Direct Observation of P(O)−C Bond Formation from (N⁀N)PdMe(P(O)(OPh)$_2$) Complexes. Rate Enhancement of Reductive Elimination by Addition of Triarylphosphines

Adam M. Levine, Robert A. Stockland, Jr.,* Robert Clark,† and Ilia Guzei†

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

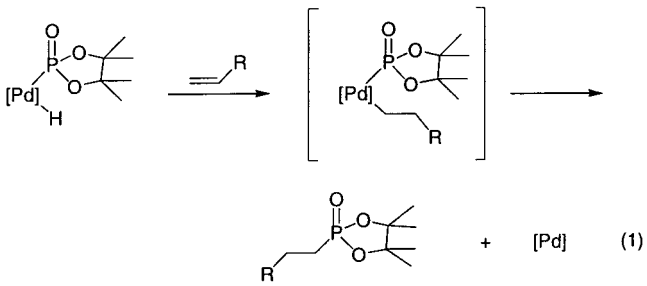
Received March 18, 2002

Complexes of the type (N⁀N)PdMe(P(O)(OPh)$_2$) (N⁀N = bipy (**1**), phen (**2**), dNbipy (**3**); bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Nbipy = 4,4′-dinonyl-2,2′-bipyridine) have been synthesized and investigated as intermediates in P(O)−C(sp^3) bond-forming reactions. Surprisingly, P(O)−C(sp^3) bond formation was not observed upon heating solutions of **1**−**3**, even under harsh conditions (toluene-d_8, 110 °C, 48 h). Complexes **1**−**3** are also resistant to reductive elimination in the presence of Lewis bases such as THF, acetonitrile, and P(O)Ph$_3$. However, the addition of PPh$_3$ to solutions of **1**−**3** afforded the alkyl phosphonate MeP(O)(OPh)$_2$. This suggests that P(O)−C(sp^3) bond formation occurs by reductive elimination from an intermediate of the type (N⁀N)(PPh$_3$)PdMe(P(O)(OPh)$_2$. The molecular structure determination of **1** is a rare example of a crystallographically characterized transition-metal complex containing a methyl group cis to a phosphonate moiety.

Introduction

Transition-metal-mediated carbon−nitrogen and carbon−oxygen bond-forming reactions are efficient methods for the preparation of heteroatom-containing compounds.[1] Analogous processes leading to the formation of phosphorus−carbon bonds have been less thoroughly investigated.[1d,2] The platinum-catalyzed hydrophosphination of acrylonitrile has been investigated by Pringle and Glueck.[3,4] Other recent examples of metal-promoted P−C(sp^2) and P(O)−C(sp^2) bond-forming reactions include the synthesis of phosphino amino acids,[5] vinyl phosphonates,[6] phosphorus-containing polymers,[7] and triarylphosphines.[8]

Compounds containing P(O)−C(sp^3) bonds are typically prepared by the Arbuzov reaction.[9] An alternative to this process is the addition of P(O)−H bonds to olefins. The transition-metal-catalyzed version of this reaction is attractive due to the ability of metal-containing catalysts to manipulate key reaction parameters such as regioselectivity and stereoselectivity by modification of ligand architecture and careful choice of metal center. For efficient atom economy, hydrogen phosphonates are attractive materials for this reaction; however, few systems are known which successfully employ these substrates.[10] Tanaka reported the use of pinacol-derived hydrogen phosphonates in these reactions (eq 1) and in the hydrophosphorylation of 1,3-



(1)

[Pd] = (PCy$_3$)$_2$Pd; R = alkyl or aryl

* To whom correspondence should be addressed. Tel: 570-577-1665. Fax: 570-577-1739. E-mail: rstockla@Bucknell.edu.
† Molecular Structure Laboratory, Department of Chemistry, University of Wisconsin, Madison, WI 53706.

(1) For recent reviews 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.

(2) (a) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748. (b) Han, L.-B.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1999**, 395. (c) Dongwei, C.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180. The lanthanide-catalyzed hydrophosphination of olefins is known: (d) Douglass, M. R.; Marks. T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (e) Takaki, K.; Takeda, M.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 6357. (f) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221.

(3) (a) Costa, E.; Pringle, P. G.; Worboys, K. *J. Chem. Soc., Chem. Commun.* **1998**, 49. (b) Costa, E.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4277. (c) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1993**, 269. (e) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701. (f) Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1096.

(4) (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039. (b) 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.

