Reductive Elimination from Metal Phosphonate Complexes: Circumvention of Competing Protonolysis Reactions

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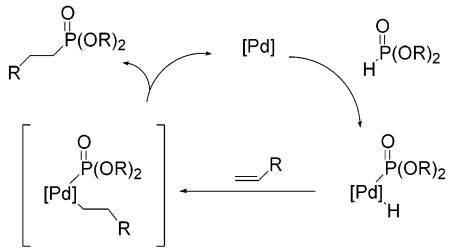
The formation of $MeP(O)(OPh)_2$ by reductive elimination from $L_2PdMe(P(O)(OPh)_2)$ species has been investigated. The electronic and steric effects of the supporting ligands were investigated by studying reductive elimination reactions from a series of discrete complexes containing nitrogen- and phosphorus-based ligands. The P(O)−C(sp^3) bond-forming reaction is slow when the intermediate species contains bidentate nitrogen ligands or small basic monodentate phosphines. Analogous complexes bearing large bite angle diphosphines such as dppf and Xantphos undergo reductive elimination at ambient temperature. The rate of $MeP(O)(OPh)_2$ formation by reductive elimination from $(dppf)PdMe(P(O)(OPh)_2)$ is not affected by the identity or concentration of added ligand (excess dppf or PPh_3), suggesting that the reductive elimination occurs from a four- or three-coordinate intermediate. When the rate of reductive elimination is slow, protonolysis reactions between $L_2PdMe(P(O)(OPh)_2)$ intermediates and $HP(O)(OPh)_2$ leads to the formation of bis-phosphonate complexes. The protonolysis reaction can be circumvented by the use of large bite angle phosphines such as dppf and Xantphos, which lead to rapid rates of P(O)−C(sp^3) bond formation. These results demonstrate that the formation of P(O)−C(sp^3) bonds by reductive elimination from $L_2PdRP(O)(OR)_2$ complexes is quite sensitive to the steric bulk of the supporting ligand and the presence of excess hydrogen phosphonate.

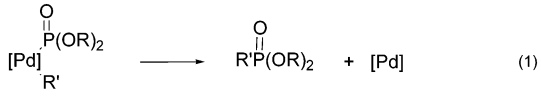
Introduction

Processes leading to the formation of P(O)−C(sp^3) bonds have been the subject of an intense amount of research, due to the myriad of applications the resulting compounds have in medicinal, organic, and agricultural chemistry.[1] Historically, these compounds are prepared by Arbusov or Pudovik type reactions;[1a,2] however, the development of a metal-mediated process is attractive, due to the ability of transition-metal catalysts to manipulate the regioselectivity and stereoselectivity of a reaction by modification of the ligand architecture. While various transition-metal-catalyzed routes are known for the formation of C−N, C−O, and P−C(sp^2,-sp^3) bonds,[3] analogous processes that form P(O)−C(sp^3) bonds are rare.[4] Of particular interest is the addition of hydrogen phosphonates to olefins (Scheme 1). Tanaka has reported the addition of a pinacol-derived hydrogen phosphonate to a variety of olefins; however, simple substrates such as $HP(O)(OR)_2$ (R = alkyl, aryl) were unreactive.[4a] Recently, Montchamp has reported the addition of hypophosphorus derivatives to alkenes and alkynes, but substrates such as $HP(O)(OBu)_2$ were unreactive.[5] Despite the screening of a number of catalysts, the factors behind this lack of reactivity remain unknown.

Scheme 1. Mechanism for the Palladium-Catalyzed Addition of a Hydrogen Phosphonate to an Olefin by Insertion of the Olefin into the Pd−H Bond[6]



A possible key step in the addition of hydrogen phosphonates to alkenes is the reductive elimination from $L_nPdR(P(O)(OR)_2)$ intermediates (eq 1).[6] We have recently found that complexes of this type are remarkably stable and can be isolated as crystalline solids.[7]



$[Pd] = L_nPd$; R = alkyl, aryl; R' = alkyl

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(1) *A Guide to Organophosphorus Chemistry*; Quin, L. D., Ed.; Wiley-Interscience: New York, 2000.

(2) The radical addition process is also known: Stiles, A. R.; Vaughan, W. E.; Rust, F. F. *J. Am. Chem. Soc.* **1958**, *80*, 714.

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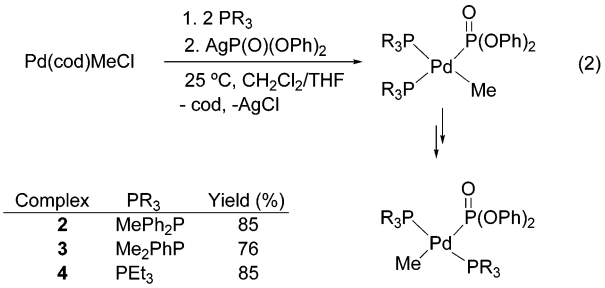
To investigate the importance of these key intermediates in P(O)−C(sp^3) bond-forming reactions and to further the understanding of the factors behind carbon−heteroelement bond-forming reactions, we have studied the reductive elimination of $MeP(O)(OPh)_2$ from a series of $L_nPdMe(P(O)(OPh)_2)$ complexes bearing monodentate and bidentate phosphine ligands.

Results and Discussion

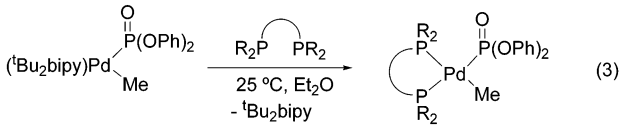
Synthesis and Characterization of Discrete Compounds. The complex (^{t}Bu$_2$bipy)PdMe(P(O)(OPh)$_2$) (**1**; ^{t}Bu$_2$bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) was prepared by treatment of (^{t}Bu$_2$bipy)PdMeCl with 1 equiv of Ag(P(O)(OPh)$_2$) in CH_2Cl_2/THF followed by filtration and drying. Compound **1** is a colorless solid that is stable in solution or the solid state for extended periods of time. No $MeP(O)(OPh)_2$ was observed upon heating **1** (toluene, 120 °C, 24 h).[7] Treatment of **1** with 2 equiv of a trialkylphosphine displaced the ^{t}Bu$_2$bipy ligand and formed complexes of the type $(PR_3)_2PdMe(P(O)(OPh)_2)$ (PR_3 = $PMePh_2$ (**2**), PMe_2Ph (**3**), PEt_3 (**4**)). Monitoring the reaction by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy showed that the displacement reaction was complete within minutes at 25 °C. The cis isomers of **2** and **4** were formed initially and slowly converted into the trans isomers upon standing in $CDCl_3$ or C_6D_6. Only the trans isomer of **3** was observed upon treatment of **1** with Me_2PhP, even with deficiencies of Me_2PhP. Excess phosphine exchanged with the coordinated phosphine and accelerated the cis to trans isomerization. Once the trans isomer was formed, conversion back into the cis isomer was not observed. No $MeP(O)(OPh)_2$ was observed at room temperature from solutions of **1**−**4**. Although treatment of **1** with small basic phosphines generated the desired $(PR_3)_2PdMe(P(O)(OPh)_2)$ complexes, analogous reactions with 2 equiv of a bulky trialkylphosphine such as PCy_3 afforded mixtures of **1**, $MeP(O)(OPh)_2$, and $Pd(PCy_3)_n$. Increasing the amount of PCy_3 increased the amount of $MeP(O)(OPh)_2$ that was formed in these reactions. Due to the difficulty of separating ^{t}Bu$_2$bipy from **3** and **4**, these complexes were isolated by starting from Pd(cod)MeCl (eq 2).



(2)

Complex	PR_3	Yield (%)
2	$MePh_2P$	85
3	Me_2PhP	76
4	PEt_3	85

Complexes containing diphosphine ligands were prepared by treatment of **1** or (dNbipy)PdMe(P(O)(OPh)$_2$)[7] (dNbipy = 4,4′-dinonyl-2,2′-bipyridine) with 1 equiv of the diphosphine in Et_2O at ambient temperature. The metal phosphonate complexes LPdMe(P(O)(OPh)$_2$) (**5**−**8**; L = dppe, dppp, dppb, dppf)[8] precipitated from solution and were isolated as analytically pure colorless to tan solids by simple filtration followed by washing with diethyl ether (eq 3). Similar to **2**−**4**, complexes **5**−**8**



(3)

were quite robust in the solid state and could be stored for long periods of time with minimal decomposition. Although free phosphine rapidly exchanged with coordinated phosphine in complexes **2**−**4,** excess bidentate phosphine did not exchange with the coordinated phosphine in **5**−**8**, as evidenced by sharp resonances in the ^{31}P and ^{1}H NMR spectra for the metal complex and the free diphosphine. Attempts to prepare a diphosphine complex containing Xantphos were unsuccessful, since $MeP(O)(OPh)_2$ was generated rapidly (quantitative formation within a few minutes at 25 °C) when 1 equiv of Xantphos was added to solutions of **1**. Carrying out this reaction at low temperature afforded mixtures.

