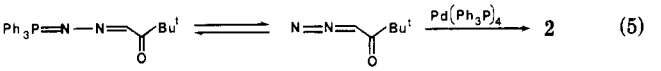
We anticipated that alternative entry to this class of alkylidenes could be obtained as depicted in eq 4. When



10

a 3.5:1 mixture of crystalline bromo enolate **10** and $Pd(PPh_3)_4$ (0.875 equiv of enolate/phosphine) dissolved in benzene-d_6 was held at 25 °C, phosphorane **2** was formed within 45 h (62% isolated yield). The reaction was inhibited by added phosphine with the rate of formation of phosphorane **2** accelerating as the palladium was stripped of PPh_3.[33] In the absence of palladium no reaction was observed between **10** and PPh_3. Treatment of enolate **10** with 5 mol % $Pd(PPh_3)_4$ in the presence of 1.0 equiv of added PPh_3 provided phosphorane **2** cleanly and catalytically (52% isolated yield) albeit at significantly reduced reaction rates (9 days).

In order to correlate the alkoxide-mediated chemistry of **1** with palladium-mediated diazo ketone chemistry, diazo ketone **11**[34] and 0.25 equiv[35] of $Pd(PPh_3)_4$ were heated in benzene-d_6 at 55 °C (eq 5). Within 0.5 h there

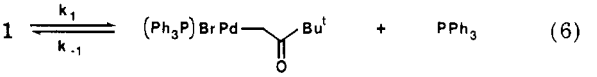


12 11

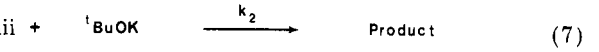
appeared a static 12:1 mixture of diazo ketone **11** and a new compound that exhibited a *tert*-butyl resonance at 1.30 ppm. Over a period of 48 h, both *tert*-butyl resonances were replaced by a *tert*-butyl resonance at 1.51 ppm that was shown to belong to phosphorane **2**. We assigned the intermediate resonance to phosphazine **12** based on well-documented phosphazine–diazoalkane equilibria.[36] When **11** and PPh_3 in benzene-d_6 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**.[37]

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



iii



$$-d[1]/dt = \frac{k_1k_2[1][t\text{-BuOK}]}{(k_{-1}[PPh_3] + k_2[t\text{-BuOK}])} \quad (8)$$

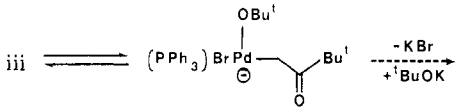
phosphine, the dehydrohalogenation of **1** was first order in **1** and zero order in *t*-BuOK and exhibited no measurable isotope effect, indicating that phosphine dissociation from **1** (eq 6) was rate-determining ($k_{-1}[PPh_3] \ll k_2[t\text{-BuOK}]$). In the presence of added PPh_3, the direct dependence on [*t*-BuOK] and inverse dependence on $[PPh_3]$ indicated that phosphine dissociation was no longer rate-determining ($k_{-1}[PPh_3] \geq k_2[t\text{-BuOK}]$). The simplest possible mechanism would involve the rate-determining