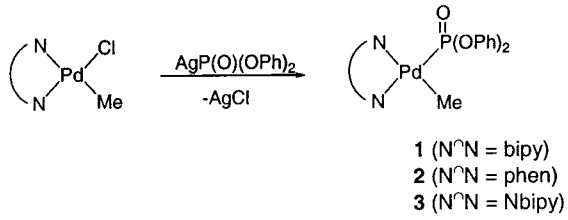
(5) (a) Kraatz, H.-B.; Pletsch, A. *Tetrahedron: Asymmetry* **2000**, *11*, 1617. (b) Gilbertson, S. R.; Starkey, G. W. *J. Org. Chem.* **1996**, *61*, 2922.

(6) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571. (b) Han, L.-B.; Zhoa, C.-Q.; Tanaka, M. *J. Org. Chem.* **2001**, *66*, 5929. (c) Han, L.-B.; Zhoa, C.-Q.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1929.

(7) (a) Lucht, B. L.; St. Onge, N. O. *J. Chem. Soc., Chem. Commun.* **2000**, 2097. (b) Kanbara, T.; Takase, S.; Izumi, K.; Kagaya, S.; Hasegawa, K. *Macromolecules* **2000**, *33*, 657.

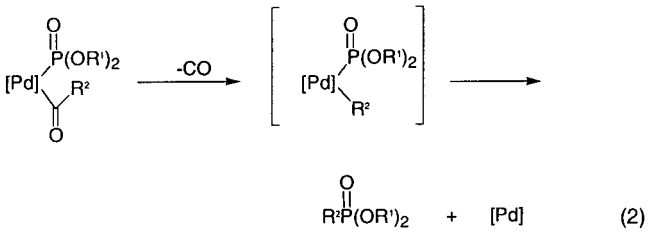
10.1021/om0202118 CCC: $22.00
Publication on Web 06/20/2002

Scheme 1



dienes and allenes.[11] Although these cyclic substrates have been successfully used, simple reagents such as HP(O)(OPh)$_2$ and HP(O)(OEt)$_2$ are unreactive.

The decarbonylation of α-ketophosphonates is an additional method for the synthesis of alkyl or aryl phosphonates.[12] Typically, phosphine-containing nickel and palladium complexes are used to promote this process. Tanaka has shown that these reactions proceed through initial oxidative addition of the α-ketophosphonate followed by deinsertion of carbon monoxide to form (PMe$_3$)$_2$PdR^2(P(O)(OR^1)$_2$) (eq 2). P(O)−C(sp^3) bond formation was proposed to occur by reductive elimination of R^{2}P(O)(OR^1)$_2$ from these 4-coordinate species.



(2)

A key step in these reactions is reductive elimination of RP(O)(OR)$_2$ from L$_2$PdR(P(O)(OR)$_2$). However, to the best of our knowledge, a complex of this type has not been isolated (R = alkyl). To probe the factors that affect the P(O)−C(sp^3) bond-forming step, we have synthesized and investigated a series of discrete organopalladium complexes of the type (N⌒N)PdMe(P(O)(OPh)$_2$).

Results and Discussion

Synthesis of Organopalladium Complexes. Complexes of the type (N⌒N)PdMe(P(O)(OPh)$_2$) (N⌒N = bipy (**1**), phen (**2**), dNbipy (**3**); bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Nbipy = 4,4′-dinonyl-2,2′-bipyridine) were synthesized in high yield by treatment of the corresponding (N⌒N)PdMeCl species with AgP(O)(OPh)$_2$ in THF/CH$_2$Cl$_2$ at room temperature (Scheme 1).

Complexes **1**−**3** exhibit a sharp singlet in the ^{31}P NMR spectrum between δ 76 and 80 ppm due to the −P(O)(OPh)$_2$ moiety. The methyl group bound to palladium gives rise to a singlet (CDCl$_3$; δ 0.83 (**1**), 0.96 (**2**), 0.79 (**3**)) in the ^{1}H NMR spectrum and a doublet in the ^{13}C NMR spectrum between δ 0.08 and −0.16 ($^2J_{PC}$ = 4.3−4.8 Hz). The resonance for one of the bipyridine aromatic hydrogens appears at unusually high frequency (CDCl$_3$; δ 10.15 (**1**), 10.49 (**2**), 9.90 (**3**)) in the ^{1}H NMR spectrum. Analysis of the 1D and 2D NMR spectra for **1**−**3** revealed this resonance to be due to the C−H group (H6′) that is part of the pyridyl ring trans to the methyl group on palladium. The ^{1}H−^{1}H NOESY of **3** is shown in Figure 1 and shows the through-space correlations between the methyl group on palladium and H6 of the bipyridine ring. The second correlation is between the methyl on palladium and the ortho hydrogens of the −OC$_6$H$_5$ group.