Compounds **5**−**8** and the cis isomers of **2** and **4** exhibit three resonances in the ^{31}P NMR spectrum (Table 1) with the high-frequency signal due to the −P(O)(OPh)$_2$ group (85.5−89.3 ppm). The coupling constant between the trans phosphorus nuclei lies between 564.3 and 602.8 Hz, while the cis coupling constant varies between 22.5 and 68.3 Hz. The signal in the ^{1}H NMR spectrum for the Pd−*Me* group in **5**−**8** and the cis isomers of **2** and **4** appears as a doublet of doublets of doublets with coupling constants between 3.1 and 9.9 Hz. The trans isomers of **2**−**4** exhibit two signals in the ^{31}P{^{1}H} NMR spectrum which appear as a doublet and triplet with coupling constants between 35.4 and 58.7 Hz. The resonance in the ^{1}H NMR spectrum for the Pd−*Me* group of the trans isomers of **2**−**4** appears as a doublet of triplets with trans couplings of 9.9−10.1 Hz and cis couplings between 6.2 and 7.0 Hz (Figure 1).

Compound **5** was further characterized by single-crystal X-ray diffraction. The asymmetric unit contains two independent molecules of **5** (**5a**,**b**) and two symmetry-independent molecules of CH_2Cl_2. The ORTEP diagram is shown in Figure 2, crystal refinement data are given in Table 2, and bond lengths and angles are

(3) For recent reviews on C−O and C−N bond-forming reactions see: (a) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (b) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (d) Baranano, D.; Mann, G.; Hartwig, J. F. *Curr. Org. Chem.* **1997**, *1*, 287. For recent reports concerning P−C(sp^2,sp^3) bond formation see: (e) Moncarz, J. R.; Laritcheva, N. F.; Glueck, D. S. *J. Am. Chem. Soc.* **2002**, *124*, 13356. (f) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039. (g) Moncarz, J. R.; Brunker, T. J.; Glueck, D. S.; Sommer, R. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1180. (h) Moncarz, J. R.; Brunker, T. J.; Jewett, J. C.; Orchowski, M.; Glueck, D. S.; Sommer, R. D.; Lam, K.-C.; Incarvito, C. D.; Concolino, T. E.; Ceccarelli, C.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 3205.

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(6) The formation of $L_nPdR(P(O)(OR)_2)$ intermediates is a result of insertion of the alkene into the Pd−H bond of a $L_nPdH(P(O)(OR)_2)$ intermediate. Insertion into the Pd−P bond is also possible: Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381.

(7) Levine, A. M.; Stockland, R. A., Jr.; Clark, R.; Guzei, I. *Organometallics* **2002**, *21*, 3278.

(8) Abbreviations: dppe = bis(diphenylphosphino)ethane, dppp = bis(diphenylphosphino)propane, dppb = bis(diphenylphosphino)butane, dppf = bis(diphenylphosphino)ferrocene.

Table 1. $^{31}P\{^1H\}$ NMR Data for $L_2PdMe(P(O)(OPh)_2)$ Complexes[a]

ligand	complex	P^b	P^c	P^d
$PMePh_2$ (cis isomer)	**2**	88.5	8.2	2.9
$PMePh_2$ (trans isomer)	**2**	99.6	16.5	16.5
PMe_2Ph (trans isomer)	**3**	99.5	−0.3	−0.3
PEt_3 (cis isomer)	**4**	87.4	12.1	10.3
PEt_3 (trans isomer)	**4**	99.8	17.8	17.8
dppe	**5**	92.9	48.3	40.1
dppp	**6**	89.3	11.0	−0.8
dppb	**7**	88.4	30.6	7.6
dppf	**8**	85.5	25.8	14.9

[a] NMR spectra recorded in $CDCl_3$ at 25 °C. For the cis isomers, P^b= −P(O)(OPh)$_2$, P^c= −PR_3 trans to −P(O)(OPh)$_2$, and P^d= −PR_3 cis to −P(O)(OPh)$_2$. For the trans isomers, P^b = −P(O)(OPh)$_2$, and P^c and P^d = cis-PR_3 groups.

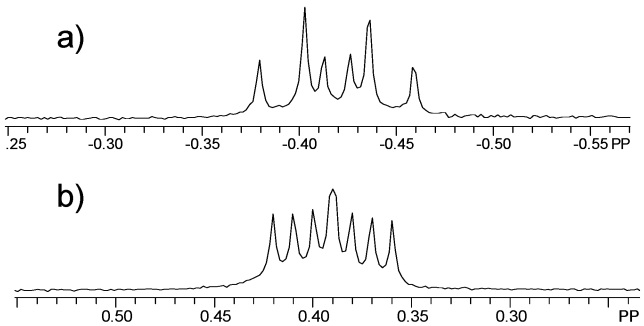


Figure 1. Representative ^1H NMR (300 MHz, $CDCl_3$, 25 °C) spectra (PdMe region): (a) *trans*-$(Me_2PhP)_2PdMe(P(O)(OPh)_2)$; (b) (dppb)PdMe(P(O)(OPh)$_2$).

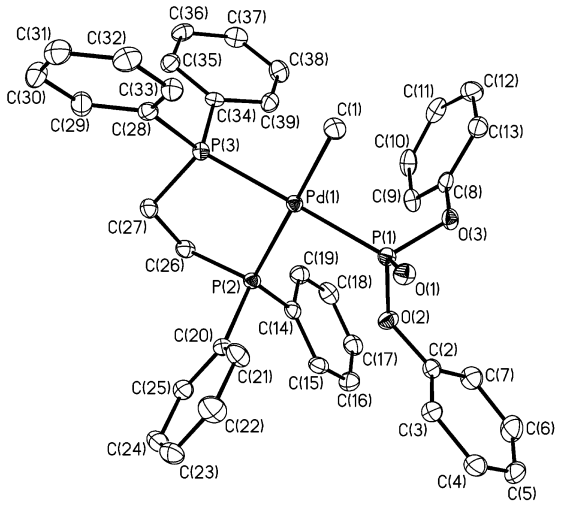


Figure 2. ORTEP diagram of one of the independent molecules of **5** with thermal ellipsoids shown at 50% probability and hydrogen atoms removed for clarity.

listed in Table 3. The major difference between the two complexes is rotation of one of the −PPh_2 aryl rings. The Pd−Me bond lengths in **5a**,**b** are indistinguishable (2.114(3) Å, **5a**; 2.110(3) Å, **5b**) and typical of methylpalladium complexes.[9] The Pd−P(O) distances are also indistinguishable in **5a**,**b** (**5a**, 2.2871(7) Å; **5b,** 2.2869(8) Å) and are similar to those in other palladium and platinum phosphonate complexes.[10] The Pd−P bonds lengths are similar (**5a**, 2.3352(7) and 2.3301(8) Å; **5b**, 2.3128(7) and 2.3293(7) Å) with the Pd−P bond trans to the methyl group slightly shorter than the Pd−P bond length trans to the P(O)(OPh)$_2^-$ group in **5a** and slightly longer in **5b**, suggesting that the trans influence of P(O)(OPh)$_2^-$ is similar to that of the methyl group.[7]

In contrast to reactions involving **1** and small basic trialkylphosphines, treatment of **1** with triarylphosphines such as PPh_3, $P(4\text{-}C_6H_4F)_3$, and $P(4\text{-}C_6H_4Cl)_3$ did not afford complexes of the type $(PR_3)_2PdMe(P(O)(OPh)_2)$. Monitoring the reaction by NMR spectroscopy revealed that the resonances in the ^1H NMR spectrum for the ^{t}Bu$_2$bipy aromatic hydrogens were broadened into the baseline. Additionally, the signals in the $^{31}P\{^1H\}$ NMR spectrum for PR_3 were broadened as well (ca. ∼80 Hz). These data suggested that the metal complex was undergoing reversible coordination of the phosphine and/or intramolecular interconversion of a five-coordinate species. This type of dynamic solution behavior is well-known for d^8 square-planar complexes.[11] After the mixture stood at 25 °C for several hours, MeP(O)(OPh)$_2$ was observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra (50% conversion by NMR). Treatment of a $(PR_3)_2PdMeCl$ precursor with 1 equiv of Ag(P(O)(OPh)$_2$) was a successful alternative method for the formation of $(PR_3)_2PdMe(P(O)(OPh)_2)$ complexes containing PEt_3 and PMe_2Ph; however, these reactions afforded an intractable mixture of metal-containing products and MeP(O)(OPh)$_2$ when PPh_3, $P(4\text{-}C_6H_4F)_3$, and $P(4\text{-}C_6H_4Cl)_3$ were used.

The reaction stoichiometry was also monitored by NMR spectroscopy using **1** + PPh_3 as the model system. Addition of 2 equiv of PPh_3 to a $CDCl_3$ solution of **1** at 25 °C under nitrogen afforded 0.5 equiv of MeP(O)(OPh)$_2$, 0.5 equiv of unreacted **1**, and 0.5 equiv of Pd(PPh_3)$_4$ after standing for 24 h (eq 4). Although Pd(PPh_3)$_4$ is known to dissociate into Pd(PPh_3)$_3$ and free PPh_3,[12] there was no further generation of MeP(O)(OPh)$_2$. The addition of 4 equiv of PPh_3 resulted in

(9) The Cambridge Structural Database contains 142 entries which have palladium−methyl bonds; Pd−Me distances range from 1.946 to 2.189 Å.