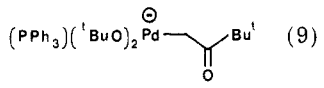
(29) Hill, G. A.; Kropa, E. L. *J. Am. Chem. Soc.* **1933**, *55*, 2509.
(30) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319.
(31) Leading references: (a) Engelter, C.; Moss, J. R.; Niven, M. L.; Nassimbeni, L. R.; Reid, G. *J. Organomet. Chem.* **1982**, *232*, C78. (b) Feser, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 940.
(32) Lappert, M. F.; Poland, J. S. *Adv. Organomet. Chem.* **1970**, *9*, 397. Mango, F. D.; Dvoretzky, I. *J. Am. Chem. Soc.* **1966**, *88*, 1654. Matsumoto, K.; Odaira, Y.; Tsutsumi, S. *J. Chem. Soc., Chem. Commun.* **1968**, 832. Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1984**, *273*, C17. Day, V. W.; Stults, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, *96*, 1227; 4008. Herrmann, W. A.; Huber, M. *J. Organomet. Chem.* **1977**, *140*, 55. Herrmann, W. A.; Huber, M. *Chem. Ber.* **1978**, *111*, 3124. Clemens, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1620.
(33) Both enolate **10** and phosphorane **2** are carbenoid equivalents except that **10** should exhibit dramatically greater nucleophilicity. Accordingly, the conversion of the putative alkylidene to phosphorane **2** could, in principle, be reversible (cf. Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43). If so, then reaction of $Pd(PPh_3)_4$ with tolyl-substituted phosphorane **4** would effect exchange of the PPh_3 and $(p\text{-tolyl})_3P$ fragments by way of a zerovalent ylide complex $(PPh_3)_xPdCH(PAr_3)C(O)$-*t*-Bu. However, phosphorane **4** was not detected (<5%) by ^1H or ^{31}P NMR when a mixture of **2**, $Pd(PPh_3)_4$, and $(p\text{-tolyl})_3P$ were heated in C_6D_6 at 110 °C for 8 days.
(34) Yates, P.; Garneau, F. X.; Lokensgard, J. P. *Tetrahedron* **1975**, *31*, 1979.
(35) The poor solubility of $(PPh_3)_4Pd$ mandated the 4.6:1 stoichiometry of **11** and $Pd(PPh_3)_4$. Complete conversion of diazo ketone **11** to phosphorane **2** illustrates the reaction to be catalytic in Pd metal.
(36) Pudovic, A. N.; Gareev, R. D. *Zh. Obshch. Khim.* **1976**, *46*, 945; **1975**, *45*, 1847, 1717. Krommes, P.; Lorberth, J. *J. Organomet. Chem.* **1977**, *127*, 19. Guziec, F. S., Jr.; Luzzio, F. A. *J. Org. Chem.* **1983**, *48*, 2434. Ramirez, F.; Levy, S. *J. Org. Chem.* **1958**, *23*, 2036.
(37) Schramm and Ibers reported that treatment of diazocyclopentadienylidene with bis(triphenylphosphine)nickel ethylene afforded the corresponding phosphorane: Schramm, K. D.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 2441.

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.[38,39a] However, an inverse first-order dependence on added phosphine would have been anticipated rather than the measured inverse *fractional* order dependence.[26] 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 deaggregation 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 PPh_3 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 PPh_3 (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 [1] 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**-d_2 to phosphorane **2**-*d* in the presence of excess PPh_3 and an additional 1.0 equiv of *t*-BuO*H* showed no proton incorporation in the methylene position of **1**-d_2 at partial conversion.[43] Most importantly, the large discrepancy between the small *intermolecular* and the large *intramolecular* isotope effects indicated that kinetic deprotonation had occurred, but 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.



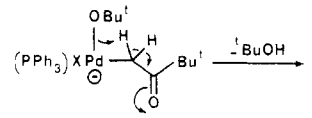


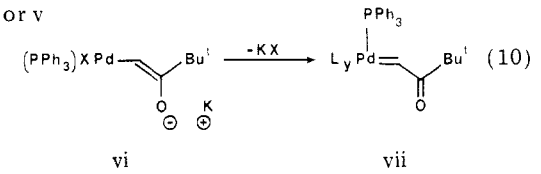
(9)

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 PPh_3) vs. those that provide $Pd(PPh_3)_4$. 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





(10)

rate-determining step.[59] Secondly, crossover experiments showed a very high degree of *intramolecularity* of phosphine–alkyl coupling. In a process that bears some relationship to metal-centered couplings of alkylidene and CO fragments,[46] sliding the phosphine toward the alkylidene carbon to afford phosphacyclopropane viii could occur with only very subtle structural reorganization and minimal charge localization (eq 11). Phosphacyclopropane viii is simply a resonance structure for a coordinated ylide complex ix.

(38) Brown, T. L.; Ladd, J. A.; Newman, G. N. *J. Organomet. Chem.* **1965**, *3*, 1. Reichle, W. T. *J. Org. Chem.* **1972**, *37*, 4254. Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737. Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086. Jackman, L. M.; DeBrosse, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 4177.

(39) (a) *t*-BuOK is reported to be a tetramer in THF: Schmidt, P.; Lochmann, L.; Schneider, B. *J. Mol. Struct.* **1971**, *9*, 403. Schlosser, M.; Jan, G.; Byrne, E.; Sicher, J. *Helv. Chim. Acta* **1973**, *56*, 1630. (b) Karsch, H. H.; Appelt, A.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1415.