Molecular Structure Determination of 1. X-ray-quality crystals of **1** were grown by slow evaporation of a CH$_2$Cl$_2$/Et$_2$O solution. The molecular structure was determined by single-crystal X-ray diffraction and is shown in Figure 2. Selected bond distances and angles are listed in Table 1, and data collection and refinement details are given in Table 2. While numerous structures of transition-metal complexes bearing cyclopentadienyl and phosphonate ligands are known, the molecular structure of **1** is a rare structural determination of a transition-metal complex with a simple alkyl group (methyl) cis to a phosphonate.[13] The arrangement of the ligands about palladium is slightly distorted from the expected square-planar geometry with the plane formed by N(1)−Pd−N(2) twisted 7.4° relative to a plane formed by P−Pd−C(23). The phosphonate group is coordinated through phosphorus and exhibits a typical P−Pd bond length of 2.2203(8) Å. The P═O bond length of 1.485(2) Å and P−O bond lengths of 1.641(2) and 1.644(2) Å are typical of other metal complexes containing phosphonate groups.[12−14] Despite being trans to different groups, both Pd−N bond lengths are identical (2.142(3) Å). This is of interest, since 4-coordinate square-planar methylpalladium complexes containing chelating dinitrogen ligands often display quite different Pd−N bond lengths according to the trans influence of the substituent adjacent to the methyl group.[15] The similarity in the Pd−N bond lengths in **1** suggests that the trans influ-

(8) Kwong, F. Y.; Chan, K. S. *J. Chem. Soc., Chem. Commun.* **2000**, 1069.

(9) Alkyl and aryl phosphonates are typically prepared by the Arbusov reaction: *A Guide to Organophosphorus Chemistry*; Quin, L. D., Ed.; Wiley-Interscience: New York, 2000. The radical hydrophosphorylation of olefins is also known: Stiles, A. R.; Vaughan, W. E.; Rust, F. F. *J. Am. Chem. Soc.* **1958**, *80*, 714.

(10) Reichwein, J. F.; Patel, M. C.; Pagenkopf, B. L. *Org. Lett.* **2001**, *26*, 4303.

(11) (a) Han, L. B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407. (b) Mirzaei, F.; Han, L. B.; Tanaka, M. *Tetrahedron Lett.* **2001**, *42*, 297. (c) Zhao, C. Q.; Han, L. B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196.

(12) (a) Nakazawa, H.; Matsuoka, Y.; Nakagawa, I.; Miyoshi, K. *Organometallics* **1992**, *11*, 1385. (b) Nakazawa, H.; Matsuoka, Y.; Yamaguchi, I.; Kuroiwa, T.; Miyoshi, K.; Yoneda, H. *Organometallics* **1989**, *8*, 2272.

(13) Other examples of structurally characterized organometallic complexes (non-Cp) include the following. Ruthenium carbene complexes: (a) Leung, W. H.; Chan, E. E. Y.; Williams, I. D.; Wong, W. T. *Organometallics* **1997**, *16*, 3234. (b) Leung, W. H.; Chan, E. E. Y.; Wong, W. T. *Organometallics* **1998**, *17*, 1245. (c) Chang, C. W.; Lin, Y. C.; Lee, G. H.; Huang, S. L.; Wang, Y. *Organometallics* **1998**, *17*, 2534. (d) Chang, C. W.; Lin, Y. C.; Lee, G. H.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 4223. η^2-Bound olefins: (e) Leung, W. H.; Chan, E. Y. Y.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 136. (f) Kläui, W.; Lenders, B.; Irmier, M.; Meyer, G. *J. Chem. Soc., Dalton Trans.* **1990**, 2069. (g) 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: (h) Zhou, Z.; Jablonski, C. R.; Bridson, J. *Organometallics* **1994**, *13*, 781. (i) Jablonski, C. R.; Huaizhu, M.; Hynes, R. *Organometallics* **1992**, *11*, 2796.

(14) (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.

(15) Rulke, R. E.; Delis, J. G. P.; Groot, A. M.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Oubitz, K.; Schenk, H. *J. Organomet. Chem.* **1996**, *508*, 109.