(10) Other examples of structurally characterized organometallic complexes (non-Cp) include: (a) Boone, B. J.; Jablonski, C. R.; Jones, P. G.; Newlands, M. J.; Yu, Y. *Organometallics* **1993**, *12*, 3042. (b) Stockland, R. A., Jr.; Maher, D. L.; Anderson, G. K.; Rath, N. P. *Polyhedron* **1999**, *18*, 1067. (c) Lin, I. J. B.; Kao, L. T. C.; Wu, F. J.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1986**, *309*, 225. Ruthenium carbene complexes: (d) Leung, W. H.; Chan, E. E. Y.; Williams, I. D.; Wong, W. T. *Organometallics* **1997**, *16*, 3234. (e) Leung, W. H.; Chan, E. E. Y.; Wong, W. T. *Organometallics* **1998**, *17*, 1245. (f) Chang, C. W.; Lin, Y. C.; Lee, G. H.; Huang, S. L.; Wang, Y. *Organometallics* **1998**, *17*, 2534. (g) Chang, C. W.; Lin, Y. C.; Lee, G. H.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 4223. η^2-Bound olefins: (h) Leung, W. H.; Chan, E. Y. Y.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 136. (i) Kläui, W.; Lenders, B.; Irmier, M.; Meyer, G. *J. Chem. Soc., Dalton Trans.* **1990**, 2069. (j) Arena, C. G.; Nicolò, F.; Drommi, D.; Bruno, G.; Faraone, F. *J. Chem. Soc., Dalton Trans.* **1996**, 4357. Acyl complexes: ref 12. Fluorinated alkyl substituents: (k) Zhou, Z.; Jablonski, C. R.; Bridson, J. *Organometallics* **1994**, *13*, 781. (l) Jablonski, C. R.; Huaizhu, M.; Hynes, R. *Organometallics* **1992**, *11*, 2796.

(11) (a) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007. (b) Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1996**, *15*, 4012. (c) Stockland, R. A., Jr.; Anderson, G. K. *Organometallics* **1998**, *17*, 4694. (d) Romeo, R. Fenech, L.; Scolaro, L. M.; Albinati, A.; Macchioni, A.; Zuccaccia, C. *Inorg. Chem.* **2001**, *40*, 3293. (e) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061. (f) Cesares, J. A.; Espinet, P. *Inorg. Chem.* **1997**, *36*, 5428. (g) Albano, V. G.; Castellari, C.; Morelli, G.; Vitagliano, A. *Gazz. Chim. Ital.* **1989**, *119*, 235−239. (h) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185. (i) Ugi, I.; Marquarding, D.; Klusacek, H.; Fillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288. (j) For a review of five-coordinate palladium complexes see: Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, *133*, 67−114.

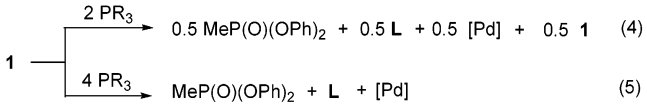
(12) Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186.

Table 2. Summary of Crystallographic Data for 5, 9, and 13

	13	5	9
empirical formula	$C_{34}H_{28}N_2O_6P_2Pd$	$C_{40}H_{39}Cl_2O_3P_3Pd$	$C_{78}H_{72}Cl_4O_8P_6Pd$
formula wt	728.92	837.92	1571.38
temp (K)	173(2)	100(2)	100(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syste	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P1$	$P2_1/c$
unit cell dimens			
a (Å)	9.3946(3)	9.4090(8)	12.5532(15)
b (Å)	34.3472(9)	11.6613(10)	16.599(2)
c (Å)	19.4549(5)	17.6423(15)	17.600(2)
α (deg)	90	93.0130(10)	90
β (deg)	101.726(1)	104.8470(10)	99.375(2)
γ (deg)	90	96.9180(10)	0
V (Å^3)	6146.7(3)	1850.4(3)	3618.2(8)
Z	8	2	2
calcd density (Mg/m^3)	1.575	1.504	1.442
abs coeff (mm^{-1})	0.758	0.814	0.593
F(000)	2960	856	1616
cryst size (mm^3)	0.38 × 0.26 × 0.18	0.39 × 0.30 × 0.19	0.39 × 0.25 × 0.18
θ range (deg)	1.22−26.36	2.05−26.50	2.35−26.46
no. of rflns collected	47 497	42 244	29 205
no. of unique rflns	12 541 (R(int) = 0.0337)	15 070 (R(int) = 0.0353)	7400 (R(int) = 0.0572)
completeness to θ	99.8%	99.0%	99.1
abs cor	empirical with DIFABS	multiscan with SADABS	multiscan with SADABS
max and min transmissn	0.8757 and 0.7616	0.8607 and 0.7420	0.9007 and 0.8016
no. of data/restraints/params	12 541/0/811	15 070/3/885	7400/0/439
goodness of fit on F^2	1.063	1.030	1.118
final R indices ($I > 2\sigma(I)$)	R1 = 0.0322	R1 = 0.0272	R1 = 0.0662
	wR2 = 0.0700	wR2 = 0.0653	wR2 = 0.1441
R indices (all data)	R1 = 0.0395	R1 = 0.0283	R1 = 0.0853
	wR2 = 0.0728	wR2 = 0.0659	wR2 = 0.1511
largest diff peak and hole (e/Å^3)	0.401 and −0.440	1.019 and −0.439	1.020 and −1.076

Table 3. Selected Bond Distances (Å) and Angles (deg) for 5

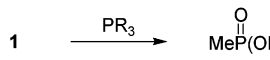
Pd(1)−C(1)	2.114(3)	Pd(2)−P(5)	2.3293(7)
Pd(1)−P(1)	2.2871(7)	P(1)−O(1)	1.4827(19)
Pd(1)−P(2)	2.3301(8)	P(1)−O(2)	1.650(2)
Pd(1)−P(3)	2.3352(7)	P(1)−O(3)	1.6553(19)
Pd(2)−C(40)	2.110(3)	P(4)−O(4)	1.484(2)
Pd(2)−P(4)	2.2869(8)	P(4)−O(6)	1.642(2)
Pd(2)−P(6)	2.3128(7)	P(4)−O(5)	1.6537(19)
C(1)−Pd(1)−P(1)	82.90(8)	C(1)−Pd(1)−P(3)	95.25(8)
C(1)−Pd(1)−P(2)	178.72(9)	P(1)−Pd(1)−P(3)	175.84(3)
P(1)−Pd(1)−P(2)	97.38(3)	P(2)−Pd(1)−P(3)	84.37(3)



L = ^{t}Bu$_2$bipy, [Pd] = Pd(PR$_3$)$_n$

complete conversion into the desired methylphosphonate and $Pd(PPh_3)_4$ (eq 5). These reactions were also sensitive to the solvent. When chlorinated solvents were used, the reductive elimination was 50% complete after 24 h when 2 equiv of PPh_3 was added. Longer reaction times or heating (110 °C) did not increase the yield of the methylphosphonate above 50%. Experiments carried out with C_6D_6 or toluene as the solvent resulted in a slight increase in the concentration of the methylphosphonate at ambient temperature (65%, 72 h, C_6D_6), while vigorous heating (120 °C) resulted in excellent yields of $MeP(O)(OPh)_2$ (quantified by NMR). The addition of excess PPh_3 (10, 100 equiv) resulted in the formation of $MeP(O)(OPh)_2$ in high yields at 25 °C (Table 4). Thus, the formation of $MeP(O)(OPh)_2$ from solutions of **1** + PR_3 was a ligand-induced process. However, reductive elimination from the isolated compound **8** (vide infra) was not a ligand-assisted process. While the overall reaction between **1** and PR_3 was an assisted process, it is likely that the role of the excess ligand was to promote displacement of the ^{t}Bu$_2$bipy ligand from the metal center, although it should be noted that the elimination from **8** could proceed through a different mechanism.

Table 4. Percent Conversion of 1 into MeP(O)(OPh)$_2$ upon Addition of PR$_3$[a]



		conversn (%) for PR$_3$ added[b]			
entry	PR$_3$	2 equiv	5 equiv	10 equiv	100 equiv
1	PPh_3	50 (60)	94 (95)	93 (96)	91 (94)
2	P(4-C$_6$H$_4$F)$_3$	50 (57)	90 (95)	97 (92)	95 (93)
3	P(4-C$_6$H$_4$Cl)$_3$	52 (55)	93 (92)	94 (92)	95 (91)
4	PPh(2-C$_6$H$_4$Cl)$_2$	0 (0)	0 (0)	0 (0)	0 (0)
5	P(2,4,6-C$_6$H$_2$Me$_3$)$_3$	0 (0)	0 (0)	0 (0)	0 (0)
6	P(2,4,6-C$_6$H$_2$(OMe)$_3$)$_3$	0 (0)	0 (0)	0 (0)	0 (0)
7	Me_2PhP	0 (0)	0 (0)	0 (0)	0 (0)
8	$MePh_2P$	0 (0)	0 (0)	0 (0)	0 (0)
9	PCy_3	37 (50)	65 (70)	70 (99)	95 (99)
10	PEt_3	0 (0)	0 (0)	0 (0)	0 (0)

[a] Reaction mixtures were stirred at 25 °C for 24 h with **1** (0.005 g, 0.08 mmol), $CDCl_3$ (0.5 mL), and the appropriate amount of phosphine. [b] Percent conversion was determined by integration of $MeP(O)(OPh)_2$ relative to an internal standard: C_6Me_6 (0.001 g, 0.012 mmol), a sealed capillary containing cyclooctadiene (1.0 μL, 0.082 mmol, DMSO-d_6 solution), or $P(O)Ph_3$ (0.003 g, 0.01 mmol). Numbers in parentheses refer to reactions carried out in toluene/C_6D_6.