(40) Rearrangement of the rate equation depicted in eq 8 leads to

$$\frac{1}{k_{obsd}} = \frac{k_{-1}[PPh_3]^x}{k_1k_2[t\text{-BuOK}]^y} + \frac{1}{k_2}$$

Plots of $1/k_{obsd}$ vs. $[PPh_3]^x/[t\text{-BuOK}]^y$ proved linear only when the calculated reaction orders in PPh_3 and *t*-BuOK were used (x = 0.58, y = 0.35). This may indicate that the fractional reaction orders arose from complex preequilibria that were not directly associated with the reaction pathway.

(41) Sugimoto, N.; Sasaki, M.; Osugi, J. *J. Am. Chem. Soc.* **1983**, *105*, 7676 and references cited therein.

(42) (a) Cram, D. J.; Kingsbury, C. A.; Rickborn, B. *J. Am. Chem. Soc.* **1961**, *83*, 3688. (b) Cram, D. J.; Uyeda, R. T. *J. Am. Chem. Soc.* **1962**, *84*, 4358. (c) Hofmann, J. E.; Schreisheim, A.; Nickols, R. E. *Tetrahedron Lett.* **1965**, 1745. (d) Streitweiser, A., Jr.; Van Sickle, D. E.; Langworthy, W. C. *J. Am. Chem. Soc.* **1962**, *84*, 244. (e) Streitweiser, A., Jr.; Van Sickle, D. E.; Reif, L. *Ibid.* **1962**, *84*, 258.

(43) Even in the event of rapid, reversible deprotonation, intimate acid–base association could preclude exchange with protic materials in the reaction medium.[42b,e]

(44) For a kinetic analysis of ate complex formation from MeLi addition to $PdMe_2(PR_3)_2$ see: Nakazawa, H.; Ozawa, F.; Yamamoto, A. *Organometallics* **1983**, *2*, 241.

(45) For leading references to the stereochemistry of three-coordinate d^8 systems, see ref 26b.

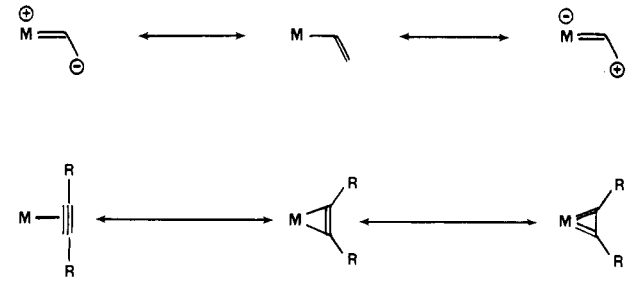
(46) Fischer, H.; Weber, L. *Chem. Ber.* **1984**, *117*, 3340.

(11)

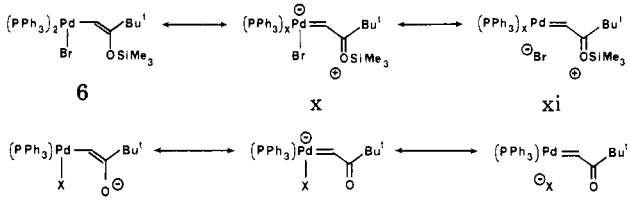
Support for the intermediacy of an alkylidene during the dehydrohalogenation of 1 comes from the common modes of reactivity observed in the reactions of $Pd(PPh_3)_4$ with enol ether 7, dibromo ketone 9, enolate 10, or diazoalkane 11. Reactions intimately related to eq 3–5 have been postulated to provide or proceed through alkylidene intermediates.[4,15,31,47] The common product (phosphorane 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 phosphorane formation involving a rate-determining reductive elimination of a phosphonium salt (e.g., Ph_3PCH_2CO-*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.[48-54] 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 10^6 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.[50] Furthermore, Kampmeier[49] 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.