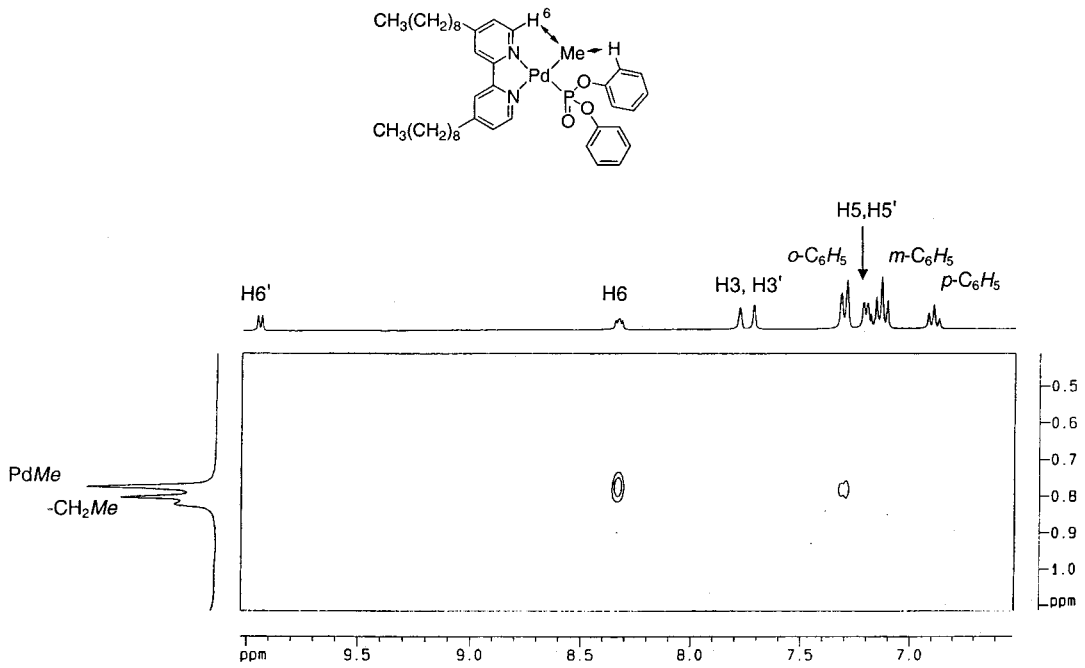


Figure 1. $^1H-^1H$ NOESY spectra (selected region, $CDCl_3$, 25 °C) of complex **3**.

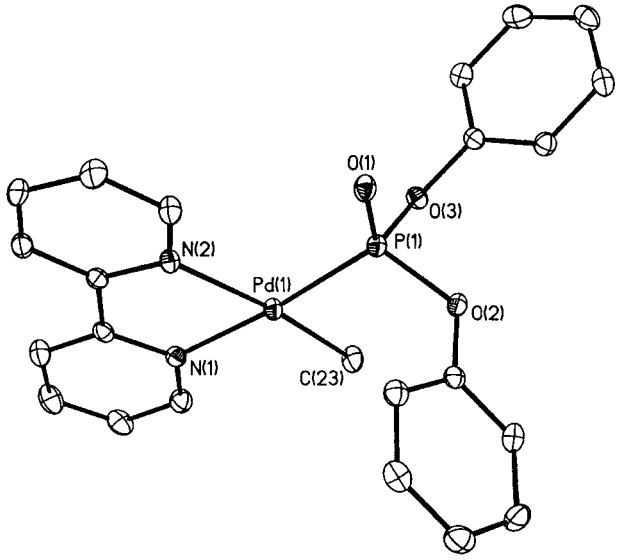


Figure 2. Molecular structure diagram (ORTEP) for **1**. Thermal ellipsoids are shown at 30% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1

Pd−C(23)	2.044(3)	P−O(1)	1.485(2)
Pd−N(1)	2.142(3)	P−O(2)	1.644(2)
Pd−N(2)	2.142(3)	P−O(3)	1.641(2)
Pd−P	2.2203(8)		
C(23)−Pd−N(1)	94.89(12)	N(2)−Pd−P	101.39(7)
C(23)−Pd−N(2)	171.98(11)	O(1)−P−O(3)	109.74(12)
N(1)−Pd−N(2)	77.09(10)	O(1)−P−O(2)	108.27(13)
C(23)−Pd−P	86.61(10)	O(3)−P−O(2)	96.44(11)
N(1)−Pd−P	174.59(7)		

ence of the diphenyl phosphonate unit in this complex is similar to that of the methyl substituent. The N−Pd−N and P−Pd−Me angles of 77.09(10) and 86.61(10)° are compressed from 90°, while the P−Pd−N(2) and Me−Pd−N(1) angles are expanded (101.39-(7), 94.89(12)°). The N(1)−Pd−P and N(2)−Pd−C(23) angles deviate from linearity (171.98(11) and 174.59(7)°).