Bulky triarylphosphines such as $PMes_3$ and P(2,4,6-$C_6H_2(OMe)_3)_3$ or weakly basic phosphines such as PPh-(2-$C_6H_4Cl)_2$[13] did not add to the palladium complex, as evidenced by sharp peaks for **1** and the free phosphine (identical with the chemical shifts for the isolated

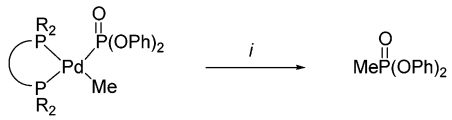
species) in the ^1H and ^{31}P NMR spectra. Treatment of **1** with up to 100 equiv of $PMes_3$ or $PPh(2\text{-}C_6H_4Cl)_2$ did not generate $MeP(O)(OPh)_2$ upon standing at 25 °C, but heating to 120 °C afforded the methylphosphonate in high yields. The use of PCy_3 as the supporting ligand afforded moderate yields of the desired product under mild conditions (Table 4, entry 9).

Thermolysis Reactions of 2−8. While heating a $CDCl_3$ solution of **2**, **3**, or **4** resulted in the formation of an intractable mixture of products with only traces of $MeP(O)(OPh)_2$ being observed, heating toluene or C_6D_6 solutions of these compounds to 120 °C generated the methylphosphonate in high yields. In the presence of up to 100 equiv of free phosphine, the only reaction products observed were the methylphosphonate and a $Pd(PR_3)_n$ species.

The relationship between the bite angle of a bidentate phosphine and the rate of reductive elimination has been the subject of numerous experimental and theoretical investigations.[14,15] In general, the larger the bite angle, the faster the rate of reductive elimination.[16] Although diphosphine bite angle effects have been well studied as they relate to carbon−carbon bond formation, their effects on P(O)−C(sp^3) bond-forming reactions have received less attention.

To investigate the relationship between the bite angle of the diphosphine and the rate of reductive elimination from $L_2PdMe(P(O)(OPh)_2)$ complexes, thermolysis reactions of **5**−**8** were carried out and monitored by NMR spectroscopy. Complexes containing small bite angles such as **5** and **6** or moderately large bite angles such as **7** did not undergo a P(O)−C(sp^3) bond-forming reaction at room temperature (Table 5). Heating $CDCl_3$ (120 °C) solutions of **5**−**7** afforded low yields of $MeP(O)(OPh)_2$. However, analogous reactions with toluene as the solvent afforded high yields of the desired product. While the reductive elimination of $MeP(O)(OPh)_2$ from **5**−**7** was sluggish at ambient temperature, complex **8** readily reductively eliminated the methylphosphonate in $CDCl_3$, toluene, or C_6D_6 at 25 °C. Additionally, treatment of **1** with 1 equiv of Xantphos (bite angle 111°) generated quantitative yields of the methylphosphonate within minutes at 25 °C in $CDCl_3$, toluene, or C_6D_6. The increased rate of reductive elimination in these reactions was attributed to either the large bite angle of the dppf or Xantphos ligand[17] or dissociation of one end of the diphosphine to generate a highly reactive three-coordinate complex. Buchwald has suggested that dissociation of one end of the Xantphos ligand was responsible for the ability of this ligand to promote coupling reactions,[18] and recent studies have shown that the formation of carbon−nitrogen bonds by reductive elimination from three-coordinate compounds was faster than from four-coordinate species.[19]

Table 5. Bite Angle and Temperature Effects on $MeP(O)(OPh)_2$ Formation[a]



entry	$R_2P\frown PR_2$	bite angle[c]	temp[b]	conversn[d]
1	dppe	85	25	0 (0)
2			120	10 (95)
3	dppp	91	25	0 (0)
4			120	20 (99)
5	dppb	98	25	0 (0)
6			120	28 (91)
7	dppf	99	25	95 (93)
8			120	73 (95)
9	Xantphos	111	25	98 (96)
10			120	95 (98)

[a] i = 1 equiv of $R_2P\frown PR_2$ as a trapping agent. Conversions listed refer to reactions carried out in $CDCl_3$, while numbers in parentheses refer to reactions carried out in toluene/C_6D_6 (5:1). Reactions were carried out using the disphosphine complex **5**, **6**, **7**, or **8** (0.005 g). Due to rapid formation of $MeP(O)(OPh)_2$ in runs 9 and 10, **1** + Xantphos was used as the model system. [b] Temperature is reported in °C. [c] Natural bite angles (in deg) were taken from ref 12. [d] Conversion (in percent) was determined by integration of $MeP(O)(OPh)_2$ relative to an internal standard: C_6Me_6 (0.001 g, 0.012 mmol), a sealed capillary containing cyclooctadiene (1.0 μL, 0.082 mmol, DMSO-d_6 solution), or $P(O)Ph_3$ (0.003 g, 0.01 mmol).

Complex **6** was used to study the thermolysis reaction in the presence of 1 equiv of the $^tBu_2$bipy ligand. Treatment of **6** with 1 equiv of $^tBu_2$bipy followed by heating to 75 °C (C_6D_6) afforded 0.5 equiv of $MeP(O)(OPh)_2$, 0.5 equiv of $(dppp)_2Pd$, and 0.5 equiv of ($^tBu_2$bipy)$PdMe(P(O)(OPh)_2)$ (eq 6). Further heating to 120

$$\mathbf{6} \xrightarrow[\text{toluene, 75 °C}]{^tBu_2\text{bipy}} 0.5\mathbf{1} + 0.5MeP(O)(OPh)_2 + 0.5[Pd] \quad (6)$$

$$[Pd] = (dppp)_2Pd$$

°C afforded moderate yields of $MeP(O)(OPh)_2$ (85%) and a mixture of $(dppp)_2Pd$, free Pd metal, and $^tBu_2$bipy. In the presence of excess dppp (5, 10, or 100 equiv), the $^tBu_2$bipy ligand did not affect the reaction outcome, and the only species observed after heating to 120 °C for 12 h was the desired methylphosphonate (>95% yield), free $^tBu_2$bipy ligand, the trapped Pd(0) species, and free dppp.

The possibility of a ligand-assisted reductive elimination reaction from **5**−**8** was investigated kinetically using **8** as the model system with 1−6 equiv of ligand (PPh_3, dppf) added to trap the generated Pd(0) species.[20] The complex, added ligand, internal standard, and solvent were added to an NMR tube, and ^1H and ^{31}P-

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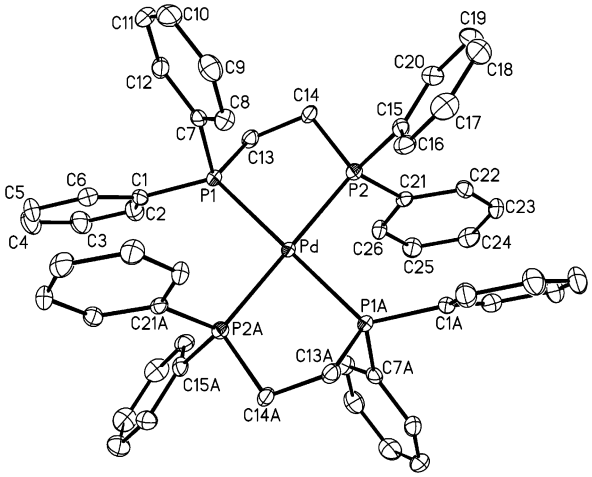


Figure 3. ORTEP of the cation of **9** with thermal ellipsoids shown at 50% probability and hydrogen atoms removed for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for the Cation of 9

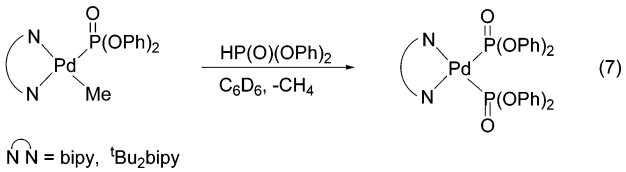
Pd−P(2)A	2.3348(10)	P(1)−C(1)	1.814(4)
Pd−P(2)	2.3348(10)	P(1)−C(7)	1.821(4)
Pd−P(1)	2.3469(10)	P(1)−C(13)	1.830(4)
Pd−P(1)A	2.3469(10)	P(2)−C(15)	1.810(4)
Cl(1)−C(39)	1.747(5)	P(2)−C(21)	1.818(4)
Cl(2)−C(39)	1.764(6)	P(2)−C(14)	1.851(4)
P(2)A−Pd−P(2)	180.00(6)	C(1)−P(1)−C(7)	103.79(19)
P(2)A−Pd−P(1)	97.34(4)	C(21)−P(2)−C(14)	105.90(19)
P(2)−Pd-P(1)	82.66(4)	C(15)−P(2)−Pd	119.01(14)
P(2)A−Pd−P(1)A	82.66(4)	C(21)−P(2)−Pd	111.31(13)
P(2)−Pd−P(1)A	97.34(4)	C(14)−P(2)−Pd	108.79(13)
P(1)−Pd−P(1)A	180.00(7)		

{^{1}H} NMR spectra were periodically recorded. The rate of the reductive elimination reaction was first order in metal complex and was not affected by the identity (PPh_3, dppf) or the concentration of the added ligand (1−6-fold excess of dppf). This suggested that the reductive elimination reaction was occurring from a three- or four-coordinate intermediate. However, our kinetic model cannot distinguish between elimination from a four-coordinate complex and dissociation of one of the arms of the diphosphine to generate a three-coordinate species which rapidly undergoes reductive elimination of $MeP(O)(OPh)_2$ followed by trapping of the Pd(0) species by free diphosphine.