Chart I



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[22] and cationic olefin π complexes[51] are sufficiently electrophilic to react with nucleophilic phosphines. However, there also exist examples of σ-vinyl complexes[52] and π-complexed acetylenes[53] 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).[54-56] Thus, *metal-centered phosphorus–carbon bond formation may prove facile only when the transition state is stabilized by alkylidene character.* The reaction of bromoenol ether 7 with $Pd(PPh_3)_4$ to give phosphorane 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.[49] 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 *intramolecularity* that was demonstrated by the crossover ex-

(47) For theoretical studies and leading references to the coupling of the X and Y fragments of X=M=Y species, see: Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632. Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.

(48) Horner, L.; Mummenthey, G.; Moser, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782. Cassar, L.; Foa, M. *J. Organomet. Chem.* **1974**, *74*, 75. Heck, R. F.; Ziegler, C. B., Jr. *J. Org. Chem.* **1978**, *43*, 2941. Mitchell, R. H.; Chaudhary, M.; Dingle, T. W.; Williams, R. V. *J. Am. Chem. Soc.* **1984**, *106*, 7776. Cramer, R.; Coulson, D. R. *J. Org. Chem.* **1975**, *40*, 2267.

(49) Kampmeier, J. A.; Harris, S. H.; Rodehurst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478.

(50) For reductive eliminations from d^8 square-planar complexes, evidence for mechanisms involving either phosphine association or dissociation have been presented: Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A. Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181 and references cited therein.

(51) Choi, H. S.; Sweigart, D. A. *Organometallics* **1982**, *1*, 60 and references cited therein. See also references cited in ref 49.

(52) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141. (b) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410. (c) Carmona, E.; Gutierrez-Puebla, E.; Monge, A.; Marin, J. M.; Panque, M.; Poveda, M. L. *Organometallics* **1984**, *3*, 1438. (d) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerehais, J. E. *Organometallics* **1983**, *2*, 1681. (e) Alt, H. G.; Schwarzle, J. A.; Kreissl, F. R. *J. Organomet. Chem.* **1978**, *152*, C57. (f) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *112*, C39. (g) Yasufuku, K.; Hamada, A.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1980**, *102*, 4363.

(53) Davidson, J. L.; Vasapollo, G.; Manojlovic-Muir, L.; Muir, K. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. See also ref 13b.

(54) Acetylenes as four-electron-donating bis(carbenes): Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766. Richard, R. L.; Weiss, R.; Newton, W. E.; Chen, G. J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. Cotton, F. A.; Hall, W. T. *Ibid.* **1979**, *101*, 5094. Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387. Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697. Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

(55) Resonance relationships of M(σ-vinyl), M(σ-aryl), and M–C$^-$ species to alkylidenes: Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869; **1983**, *3*, 1336; *J. Am. Chem. Soc.* **1981**, *103*, 3589. Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289. Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 387. Brown, K. L.; Ngamelue, M. *J. Organomet. Chem.* **1983**, *243*, 339.

(56) Metallacyclopropene/σ-vinyl metal equilibria: Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267. Davidson, J. L.; Wilson, W. F.; Manojlovic-Muir, L.; Murir, K. W. *J. Organomet. Chem.* **1983**, *254*, C6 and references cited therein.

periments. We have begun to question whether the role of *intramolecularity* in alkylidene-to-phosphorane conversions has been underestimated[57] and, in turn, whether this has resulted in the importance of the alkylidene charge polarizations to be overestimated. In this connection, the calculations of Nakatsuji et al. suggest that alkylidene philicities are determined by frontier orbital control rather than charge distribution.[3b]

Experimental Section

General Data. ^{13}C and ^{31}P NMR spectra were recorded on a JEOL FX-90Q spectrometer. Routine ^1H NMR spectra were recorded on a Varian CFT-20 (80 MHz) spectrometer. The low-temperature reaction kinetics were monitored on a Brucker 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-d_9 was prepared from commercially available *tert*-butyl-d_{10} alcohol (Aldrich) with oil-free potassium hydride in THF and was sublimed before use. Tetrakis(triphenylphosphine)palladium and tetrakis(tri-*p*-tolylphosphine)-palladium were prepared by standard literature procedures.[58] Benzene, benzene-d_6, tetrahydrofuran, and tetrahydrofuran-d_8 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-butanone (3). Bromo ketone **3** was prepared by using a nondescript literature procedure as follows.[29] (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 sequentially with anhydrous $CuBr_2$ (81.2 g, 363 mmol), 220 mL of 1:1 ethyl acetate/chloroform, and 26 mL (210 mmol) of pinacolone (Aldrich). The contents were held at reflux under a $CaCl_2$ drying tube for 24 h, at which time the slurry was filtered free of solids with ethyl acetate rinsings. Concentration of the filtrate followed by fractional distillation afforded 23 g (71% yield) of **3** as a colorless oil (bp 78 °C at 11 mm): ^1H NMR (80 MHz, $CDCl_3$) δ 4.15 (s, 2 H), 1.21 (s, 9 H).