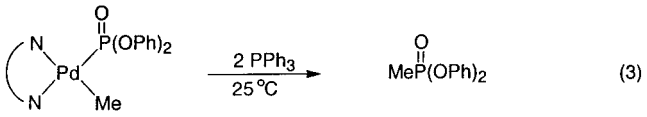
Table 2. Summary of Data Collection and Refinement for Complex 1

empirical formula	$C_{23}H_{21}N_2O_3PPd$
fw	510.79
temp	173(2) K
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a	8.9357(8) Å
b	9.8918(9) Å
c	12.9092(12) Å
α	87.751(2)°
β	71.953(2)°
γ	70.122(2)°
V	1017.48(16) Å^3
Z	2
density (calcd)	1.667 Mg/m^3
abs coeff	1.019 mm^{-1}
F(000)	516
cryst size	0.40 × 0.30 × 0.30 mm^3
θ range for data collecn	2.55−26.40°
index ranges	$-10 \le h \le 11$, $-12 \le k \le 12$, $0 \le l \le 16$
no. of rflns collected	6427
no. of indep rflns	3910 (R(int) = 0.0212)
completeness to $\theta = 26.40°$	93.3%
abs cor	empirical with SADABS
max and min transmissn	0.7497 and 0.6860
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3910/0/272
goodness of fit on F^2	1.072
final R indices ($I > 2\sigma(I)$)	R1 = 0.0329, wR2 = 0.0780
R indices (all data)	R1 = 0.0382, wR2 = 0.0801
largest diff peak and hole	0.759 and −0.498 e Å^{-3}

Thermolysis Reactions of 1−3. Complexes **1**−**3** are remarkably stable. Heating a solution of **1** ($CDCl_3$, 70 °C, 2 days) resulted in recovery of **1** (97% by NMR, C_6Me_6 as internal standard). The use of acetone-d_6 as the solvent generated a mixture of products, presumably due to nucleophilic attack of the phosphoryl oxygen on the carbonyl carbon of acetone.[12] The increased solubility of **3** facilitated studies in nonpolar solvents. No

reaction was observed when a C_6D_6 solution of **3** was heated (80 °C, 72 h).[16]

Treatment of **1** ($CDCl_3$ solution) with 1−100 equiv of THF followed by heating (70 °C, 24 h) resulted in complete recovery of **1** (quantitative by NMR). Similar results were observed with acetonitrile or pyridine. Treatment of a $CDCl_3$ solution of **1** with 1 equiv of PPh_3 resulted in collapse of the resonances for the bipy hydrogens in the ^{1}H NMR spectrum. A broad peak for PPh_3 was observed in the ^{31}P NMR spectrum. This fluxional behavior is consistent with reversible coordination of PPh_3 and or interconversion of the 5-coordinate species.[17] Addition of a second equivalent of PPh_3 only slightly increased the intensity of the broad resonance in the ^{31}P spectrum for PPh_3. It was of interest that 2 equiv of PPh_3 did not displace the dinitrogen ligand and form $(PPh_3)_2$PdMe(P(O)(OPh)$_2$). Within a few minutes of the addition of PPh_3 to solutions of **1**−**3**, MeP(O)(OPh)$_2$ was observed (^{31}P NMR, δ 23; ^{1}H NMR, δ 1.73, d, $^2J_{HP}$ = 17.6 Hz, P*Me*). After standing for 12 h at 25 °C, the resonance in the ^{31}P NMR spectrum for **1** was not present (eq 3; 50% yield of MeP(O)(OPh)$_2$ by NMR).

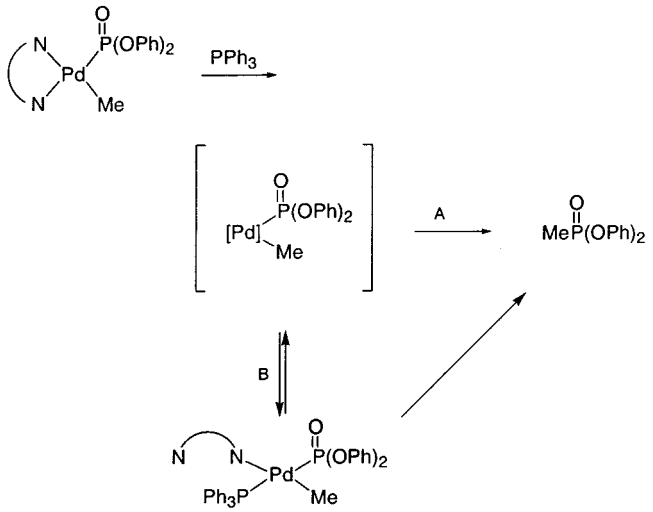


(3)