Sensitivity of Phosphine-Containing Complexes. While quite robust in the solid state, complexes **2**−**8** were very sensitive to oxygen and moisture in solution. A solution of **5** (CH_2Cl_2) afforded a mixture of compounds after stirring at room temperature for 24 h. Cooling of the solution to −40 °C afforded crystals of $[Pd(dppe)_2][PO_2(OPh)_2]_2$ (**9**; ∼2% yield), which were separated by filtration. The ORTEP diagram of **9** is shown in Figure 3, crystal refinement data are listed in Table 2, and bond lengths and angles are listed in Table 6. The complex $[Pd(dppe)_2][PO_2(OPh)_2]_2 \cdot 2CH_2Cl_2$ crystallized as discrete anions and cations. The Pd(II) atom occupies a crystallographic inversion center, rendering the geometry about the metal center square planar. The Pd−P distance in **9** is 2.341(7) Å (average) and the ligand bite angle, P1−Pd−P2, is 82.66(4)° (average).

Protonolysis Reactions of Metal Phosphonate Complexes. The protonolysis of metal alkyl complexes is an efficient way to generate unsaturated metal complexes and metal−heteroelement bonds.[21] Thus, it is conceivable that treatment of $L_2PdR(P(O)(OR)_2)$ with $HP(O)(OR)_2$ could generate RH and $L_2Pd(P(O)(OR)_2)_2$. Additionally, if the rate of the protonolysis reaction was comparable to the reductive elimination reaction, it could compete with the P(O)−C(sp^3) bond-forming reaction. This process was realized in several recent reports. Treatment of $ZnMe_2$ with phenylphosphonic acid resulted in the formation of methane and $Zn(O_3PC_6H_5)$.[22] Tanaka reported that treatment of $(dppe)PdMe_2$ with 1 equiv of diphenylphosphinic acid afforded $(dppe)PdMe(OP(O)Ph_2)$,[23] and Schmidbaur has shown that PPh_3AuMe reacted with $HP(O)R_2$ (R = alkyl, alkoxy, aryl) complexes to generate gold phosphonate complexes of the type $Ph_3PAuP(O)R_2$.[24] To investigate the scope of this reaction as it relates to potential side reactions in metal-mediated P(O)−C(sp^3) bond-forming reactions, we have investigated the reaction of $L_2PdMe(P(O)(OPh)_2)$ (L = nitrogen- or phosphorus-based ligand) with the representative hydrogen phosphonate $HP(O)(OPh)_2$.

Since complexes of the type $(N\frown N)PdMe(P(O)(OPh)_2)$ ($N\frown N$ = bipy, ^{t}Bu$_2$bipy, dNbipy) did not reductively eliminate $MeP(O)(OPh)_2$ upon standing or heating, they provide a discrete system by which the protonation reaction can be studied in the absence of P(O)−C(sp^3) bond-forming reactions. Treatment of $(bipy)PdMe(P(O)(OPh)_2$ or **1** with $HP(O)(OPh)_2$ (CH_2Cl_2, 25 °C, 72 h) afforded methane and a mixture of palladium-containing complexes. Addition of diethyl ether to this mixture precipitated the bis-phosphonate complexes $(N\frown N)Pd(P(O)(OPh)_2)_2$ (bipy (**13**), 45% yield; ^{t}Bu$_2$bipy (**14**), 54%yield; eq 7). Although hydrogen phosphonates can



(7)

tautomerize into $P(OH)(OR)_2$ species and coordinate to metals,[25] no $MeP(O)(OPh)_2$ was observed in these reactions. Analogous reactions in $CDCl_3$ at higher temperatures (70 °C) yielded a mixture of compounds, with **13** and **14** being formed in lower yields. Due to the poor solubility of $(bipy)PdMe(P(O)(OPh)_2)$ in nonhalogenated solvents, **1** was used as the discrete model complex for reactions carried out in toluene and benzene. Treatment of **1** with 1 equiv of $HP(O)(OPh)_2$ in toluene (25 °C, 72 h) afforded the bis-phosphonate species in high yield

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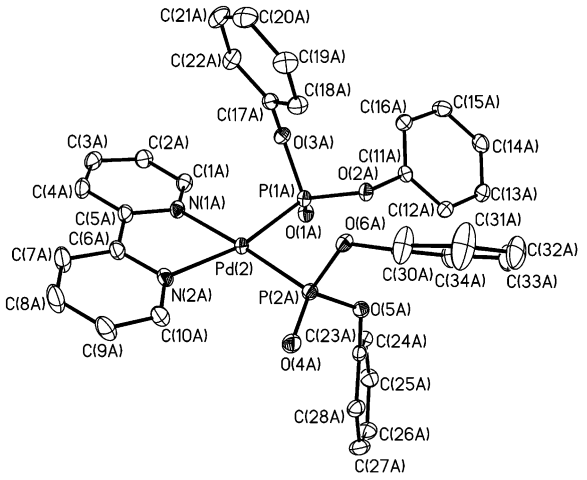


Figure 4. ORTEP diagram of one of the independent molecules of **13** with thermal ellipsoids shown at 50% probability and hydrogen atoms removed for clarity.

Table 7. Selected Bond Distances (Å) and Angles (deg) for 13

Pd(1)−N(2)	2.160(2)	Pd(2)−N(2A)	2.144(2)
Pd(1)−N(1)	2.165(2)	Pd(2)−N(1A)	2.151(2)
Pd(1)−P(1)	2.2377(6)	Pd(2)−P(1A)	2.2369(6)
Pd(1)−P(2)	2.2466(7)	Pd(2)−P(2A)	2.2509(6)
N(2)−Pd(1)−N(1)	76.70(8)	N(2A)−Pd(2)−N(1A)	77.23(8)
N(2)−Pd(1)−P(1)	168.62(6)	N(2A)−Pd(2)−P(1A)	166.68(6)
N(1)−Pd(1)−P(1)	92.97(6)	N(1A)−Pd(2)−P(1A)	90.88(6)
N(2)−Pd(1)−P(2)	100.05(6)	N(2A)−Pd(2)−P(2A)	100.36(6)
N(1)−Pd(1)−P(2)	174.57(6)	N(1A)−Pd(2)−P(2A)	176.43(6)
P(1)−Pd(1)−P(2)	90.60(2)	P(1A)−Pd(2)−P(2A)	91.78(2)

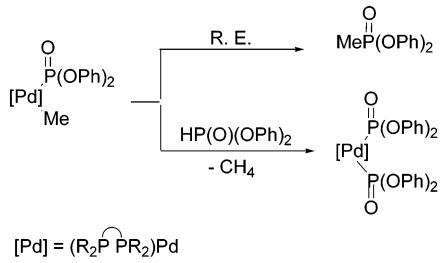
(quantified by NMR, 91% isolated). Heating **1** with 1 equiv of $HP(O)(OPh)_2$ (75 °C, 6 h, toluene) also formed **14** in high yield (85%).

Complex **13** was further characterized by single-crystal X-ray diffraction. The ORTEP diagram is shown in Figure 4, crystal refinement data are listed in Table 2, and bond lengths and angles are listed in Table 7. The asymmetric unit contains two independent molecules of **13** (**13a**,**b**), with the tilt of one of the P−OPh rings being the largest difference. The Pd−P bond lengths (**13a**, 2.2377(6) and 2.2466(7) Å; **13b**, 2.2369(6) and 2.2509(6) Å) are typical of those found in palladium and platinum phosphonate complexes.

Since complexes **5**−**8** reductively eliminated $MeP(O)(OPh)_2$ with rates dependent upon the identity of the diphosphine, these complexes were excellent model systems for comparing electrophilic alkyl abstraction vs reductive elimination. The results of a competition experiment would provide valuable information for the circumvention of the protonolysis reaction and give direction to the design of a successful olefin hydrophosphorylation catalyst.