$(PPh_3)_2$(Br)PdCH$_2$C(O)-*t*-Bu (1). To a solution of $Pd(PPh_3)_4$ (1.85 g, 1.60 mmol) slurried in 40 mL of benzene under argon at 25 °C was added ketone **3** (256 μL, 1.90 mmol). After 1.0 h the clear yellow solution was concentrated in vacuo. The resulting yellow solid was washed once with hexane and then recrystallized from THF/hexane or CH_2Cl_2 to afford **1** (1.20 g, 85% yield) as a microcrystalline solvate: ^1H NMR ($CDCl_3$) δ 8.0–7.0 (m, 30 H), 2.45 (br s, 2 H), 0.25 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 220.1 (CO), 135.1–127.9 (envelope of phenyl carbons), 44.23 (quaternary C), 31.3 (CH_2), 26.8 (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 27.60 (s). IR (Nujol) 1670, 1090 cm^{-1}. Anal. Calcd for $C_{46}H_{49}BrO_2P_2Pd\cdot CH_2Cl_2$: C, 57.78; H, 4.85; P, 6.94; Pd, 11.91. Found: C, 57.84; H, 4.79; P, 6.97; Pd, 12.10.

Reaction of 1 with *t*-BuOK in the Presence of PPh_3. To a 25-mL round-bottom flask charged with **1** (400 mg, 0.48 mmol), PPh_3 (393 mg, 1.50 mmol), and freshly sublimed *t*-BuOK (56 mg, 0.50 mmol) was vacuum transferred 20 mL of THF at −78 °C. After the reaction vessel was allowed to slowly warm to room temperature over 4 h, the solvent was removed from the resulting yellow slurry to afford a pale yellow solid. The yellow solid was extracted twice with diethyl ether and once with THF. The remaining solid (480 mg, 84% yield) was shown to be spectroscopically homogeneous and indistinguishable from an authentic sample of $Pd(PPh_3)_4$ prepared by a literature procedure.[58] The extracts were concentrated in vacuo and the resulting yellow solid recrystallized from ether and hexane, affording 141 mg (82% yield) of phosphorane **2** that was identical with an authentic sample prepared by a literature procedure.[17] When the reaction was run in THF-d_8 with *t*-BuOK-d_9 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.

3,3-Dimethyl-1,1,1-trideuterio-2-butanone. A two-phase mixture of pinacolone (25 mL, 200 mmol), anhydrous potassium carbonate (500 mg, 3.62 mmol), and D_2O (99.8% d, 50 mL) was held at reflux for 48 h under N_2. The aqueous phase was removed, and the pinacolone was carried through two additional cycles using fresh potassium carbonate and fresh D_2O each time. After the third cycle, the organic layer was dried over anhydrous Na_2SO_4 and distilled (105 °C, 760 mm) to afford 14 g of 3,3-dimethyl-1,1,1-trideuterio-2-butanone (68% yield) with >99% deuteration at the methyl group as shown by 300-MHz ^1H NMR.

1-Bromo-1,1-dideuterio-3,3-dimethyl-2-butanone (3-d_2). Doubly deuterated **3**-d_2 was prepared in 68% yield from the trideuterated pinacolone (vide supra) by the procedure used to prepare **3** with substitution of $CDCl_3$ for $CHCl_3$ as reaction solvent. 300-MHz ^1H NMR ($CDCl_3$) showed 98% deuteration of the bromomethyl moiety of **3**-d_2.

$(PPh_3)_2$(Br)PdCD$_2$C(O)-*t*-Bu (1-d_2). Complex **1**-d_2 was prepared from **3**-d_2 by the procedure used to prepare **1**. The 300-MHz ^1H NMR showed 1.92 deuteria per methylene moiety.