The use of $CDCl_3$ that was not deoxygenated resulted in incomplete conversion of **1** into MeP(O)(OPh)$_2$ (70 °C, 48 h, 21% conversion by NMR) due to oxidation of PPh_3. Complex **1** was recovered (77% by NMR) in this reaction. The inability of $P(O)Ph_3$ to catalyze this reaction was confirmed by heating a C_6D_6 solution of **1** with P(O)Ph_3 (70 °C, 48 h, quantitative recovery of **1**). The increased solubility of **3** facilitated studies in nonpolar solvents. Addition of 2 equiv of PPh_3 to a C_6D_6 solution of **3** resulted in a similar collapse of the Nbipy hydrogens in the ^{1}H NMR spectrum as well as a broad resonance in the ^{31}P NMR spectrum for the added PPh_3. Upon standing (25 °C, 12 h), MeP(O)(OPh)$_2$ (70% by NMR) was observed.[18]

The precise mechanism for the rate enhancement of P(O)−C(sp^3) formation due to the addition of phosphine is not clear. One possibility involves coordination of the added phosphine to palladium to form the 5-coordinate complex (N⁀N)(PPh_3)PdMe(P(O)(OPh)$_2$), which undergoes P(O)−C(sp^3) bond formation by reductive elimination of MeP(O)(OPh)$_2$ (path A, Scheme 2). Many experimental and theoretical studies have been carried out on analogous processes involving the formation of C−C or C−H bonds by reductive elimination from palladium and platinum complexes.[19] While some bond-forming reactions proceed by direct reductive elimination from a 4-coordinate complex,[20] reductive elimination is often more facile from a 3-coordinate species.[21] In some cases, excess ligand was found to promote reductive elimination reactions, presumably through the formation of 5-coordinate intermediates.[22] For our system, the formation of a 5-coordinate species is supported by the fluxional behavior observed in the ^{1}H NMR spectrum for the bipyridine hydrogens upon addition of PPh_3. However, the precise geometry of the proposed 5-coordinate complex is not known. Chelating dinitrogen ligands have been found to occupy adjacent sites in the equatorial plane or an equatorial and axial site.[23]

Scheme 2[a]



[a] [Pd] = (N⁀N)(PPh_3)Pd.

An additional mechanistic possibility for the rate enhancement of reductive elimination of MeP(O)(OPh)$_2$ upon the addition of PPh_3 entailed complete displacement of the N⁀N ligand by PPh_3 to form trace amounts of $(PPh_3)_2$PdMe(P(O)(OPh)$_2$).[24] P(O)−C(sp^3) bond formation would be favored in this complex due to the increased trans influence and trans effect of the phosphine donors. To investigate this possibility, we sought to prepare complexes of the type $(PR_3)_2$PdMe(P(O)(OPh)$_2$). Since the addition of PPh_3 to solutions of **1**−**3** was unsuccessful in completely displacing the dinitrogen ligand, a more basic phosphine ($MePPh_2$) and a chelat-

(16) Similar results were obtained in toluene-d_8 at 110 °C.

(17) The fluxional process displayed by treatment of **1**−**3** with various phosphine ligands is currently under investigation and will be presented shortly.

(18) The fate of the palladium has not been determined in these reactions.

(19) (a) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (b) Stahl, S. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (c) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609. (d) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (e) Hill, G. S.; Redina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (f) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (g) O'Reilly, A. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (h) Goldberg, K. I.; Yan, J.; Breutung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889. (i) Goldberg, K. I.; Yan, J.; Winter, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 1573.

(20) (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (b) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (c) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892. (d) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356. (e) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

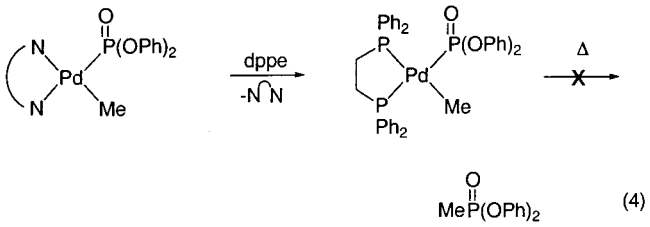
(21) (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (c) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (d) Dicosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601.

(22) (a) Komiya, S.; Yoshihiro, A.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466. (b) Yamamoto, T.; Abla, M. *J. Organomet. Chem.* **1997**, *535*, 209. (c) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181.