The identity and concentration of the products from the reaction between **5**−**8** and $HP(O)(OPh)_2$ were dependent upon the solvent, phosphine, and temperature. No reaction was observed between **5**, **6**, or **7** and $HP(O)(OPh)_2$ at room temperature in toluene (12 h); however, heating these solutions gave varying yields of $MeP(O)(OPh)_2$ and the bis-phosphonate species depending upon the bite angle of the phosphine (Table 8). Addition of ether to reaction mixtures employing **5** and **6** precipitated $L_2Pd(P(O)(OPh)_2)_2$ (L_2 = dppe (**15**), dppp (**16**)). Increasing the concentration of $HP(O)(OPh)_2$ to

Table 8. Competing Processes: Reductive Elimination vs Protonation[a]



	conversn (%)	
diphosphine	bis-phosphonate	$MeP(O)(OPh)_2$
dppe	95	0
dppp	45	19
dppb	30	40
dppf	0	95
	0	90[c]
Xantphos	0	99[b]
	0	99[b,c]

[a] Reactions were carried out in C_6D_6 or toluene/C_6D_6 (5:1) with **5**−**7** (0.005 g). The appropriate amount of degassed $HP(O)(OPh)_2$ was added by syringe. [b] **1** + 2 equiv of Xantphos was used as the test case due to the rapid reductive elimination of $MeP(O)(OPh)_2$. [c] 10 equiv of $HP(O)(OPh)_2$ was used. Conversion was determined by integration of $MeP(O)(OPh)_2$ relative to an internal standard: C_6Me_6 (0.001 g, 0.012 mmol) or $P(O)Ph_3$ (0.003 g, 0.01 mmol).

10 equiv per Pd complex resulted in no methylphosphonate from **5**−**7**, even under rigorous conditions (toluene, 120 °C, 24 h), showing that the tautomer of diphenylphosphite ($P(OH)(OPh)_2$) does not promote this reaction.[25] These results demonstrated that the protonolysis reaction between $L_2PdMe(P(O)(OPh)_2)$ and $HP(O)(OPh)_2$ was competitive with reductive elimination when the methylphosphonate complex contains bipyridine-based or small bite angle phosphines and dominates at high concentrations of the hydrogenphosphonate.

In contrast to reductive elimination from **1**−**7**, complexes containing large bite angle diphosphines underwent the rapid reductive elimination of $MeP(O)(OPh)_2$ at room temperature. Since the protonolysis reaction between **1**−**7** and $HP(O)(OPh)_2$ was slow at 25 °C, and the reductive elimination of $MeP(O)(OPh)_2$ from **8** and solutions of **1** + Xantphos was rapid at this temperature, complexes with large bite angle phosphines offered the best chance of circumventing the protonolysis reaction. Treatment of **8** with 1 or 10 equiv of $HP(O)(OPh)_2$ did not effect the reductive elimination reaction (Table 8), and no protonolysis product was observed. Similarly, the addition of 1 or 10 equiv of $HP(O)(OPh)_2$ (premixed in toluene) to solid **1** + Xantphos afforded high yields of the methylphosphonate (quantified by NMR) within minutes.

Conclusions

The studies presented here enable several conclusions to be made about the formation of methylphosphonates from $[Pd]Me(P(O)(OPh)_2$ intermediates. The reductive elimination from $[Pd]R(P(O)(OR)_2)$ species can be quite facile, depending upon the ligand architecture and solvent. The fastest reductive elimination reactions were observed with large bite angle diphosphines such as Xantphos. These studies have also increased the understanding of the competing protonolysis reaction

between [Pd]R(P(O)(OR)$_2$) intermediates and free HP(O)(OR)$_2$, which is critical to the design of a successful catalyst, since a reaction mixture contains a large excess of hydrogen phosphonate relative to the metal complex. The results presented here demonstrate that the competing protonolysis reactions are only problematic when the rate of reductive elimination is slow. This secondary chemistry can be circumvented through the use of dppf or Xantphos as the supporting ligand. Current studies are focused on using this information to design a general catalytic system for the addition of simple hydrogen-phosphonates such as HP(O)(OR)$_2$ (R = Ph, Et) to alkenes.

Experimental Section

General Considerations. All reactions were performed under N_2 or vacuum using standard Schlenk techniques or in an N_2-filled drybox. Diethyl ether, CH_2Cl_2, benzene, and toluene were dried using a Grubbs-type solvent purification system. Toluene-d_8 and benzene-d_6 were distilled from sodium/benzophenone. $CDCl_3$ was dried over calcium hydride. Nitrogen was purified by passage through columns containing activated molecular analytical columns from Chromatography Research Supplies. The bipy, ^{t}Bu$_2$bipy, dNbipy, and phosphine ligands were obtained from Aldrich and used as received. The complexes Ag(P(O)(OPh)$_2$,[26] (^{t}Bu$_2$bipy)PdMeCl,[27] (bipy)PdMe(P(O)(OPh)$_2$),[7] and (dNbipy)PdMe(P(O)(OPh)$_2$)[7] were prepared as described previously. Elemental analyses were performed by Midwest Microlabs.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at ambient temperature unless specified otherwise. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent resonances, and all coupling constants are given in hertz. ^{31}P NMR spectra were referenced to external H_3PO_4 (0 ppm). Quantitative ^{31}P{^{1}H} NMR was obtained using an inverse-gated pulse program with a recycle delay of 30 s.

Preparation of (^{t}Bu$_2$bipy)PdMe(P(O)(OPh)$_2$) (1). A round-bottom flask was charged with (^{t}Bu$_2$bipy)PdMeCl (0.500 g, 1.18 mmol), Ag(P(O)(OPh)$_2$) (0.401 g, 1.18 mmol), THF (50 mL), and CH_2Cl_2 (50 mL). After the mixture was stirred for 3 h at 25 °C, the solvent was removed under vacuum and the residue extracted with CH_2Cl_2. Removal of the volatiles afforded **1** as an off-white solid (0.61 g, 83%). Anal. Calcd for $C_{31}H_{37}N_2O_3PPd$: C, 59.77; H, 5.94. Found: C, 59.76; H, 5.91. ^{1}H NMR spectrum ($CDCl_3$, 25 °C): δ 10.0 (d, 1H, J = 5.7, H6′), 8.43 (dd, 1H, J = 5.7, 3.6, H6), 7.92 (s, 1H, H3 or H3′), 7.86 (s, 1H, H3 or H3′), 7.43 (m, 2H, H5 and H5′), 7.32 (d, 4H, J = 8.4, *o*-C$_6H_5$), 7.14 (t, 4H, J = 7.8, *m*-C$_6H_5$), 6.91 (t, 2H, J = 7.3, *p*-C$_6H_5$), 1.35 (s, 9H, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu), 0.80 (s, 3H, Pd*Me*). ^{31}P{^{1}H} NMR spectrum ($CDCl_3$, 25 °C): δ 77.3. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 164.0 (s, quat), 162.8 (s, quat), 156.1 (s, quat), 153.7 (s, quat), 153.3 (s, C6′), 152.8 (d, J = 7.3, *ipso*-*C*$_6$H$_5$), 147.2 (s, C6), 128.8 (s, *m*-*C*$_6$H$_5$), 123.8 (s, C5 or C5′), 122.9 (s, C5 or C5′), 122.5 (s, *p*-C$_6$H$_5$), 121.5 (d, J = 5.4, *o*-*C*$_6$H$_5$), 118.2 (s, C3 or C3′), 117.7 (s, C3 or C3′), 35.5 (s, -*C*Me$_3$), 35.3 (s, -*C*Me$_3$), 30.3 (s, −C*Me*$_3$), −0.2 (d, J = 4.9, Pd*Me*). ^{1}H NMR spectrum (C_6D_6, 25 °C): δ 10.84 (d, 1H, J = 5.6, H6′), 8.07 (dd, 1H, J = 5.6, 3.3, H6), 7.99 (d, 4H, J = 8.4, *o*-C$_6H_5$), 7.33 (s, 2H, H3 and H3′), 7.15 (t, 4H, J = 7.3, *m*-C$_6H_5$), 6.82 (t, 2H, J = 7.3, *p*-C$_6H_5$), 6.75 (d, 1H, J = 6.7, H5 or H5′), 6.45 (d, 1H, J = 6.0, H5 or H5′), 0.90 (s, 18H, CMe$_3$), 0.73 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 162.6 (s, quat), 161.6 (s, quat), 156.1 (s, quat), 154.3 (d, J = 9.7, *ipso*-*C*$_6$H$_5$), 154.3 (s, C6′), 153.7 (s, quat), 147.1 (s, C6), 129.3 (s, *m*-C$_6$H$_5$), 123.8 (s, C5 or C5′), 122.8 (s, *p*-C$_6$H$_5$), 122.5 (d, J = 3.5, C5 or C5′), 122.4 (d, J = 5.4, *o*-C$_6$H$_5$), 117.7 (d, J = 3.0, C3 or C3), 117.2 (s, C3 or C3), 34.8 (s, −*C*Me$_3$), 34.7 (s, −*C*Me$_3$), 29.9 (s, −C*Me*$_3$), 29.8 (s, −C*Me*$_3$), 0.3 (d, J = 4.3, Pd*Me*). ^{31}P NMR spectrum (C_6D_6, 25 °C): δ 74.5.

General Method for the Preparation of Phosphine Complexes. A flask was charged with **1**, the appropriate amount of the phosphine, and Et_2O (10 mL). After it was stirred at 25 °C for 1 h, the solution was filtered and the resulting solid washed with diethyl ether and dried under vacuum.