1-Bromo-1-deuterio-3,3-dimethyl-2-butanone (3-d_1). To a solution of lithium diisopropylamide (3.80 mmol) in 15 mL of anhydrous THF at −78 °C under N_2 was added **1**-d_2 (405 μL, 3.00 mmol) in 1.0 mL of THF. After being stirred at −78 °C for 45 min, the contents of the reaction were transferred by cannulation into 20 mL of 1:1 THF/H_2O. Following extraction with CH_2Cl_2 (3 × 20 mL), the combined organic layers were dried (Na_2SO_4) and concentrated. Kugelrohr distillation (11 mm, 75–85 °C) afforded 470 mg (87% yield) of **3**-d_1 exhibiting 1.08 deuteria per bromomethyl moiety as shown by 300-MHz ^1H NMR spectroscopy.

$(PPh_3)_2$(Br)PdC(D)HC(O)-*t*-Bu (1-d_1). **1**-d_1 was prepared from **3**-d_1 as described above for **1**. The 300-MHz ^1H NMR analysis showed an average of 1.0 deuteria per methylene moiety.

[P(*p*-tolyl)$_3$]$_2$(Br)PdCH$_2$C(O)-*t*-Bu (5). Complex **5** was prepared analogously to **1** by starting with $(p\text{-tolyl}_3P)_4Pd$.[58] Recrystallization from hexane/ether afforded the product as off-white microcrystals (71% yield): ^1H NMR (C_6D_6) δ 7.90 (br m, 12 H), 6.97 (m, 12 H), 2.00 (s, 18 H), 0.55 (s, 9 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 25.31; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 219.0 (CO), 140–126 (envelope of aryl carbons), 44.6 (quaternary C), 32.0 (CH_2), 27.4 (CH_3), 21.2 (aryl-CH_3). Anal. Calcd for $C_{48}H_{53}BrP_2PdO$: C, 64.50; H, 5.98; P, 6.94; Pd, 11.91. Found: C, 64.43; H, 5.96; P, 7.04; Pd, 11.85.

[P(p-tolyl)$_3$]$_2$(Br)PdCD$_2$C(O)-*t*-Bu (5-d_2). **5**-d_2 was prepared as described for **5**. The 300-MHz ^1H NMR analysis showed an average of 1.90 deuteria per molecule.

Authentic $Ph_3P{=}CHC(O)$-*t*-Bu (2).[17] Phosphorane **2** prepared by a standard literature procedure exhibited the following spectroscopic characteristics: ^1H NMR (THF-d_8) δ 7.7–6.8 (m, 15 H), 3.64 (d, J_{P-H} = 28 Hz, 1 H), 0.12 (s, 9 H); ^1H NMR (C_6D_6) δ 7.85–6.80 (m, 15 H), 3.96 (d, J_{P-H} = 28 Hz, 1 H), 1.51 (s, 9 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.38 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 199.6 (CO), 133.6–126.9 (envelope of aryl carbons), 45.9 (d, J_{P-C} = 110 Hz, CH), 40.9 (d, J_{P-C} = 12 Hz, quaternary carbon), 29.3 (CH_3).

Authentic (*p*-Tolyl)$_3$P=CHC(O)-*t*-Bu (4). A solution of 1-bromo-3,3-dimethyl-2-butanone (**3**; 135 μL, 1.0 mmol) and tri-*p*-tolylphosphine (300 mg, 1.0 mmol) in anhydrous THF under N_2 was heated at 60 °C for 3 h. After the mixture was cooled to −78 °C, 10 mL of THF followed by oil-free KH (60 mg, 1.50 mmol) was added sequentially. The solvent was removed in vacuo to afford a pale yellow oil. Recrystallization from hexane provided 280 mg of **4** (70% yield) as white crystals: ^1H NMR (THF-d_8) δ 7.72 (dd, J_{H-H} = 8.1 Hz, J_{P-H} = 12.1 Hz, 2 H), 6.88 (dd, J_{H-H} = 8.1, J_{P-H} = 2.4 Hz, 2 H), 4.04 (d, J_{P-H} = 27.5 Hz, 1 H), 1.94 (s,

(57) Although metal-centered P–C bond formation has been suspected to occur intramolecularly in several instances (cf. ref 1d, 31b, 49, 52d), we are unaware of any fully documented examples. A recent publication cites such a migration as unpublished work from R. R. Schrock's laboratories (Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 3913). However, the necessary control experiments had not been carried out. Schrock, R. R., personal communication.