(23) (a) Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, *133*, 67. (b) Albano, V. G.; Monari, M.; Orabona, I.; Rufo, F.; Vitagliano, A. *Inorg. Chim. Acta* **1997**, *265*, 35.

(24) Although $(PPh_3)_2$PdMe(P(O)(OPh)$_2$) was not observed in these reactions, it could have been formed in small amounts; however, the lack of MeP(O)(OPh)$_2$ formation from **4** and **5** suggest that reductive elimination from the 4-coordinate complex $(PPh_3)_2$PdMe(P(O)(OPh)$_2$) is less likely.

ing diphosphine (dppe) were used. Addition of 2 equiv of $MePPh_2$ or 1 equiv of dppe to solutions ($CDCl_3$) of **1**−**3** resulted in the complete displacement of the N⌒N ligand and formation of $(PMePh_2)_2PdMe(P(O)(OPh)_2)$ (**4**) and $(dppe)PdMe(P(O)(OPh)_2)$ (**5**). Sharp resonances in the ^1H NMR spectrum for the bipy ligand (identical to free bipy) indicated that it did not effectively compete with $MePPh_2$ or dppe for sites on palladium. Upon standing ($CDCl_3$, 25 °C, 48 h), $MeP(O)(OPh)_2$ was not observed from solutions of **4** and **5**. Heating **4** or **5** ($CDCl_3$, 70 °C, 10 h) did not induce the formation of $MeP(O)(OPh)_2$ (eq 4). These results suggested that the



$$MeP(O)(OPh)_2 \qquad (4)$$

P(O)−C(sp^3) bond formation observed when PPh_3 is added to solutions of **1**−**3** did not occur from a 4-coordinate complex of the type $(PPh_3)_2PdMe(P(O)(OPh)_2)$.

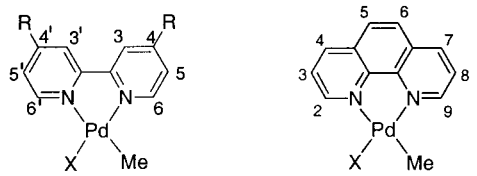
An additional mechanistic possibility involves the dissociation of one of the nitrogen donors upon coordination of the PPh_3 to generate a 4-coordinate species as shown in Scheme 2 (path B). The greater trans influence and trans effect of the phosphine ligand could facilitate P(O)−C(sp^3) bond formation. While our data do not completely rule out this possibility, the lack of $MeP(O)(OPh)_2$ formation from **1**−**3** or from samples of $(PMePh_2)_2PdMe(P(O)(OPh)_2)$ and $(dppe)PdMe(P(O)(OPh)_2)$ suggest this possibility is not as likely.

In conclusion, we have isolated and characterized complexes of the type (N⌒N)PdMe($P(O)(OR)_2$). While these 4-coordinate complexes are quite robust, the addition of weakly basic phosphine ligands promotes the formation of $MeP(O)(OPh)_2$. This is presumably due to reductive elimination from $(N⌒N)(PPh_3)PdMe(P(O)(OPh)_2)$. Further studies are underway to elucidate the precise mechanism of the P(O)−C(sp^3) bond-forming step and to determine the effect of electronic and steric variation of the added phosphine.

Experimental Section

All reactions were performed under a nitrogen atmosphere on a vacuum line or in a nitrogen-filled drybox. Hexane, toluene, toluene-d_8, and benzene-d_6 were distilled from sodium/benzophenone. Dichloromethane and $CDCl_3$ were dried over CaH_2 and distilled. Nitrogen was purified by passage through purification columns (oxygen and moisture) from Chromatography Research Supplies. 2,2′-Bipyridine, 1,10-phenanthroline, and 4,4′-dinonyl-2,2′-bipyridine were obtained from Aldrich and used as received. $Ag(P(O)(OPh)_2)$,[25] (bipy)PdMeCl,[15] and (phen)PdMeCl[15] were prepared as described previously. Due to its limited stability, the silver salt must be used within 48 h of preparation. Elemental analyses were performed by Midwest Microlabs.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at ambient temperature unless specified otherwise. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Coupling constants are given in Hz. The connectivity of **1**−**3** was established using a series of $^1H-^1H$ and $^1H-^{13}C$ correlation experiments. The numbering scheme is shown in Figure 3.



X = P(O)(OPh)$_2$, Cl; R = H, nonyl

Figure 3. Atom-labeling scheme for complexes **1**−**3**.