Preparation of (MePh$_2$P)$_2$PdMe(P(O)(OPh)$_2$) (2).[7] The general method was followed using **1** (0.10 g, 0.16 mmol) and $PMePh_2$ (59.8 μL, 0.32 mmol) to afford the title compound as a colorless solid (0.11 g, 91%). Anal. Calcd for $C_{39}H_{39}O_3P_3Pd$: C, 62.04; H, 5.17. Found: C, 62.00; 5.37. See ref 7 for the NMR data of the cis isomer. Data for the trans isomer are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.50−6.80 (m, 30H, P*Ph*$_2$), 2.23 (m, 6H, P*Me*), −0.55 (dt, 3H, J = 10.1, 6.6, Pd*Me*). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 99.6 (t, 1P, J = 58.8, −P(O)(OPh)$_2$), 16.5 (d, 2P, J = 58.8, $PMePh_2$). Alternatively, the title compound can be prepared by treatment of Pd(cod)MeCl with 2 equiv of $MePh_2P$ and 1 equiv of AgP(O)(OPh)$_2$ in CH_2Cl_2/THF. After filtration to remove the silver chloride and drying, **2** was isolated in high yield (0.23 g, 85%).

Preparation of (Me$_2$PhP)$_2$PdMe(P(O)(OPh)$_2$) (3). Due to the difficulty in separating ^{t}Bu$_2$bipy from the title compound, the following preparation was used. A round-bottom flask was charged with Pd(cod)MeCl (0.10 g, 0.38 mmol), degassed CH_2Cl_2 (10 mL), degassed THF (10 mL), PMe_2Ph (107 μL, 0.76 mmol), and Ag(P(O)(OPh)$_2$) (0.13 g, 0.38 mmol). After the mixture was stirred at 25 °C for 4 h, the volatiles were removed and the residue was extracted with degassed hexane (3 × 25 mL). The hexane was removed under vacuum to afford an oily colorless solid (0.180 g, 76%). Anal. Calcd for $C_{29}H_{35}O_3P_3Pd$: C, 55.20; H, 5.55. Found: C, 54.75; H, 5.50. Only the trans isomer was observed in these experiments (see text); data for this isomer are as follows. ^{1}H NMR spectrum ($CDCl_3$, 25 °C): δ 7.50−7.30 (m, 10 H, Ar H), 7.15 (t, 4H, J = 7.6 Hz, *m*-C$_6$H$_5$), 7.04 (d, 4H, J = 8.0 Hz, *o*-C$_6$H$_5$), 6.98 (t, 2H, J = 7.6 Hz, *p*-C$_6$H$_5$), 1.80 (t, 12H, J = 3.3 Hz, −PPhMe$_2$), −0.27 (dt, 3H, J = 9.9, 7.0, PdMe). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 99.5 (t, 1P, J = 35.4, −P(O)(OPh)$_2$), −0.15 (d, 2P, J = 35.4, −P*Me*$_2$Ph).

Preparation of (Et$_3$P)$_2$PdMe(P(O)(OPh)$_2$) (4). Due to difficulty in separating ^{t}Bu$_2$bipy from the title compound, the following preparation was used. A round-bottom flask was charged with Pd(cod)MeCl (0.10 g, 0.38 mmol), degassed CH_2Cl_2 (10 mL), degassed THF (10 mL), PEt_3 (112 μL, 0.76 mmol), and Ag(P(O)(OPh)$_2$) (0.13 g, 0.38 mmol). After the mixture was stirred at 25 °C for 4 h, the volatiles were removed and the residue was extracted with degassed hexane (3 × 25 mL). The hexane was removed under vacuum to afford an oily colorless solid (0.190 g, 85%). Anal. Calcd for $C_{25}H_{43}O_3P_3Pd$: C, 50.81; H, 7.28. Found: C, 51.03; H, 6.80. Data for the cis isomer are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.09 (m, 8H, *o* and *m*-C$_6H_5$), 6.89 (m, 2H, J = 4.3, *p*-C$_6H_5$), 1.87 (m, 12H, −C*H*$_2$-CH$_3$), 0.99 (t, 18H, J = 7.9, −CH$_2$C*H*$_3$), −0.10 (ddd, 3H, J = 9.9, 6.2, 3.1, PdMe). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): 87.4 (dd, J = 597.3, 68.3, −*P*(O)(OPh)$_2$), 12.1, (dd, J = 597.3, 33.4, *trans*-PEt$_3$), 10.3 (dd, J = 68.4, 33.8, cis-*P*Et$_3$). Data for the trans isomer are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.09 (m, 8H, *o*- and *m*-C$_6H_5$), 6.87 (t, 2H, J = 4.3, *p*-C$_6H_5$), 1.87 (m, 12H, −C*H*$_2$CH$_3$), 0.99 (m, 18H, J = 7.9, −CH$_2$C*H*$_3$), −0.11 (dt, 3H, J = 9.9, 6.2, PdMe). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 99.8 (t, J = 54.0, −*P*(O)(OPh)$_2$), 17.8 (d, J = 54.0, −*P*Et$_3$).

Preparation of (dppp)PdMe(P(O)(OPh)$_2$) (6). The general method was followed using **1** (0.11 g, 0.18 mmol) and dppp (0.073 g, 0.18 mmol) to afford the title compound as a colorless solid (0.128 g, 94%). Anal. Calcd for $C_{40}H_{39}O_3P_3Pd$: C, 62.63; H, 5.09. Found: C, 62.49; H, 5.22. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.64 (m, 4H, −C$_6H_5$), 7.50−7.30 (m, 16H, −C$_6H_5$), 7.07 (t, 4H,

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J = 7.7, $-C_6H_5$), 6.94 (t, 2H, J = 7.3, $-C_6H_5$), 6.77 (d, 4H, J = 8.2, $-C_6H_5$), 2.42 (m, 2H, $-CH_2-$), 2.29 (m, 2H, $-CH_2-$), 1.92 (m, 2H, $-CH_2-$), 0.55 (ddd, 3H, J = 8.2, 6.0, 4.1, PdMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 89.3 (dd, J = 582.7, 47.3, $-P(O)(OPh)_2$), 11.0 (dd, J = 583.5, 47.5, trans-PPh_2), −0.8 (dd, J = 46.9, 47.1, cis-PPh_2).

Preparation of (dppb)PdMe(P(O)(OPh)$_2$) (7). The general method was followed with **1** (0.11 g, 0.18 mmol) and dppb (0.075 g, 0.18 mmol) to afford the title compound as a colorless solid (0.13 g, 94%). Anal. Calcd for $C_{41}H_{41}O_3P_3Pd$: C, 63.04; H, 5.25. Found: C, 62.44; H, 5.55. ^1H NMR ($CDCl_3$, 25 °C): δ 7.65−7.20 (m, 20H, $-C_6H_5$), 6.95 (m, 6H, *m*-, *p*-C_6H_5), 6.59 (d, 4H, J = 7.9, *o*-C_6H_5), 2.53 (m, 2H, $-CH_2-$), 2.23 (m, 2H, $-CH_2-$), 2.07 (m, 2H, $-CH_2-$), 1.51 (m, 2H, $-CH_2-$), 0.43 (ddd, 3H, J = 8.9, 6.2, 3.1, PdMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 88.4 (dd, 1P, J = 573.3, 51.7, $-P(O)(OPh)_2$), 30.6 (dd, 1P, J = 573.3, 35.6, trans-CH_2PPh_2), 7.6 (dd, 1P, J = 51.7, 35.7, cis-CH_2PPh_2).

Preparation of (dppf)PdMe(P(O)(OPh)$_2$) (8). A round-bottom flask was charged with **1** (0.11 g, 0.18 mmol), dppf (0.098 g, 0.18 mmol), and CH_2Cl_2 (3 mL). After the mixture was stirred at −43 °C for 24 h, Et_2O (20 mL; precooled to −43 °C) was added. After standing at − 43 °C for 24 h, a colorless solid formed and was separated by filtration. The residue was washed with chilled (−45 °C) ether and hexane and dried under vacuum (0.01 g, 63%). Anal. Calcd for $C_{47}H_{41}O_3P_3Pd$: C, 62.10; H, 4.51. Found: C, 61.91; H, 4.84. ^1H NMR ($CDCl_3$, 25 °C): δ 7.60−7.20 (m, 20H, $-C_6H_5$), 6.92 (t, 4H, $^3J_{HH}$ = 7.9, *m*-C_6H_5), 6.84 (t, 2H, $^3J_{HH}$ = 7.0, *p*-C_6H_5), 6.73 (d, 4H, $^3J_{HH}$ = 8.0, *o*-C_6H_5), 4.35−4.0 (m, 6H, $-C_5H_4$), 3.64 (m, 2H, $-C_5H_4$), 0.69 (m, 3H, PdMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 85.4 (dd, 1P, J = 602.8, 58.8, $-P(O)(OPh)_2$), 25.8 (dd, 1P, J = 602.8, 32.6, trans-*P*Ph_2), 14.9 (dd, 1P, J = 58.9, 32.8, cis-*P*Ph_2).