(58) Garrou, P.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115. Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(59) **Note Added in Proof.** Cp(CO)(NO)ReCH$_2$CN can be deprotonated (*n*-BuLi) and alkylated to give Cp(CO)(NO)ReCH(CH$_3$)CN. Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103.

9 H, Ar-Me), 1.54 (s, 9 H, *t*-Bu); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 14.5 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 199.5 (s, CO), 142–124 (envelope of aryl carbons), 46.8 (d, J_{P-C} = 110 Hz), 41.0 (d, J_{P-C} = 10 Hz, quaternary C), 29.4 (s, CH_3), 21.3 (s, CH_3-aryl); IR (film) 1595 (m), 1525 (s), 1480 (s), 1100 (s) cm^{-1}; exact mass calcd for $C_{27}H_{31}OP$ 402.2112, found 402.2091.

Crossover Experiment. To an argon-flushed NMR tube at −95 °C were added **1** (5 mg) and **5**-d_2 (5 mg) each in 175 μL of THF-d_8, followed by *t*-BuOK-d_9 (14 mg) in 200 μL of THF-d_8. 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 3.64 ppm corresponding 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**-d_2, 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 10 mg (0.012 mmol) of complex **1**·(CH_2Cl_2) and PPh_3 (32 mg, 0.12 mmol) in THF-d_8 (250 μL) and capped with a septum. After cooling the tube to −78 °C under argon, a solution of freshly sublimed *t*-BuOK (14 mg, 0.12 mmol) in THF-d_8 (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 ≤4 min.) The reaction was monitored for loss of the *tert*-butyl resonance of **1** at 0.12 ppm relative to a CH_2Cl_2 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=C(OSiMe$_3$)Bu (7). To a solution of lithium diisopropylamide (1.00 mmol) in THF (3 mL) at −78 °C under nitrogen was added neat bromo ketone **1** (135 μL, 1.00 mmol). (Note: a procedure for the generation and isolation of the solvent free enolate **10** as a stable crystalline solid is described later.) After 0.5 h the reaction was quenched with freshly distilled trimethylsilyl chloride (130 μL, 1.10 mmol). The reaction was warmed to room temperature and partitioned between ethyl acetate and aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4), stripped to an oil, and flash chromatographed (hexane) to afford 140 mg (56% yield) of **7**. ^1H NMR (C_6D_6) δ 5.24 (s, 1 H), 0.91 (s, 9 H), 0.30 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 162.3 (C-OMe$_3$Si), 83.0 (CHBr), 38.0 ($C(CH_3)_3$), 28.1 (CH_3 of *t*-Bu), 1.3 ($SiCH_3$); IR (film) 3120 (w), 2960 (s), 1620 (s) cm^{-1}; exact mass calcd for $C_9H_{19}BrOSi$ 250.0389, found 250.0385. Irradiation of the silyl resonance at 0.30 ppm in the ^1H NMR spectrum had no measurable affect on the vinyl resonance at 5.24 ppm. However, irradiation of the *tert*-butyl resonance at 0.91 ppm led to a 21% NOE enhancement of the vinyl resonance.

Reaction of 7 with Pd(PPh$_3$)$_4$. A solution of enol ether **7** (5 mg, 0.020 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in benzene-d_6 (0.5 mL) in a sealed NMR tube under N_2 was heated in a 100 °C oil bath. Aside from aromatic resonances derived from triphenylphosphine-containing materials, the only products observable by 80-MHz ^1H NMR spectroscopy were those derived from phosphorane **2** and an envelope of trimethylsilyl fragments (0.4–0.1 ppm).

Reaction of 9 with Pd(PPh$_3$)$_4$. To an NMR tube charge with $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) was added dibromo ketone **9**[29] (6 mg, 0.023 mmol) in 0.5 mL of C_6D_6 at 25 °C. Rapid reaction lead to a 2:3 mixture of isomeric oxidative adducts. *cis*-**8** (minor isomer): ^1H NMR (300 MHz) δ 8.1–6.9 (br m), 4.55 (dd, J_{P-H} = 14.3 Hz, 9.5 Hz, 1 H), 1.42 (s, 9 H). *trans*-**8** (major isomer): ^1H NMR (300 MHz) δ 8.1–6.9 (br m), 4.81 (t, J_{P-H} = 8 Hz, 1 H), 1.02 (s, 9 H). Upon standing for 2 days at 25 °C *cis*-**8** and *trans*-**8** disappeared with concomitant appearance of phosphorane **2**. (See preparation of authentic **2** for NMR shifts in C_6D_6.)

Bromo Enolate 10. To a solution of $(Me_3Si)_2NH$ (1.0 mL, 4.76 mmol) in 35 mL of toluene under argon at −78 °C was added 2.2 M *n*-BuLi in hexane (4.50 mmol). After the solution was stirred at −78 °C for 15 min, bromo ketone **3** (607 μL, 4.50 mmol) in hexane (0.40 mL) was added. After an additional 1.0 h at −78 °C the vessel was warmed to 25 °C and the contents were stirred for 0.5 h. The solution was then stripped in vacuo to approximately 15 mL and diluted with 30 mL of hexane by vacuum transfer to afford white crystals. After the mixture was cooled to −78 °C, the crystals of enolate **10** were filtered and dried in vacuo (yield 570 mg, 68%): ^1H NMR (80 MHz, C_6D_6) δ 4.98 (s, 1 H), 1.06 (s, 9 H).

Addition of 10 to Pd(PPh$_3$)$_4$: Stoichiometric. An argon-flushed NMR tube was charged with $(PPh_3)_4Pd$ (40 mg, 0.035 mmol), bromo enolate **10** (23 mg, 0.12 mmol), and C_6D_6 (2.0 mL) and then sealed under vacuum with a flame. After 45 h at 25 °C proton NMR analysis showed the complete disappearance of the resonances corresponding to enolate **10** and the concomitant clean formation of resonances corresponding to phosphorane **2** (to the exclusion of significant quantities of other resonances). The resulting black reaction mixture was passed through a short column of silica gel (methanol elution) to removed the Pd metal, and the eluate was flash chromatographed (5% ethanol/ethyl acetate) on silica gel to afford phosphorane **2** (27 mg, 62% yield) that was pure by proton NMR.

Addition of 10 to Pd(PPh$_3$)$_4$: Catalytic. An NMR tube was charged with PPh_3 (46 mg, 0.176 mmol), enolate **10** (30 mg, 0.16 mmol), $(PPh_3)_4Pd$ (9 mg, 0.008 mmol), and C_6D_6 (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 95% conversion).

Diazo Ketone 11.[34] Diazo ketone **11** was prepared by a nondescript literature procedure as follows. To a solution of pivaloyl chloride (590 mg, 4.90 mmol) in 20 mL of anhydrous diethyl ether at 0 °C under N_2 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 (C_6D_6) δ 4.35 (s, 1 H), 0.91 (s, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 200.4 (CO), 51.0 (br s, CHN_2), 41.7 (quaternary C), 26.2 (CH_3); IR (film) 3000, 2100, 1630, 1480 cm^{-1}.

Reaction of 11 with Pd(PPh$_3$)$_4$. A solution of $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) and diazo ketone **11** (15 mg, 0.12 mmol)[35] in benzene-d_6 under N_2 was heated in a sealed NMR tube at 55 °C with monitoring by 80-MHz ^1H NMR spectroscopy. (The reaction darkened from the deposition of Pd metal.) Minor resonances attributable to phosphazine **12** appeared: δ 1.31 (s, 9 H), 8.55 (d, J_{P-H} = 3 H; or uncoupled syn and anti isomers). These were slowly replaced with resonances corresponding to phosphorane **2** over a period of 48 h.[35] When an experiment was performed in the absence of $Pd(PPh_3)_4$, the resonances assigned to phosphazine **12** and diazo ketone **11** (approximate 1:1 ratio) persisted unchanged for up to 72 h at 60 °C/h.

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