Preparation of (bipy)Pd(P(O)(OPh)$_2$)$_2$ (13). A round-bottom flask was charged with (bipy)PdMe(P(O)(OPh)$_2$) (0.050 g, 0.098 mmol), HP(O)(OPh)$_2$ (18.8 μL, 0.098 mmol), and CH_2Cl_2 (5 mL). After the mixture was stirred for 48 h at 75 °C, the solvent was evaporated and the solid washed with diethyl ether (10 mL) to afford the title compound as a white solid (0.057 g, 45%). Anal. Calcd for $C_{34}H_{28}N_2O_6P_2Pd$: C, 56.01; H, 3.87. Found: C, 55.65; H, 3.87. ^1H NMR ($CDCl_3$, 25 °C): δ 9.68 (dt, 2H, J = 3.0, J = 5.5, H6, H6′), 7.93 (d, 2H, J = 7.8, H3, H3′), 7.86 (t, 2H, J = 7.9, H4, H4′), 7.27 (m, 2H, H5, H5′), 7.25 (d, 8H, J = 8.2, *o*-C_6H_5), 7.11 (t, 8H, J = 8.2, *m*-C_6H_5), 6.94 (t, 4H, J = 7.3, *p*-C_6H_5). ^{13}C NMR ($CDCl_3$, 25 °C): δ 154.5 (s, quat), 154.0 (s, C6, C6′), 151.8 (t, J = 4.8, *ipso*-C_6H_5), 139.9 (s, C4 and C4′), 129.2 (s, *m*-C_6H_5), 126.1 (t, J = 2.5, C5, C5′), 123.7 (s, *p*-C_6H_5), 122.2 (s, C3, C3′), 121.7 (t, J = 2.4, *o*-C_6H_5). ^{31}P NMR ($CDCl_3$, 25 °C): δ 53.1.

Preparation of (^{t}Bu$_2$bipy)Pd(P(O)(OPh)$_2$)$_2$ (14). A round-bottom flask was charged with (^{t}Bu$_2$bipy)PdMe(P(O)(OPh)$_2$) (0.05 g, 0.08 mmol), HP(O)(OPh)$_2$ (15.4 μL, 0.08 mmol), and benzene (5 mL). After the mixture was stirred for 12 h at 75 °C, the solvent was evaporated and the solid washed with 10 mL of diethyl ether to afford the title compound as a white solid (0.062 g, 91%). Anal. Calcd for $C_{42}H_{44}N_2O_6P_2Pd$: C, 59.97; H, 5.23. Found: C, 59.58; H, 5.29. ^1H NMR ($CDCl_3$, 25 °C): δ 9.80 (dt, 2H, J = 3.0, 5.9, H6, H6′), 7.90 (s, 2H, H3, H3′), 7.41 (d, 2H, J = 5.9, H5, H5′), 7.33 (d, 8H, J = 8.1, *o*-C_6H_5), 7.19 (t, 8H, J = 7.9, *m*-C_6H_5), 7.01 (t, 4H, J = 7.4, *p*-C_6H_5), 1.39 (s, 18H, $-CMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 164.2 (s, quat), 155.0 (s, quat), 153.9 (s, C6, C6′), 152.1 (t, J = 4.8, *ipso*-C_6H_5), 129.1 (s, *m*-C_6H_5), 123.5 (s, *p*-C_6H_5), 123.4 (s, C5, C5′), 121.8 (t, J = 2.4, *o*-C_6H_5), 118.1, (s, C3, C3′), 35.5 (s, $-CMe_3$), 30.3 (s, $-CMe_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 54.0.

Preparation of (dppe)Pd(P(O)(OPh)$_2$)$_2$ (15). A round-bottom flask was charged with (dppe)PdMe(P(O)(OPh)$_2$) (0.05 g, 0.066 mmol), HP(O)(OPh)$_2$ (12.7 μL, 0.066 mmol), and benzene (3 mL). After the mixture was stirred for 12 h at 120 °C, the solvent was evaporated and the solid washed with 10 mL of diethyl ether to afford the title compound as an off-white solid (0.052 g, 81%). Anal. Calcd for $C_{50}H_{44}O_6P_4Pd$: C, 61.83; H, 4.53. Found: C, 61.56; H, 4.88. ^1H NMR ($CDCl_3$, 25 °C): δ 7.60−6.88 (m, 40H, $-C_6H_5$), 2.19−2.12 (m, 4H, $-CH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, AA′XX′ pattern): δ 66.5 ($-P(O)(OPh)_2$), 43.37 ($-PPh_2$); $J_{AA'}$ = ±29.0, J_{AX} = 555, $J_{AX'}$ = −29.0, $J_{XX'}$ = ±51.0.[28]

Preparation of (dppp)Pd(P(O)(OPh)$_2$)$_2$ (16). A round-bottom flask was charged with (dppp)PdMe(P(O)(OPh)$_2$) (0.05 g, 0.065 mmol), HP(O)(OPh)$_2$ (12.5 μL, 0.065 mmol), and benzene (5 mL). After the mixture was stirred for 12 h at 80 °C, the solvent was evaporated and the solid washed with 10 mL of diethyl ether to afford the title compound as a white solid (0.029 g, 45%). Anal. Calcd for $C_{51}H_{46}O_6P_4Pd$: C, 62.17; H, 4.67. Found: C, 62.13; H, 4.74. ^1H NMR ($CDCl_3$, 25 °C): δ 7.55−6.80 (m, 40 H, $-C_6H_5$), 2.19 (m, 2H, $-CH_2-$), 1.86−1.70 (m, 4H, $-CH_2-$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, AA′XX′ pattern): δ 63.2 ($-P(O)(OPh)_2$), −0.8 ($-PPh_2$); $J_{AA'}$ = ±76, J_{AX} = 563, $J_{AX'}$ = −31.0, $J_{XX'}$ = ±54.0.[28]

Reaction of Triarylphosphines with 1. An NMR tube was charged with **1**, an appropriate amount of triarylphosphine, solvent (0.5 mL), and $P(O)Ph_3$ (0.003 g, 0.011 mmol, internal standard for reactions carried out in protonated toluene) or C_6Me_6 (0.001 g, 0.012 mmol). Two drops of C_6D_6 were added to reaction mixtures when protonated toluene was used as the solvent. A comparison of the integrals for the metal complex, internal standard, and $MeP(O)(OPh)_2$ before and after stirring at the desired temperature gave the percent conversion of the reaction.

Thermolysis Reactions of 2−8. An NMR tube was charged with the palladium complex (0.005 g), $P(O)Ph_3$ (0.003 g, 0.011 mmol, internal standard for reactions carried out in protonated toluene) or C_6Me_6 (0.001 g, 0.012 mmol), and the appropriate solvent (0.5 mL). Two drops of C_6D_6 were added to reaction mixtures when protonated toluene was used as the solvent. After heating in an oil bath for the desired amount of time, the amount of $MeP(O)(OPh)_2$ formed in the reaction was determined by a comparison of the integrals for the metal complex, internal standard, and $MeP(O)(OPh)_2$ before and after stirring at the desired temperature.

Kinetic Analysis of the Reductive Elimination from 8. Since compound **8** readily eliminates $MeP(O)(OPh)_2$ at room temperature in solution, it was generated in situ from the reaction of **1** with dppf. Monitoring the reaction by NMR revealed that the displacement reaction was complete within a few minutes at 25 °C, and control reactions demonstrated that free ^{t}Bu$_2$bipy does not affect the rate of the reaction. An NMR tube was charged with **1** (0.005 g, 8.0 μmol), appropriate amount of dppf (2−6 equiv), $P(O)Ph_3$ (0.003 g, 0.011 mmol, internal standard when reactions were carried out in protonated toluene) or C_6Me_6 (0.001 g, 0.012 mmol), and the appropriate solvent (0.5 mL). Two drops of C_6D_6 were added to reaction mixtures for a spectrometer lock when reactions were carried out in protonated toluene. NMR data were collected at regular intervals over 3 half-lives. The concentrations of **8**, excess dppf, $MeP(O)(OPh)_2$, and $Pd(dppf)_2$ were determined by comparison of the integrals of the species relative to the internal standard. The rate of $MeP(O)(OPh)_2$ formation varied by less than 5% between reactions with 2−6 equiv of dppf. Similar results were obtained using PPh_3 as the trapping agent.

Reductive Elimination vs Protonolysis Reactions. An NMR tube was charged with the appropriate metal complex, $HP(O)(OPh)_2$ (1 equiv), solvent, $P(O)Ph_3$ (0.003 g, 0.011 mmol, internal standard when reactions were carried out in protonated toluene) or C_6Me_6 (0.001 g, 0.012 mmol), and the

(28) To simulate the spectrum, the cis couplings between the phosphonate groups and between the phosphorus atoms of the diphosphine ($J_{XX'}$ and $J_{AA'}$) must have opposite signs. For further explanation and discussion of AA′XX′ NMR spectral patterns see: Becker, E. D. *High-Resolution NMR: Theory and Chemical Applications*, 3rd ed.; Academic Press: San Diego, CA, 2000; pp 176−177.

appropriate solvent (0.5 mL). Two drops of C_6D_6 were added to reactions for a spectrometer lock when reactions were carried out in protonated toluene. A comparison of the integrals before and after stirring at the desired temperature afforded amounts of the bis-phosphonate complex and $MeP(O)(OPh)_2$.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates, and all bond lengths and angles for **5**, **9**, and **13**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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