Synthesis of (bipy)PdMe(P(O)(OPh)$_2$) (1). A round-bottom flask was charged with (bipy)PdMeCl (0.110 g, 0.352 mmol), $Ag(P(O)(OPh)_2)$ (0.12 g, 0.352 mmol), CH_2Cl_2 (20 mL), and THF (10 mL). The mixture was stirred (1 h, 25 °C) in the absence of light. After filtration, the volatiles were removed under vacuum. The resulting dark yellow solid was washed with diethyl ether and dried in vacuo to afford 0.171 g (95.3%) of a dark yellow solid. Anal. Calcd for $C_{23}H_{21}N_2O_3PPd$: C, 54.07; H, 4.11. Found: C, 53.67; H, 3.87. ^1H NMR ($CDCl_3$): δ 10.15 (d, 1H, $^3J_{HH} = 5.5$, H6′), 8.51 (dd, 1H, $^3J_{HH} = 5.5$, $^4J_{PH} = 5.5$, H6), 8.03 (d, 1H, $^3J_{HH} = 8.1$, H3 or H3′), 7.95 (d, $^3J_{HH} = 7.5$, 1H, H3 or H3′), 7.91 (t, $^3J_{HH} = 8.2$, H4 or H4′), 7.85 (t, $^3J_{HH} = 7.9$, H4 or H4′), 7.45 (t, 2H, $^3J_{HH} = 6.6$, H5 and H5′), 7.31 (d, 4H, $^3J_{HH} = 8.2$, *o*-C_6H_5), 7.15 (t, 4H, $^3J_{HH} = 8.3$, *m*-C_6H_5), 6.92 (t, 2H, $^3J_{HH} = 8.0$, *p*-C_6H_5), 0.83 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 155.9 (s, quat), 154.0 (s, C6′), 153.4 (s, quat), 152.8 (d, $^2J_{CP} = 7.2$, *ipso*-C_6H_5), 147.5 (d, $^3J_{PC} = 1.9$, C6), 139.4 (s, C4 or C4′), 138.3 (s, C4 or C4′), 128.9 (s, *m*-C_6H_5), 126.7 (s, C5 or C5′), 125.8 (d $^4J_{PC} = 3.8$, C5 or C5′), 122.7 (s, *p*-C_6H_5), 121.8 (d, $^4J_{PC} = 3.0$, C3 or C3′), 121.5 (d, $^3J_{PC} = 5.4$, *o*-C_6H_5), 121.2 (s, C3 or C3′), 0.2 (d, $^2J_{CP} = 4.3$, Pd*Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 76.0 (s).

Synthesis of (phen)PdMe(P(O)(OPh)$_2$) (2). A round-bottom flask was charged with (phen)PdMeCl (0.11 g, 0.326 mmol), $AgP(O)(OPh)_2$ (0.11 g, 0.326 mmol), CH_2Cl_2 (100 mL), and THF (100 mL). The reaction mixture was stirred (25 °C, 2 h) in the absence of light. After removal of the solvent under vacuum, the solid residue was washed with hexane. The resulting solid was dried under vacuum, affording 0.098 g (56.3%) of a pale yellow powder. Anal. Calcd for $C_{25}H_{21}N_2O_3PPd$: C, 56.14; H, 3.93. Found: C, 55.97; H, 3.88. ^1H NMR ($CDCl_3$): δ 10.49 (d, 1H, $^3J_{HH} = 4.4$, H2), 8.86 (dd, 1H, $^3J_{HH} = 4.5$, $^4J_{PH} = 4.5$ H9), 8.42 (d, 1H, $^3J_{HH} = 8.2$, H7), 8.34 (d, 1H, $^3J_{HH} = 8.2$, H4), 7.86 (s, 1H, H5 or H6), 7.85 (s, 1H, H5 or H6), 7.79 (m, 2H, H3 and H8), 7.36 (d, 4H, $^3J_{HH} = 8.2$, *o*-C_6H_5), 7.15 (t, 4H, $^3J_{HH} = 7.5$, *m*-C_6H_5), 6.91 (t, 4H, $^3J_{HH} = 7.37$, *p*-C_6H_5), 0.96 (s, 3H, Pd*Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 92.5.

Synthesis of (Nbipy)PdMeCl. A round-bottom flask was charged with (cod)PdMeCl (0.51 g, 1.79 mmol), Nbipy (0.73 g, 1.79 mmol), and CH_2Cl_2 (100 mL). The reaction mixture was stirred at 25 °C for 2 h. After removal of the solvent under vacuum, the solid residue was extracted with hexane. The resulting solid was dried under vacuum to afford 0.94 g (93.2%) of a pale yellow powder. Anal. Calcd for $C_{29}H_{47}N_2ClPd$: C, 61.65; H, 8.32. Found: C, 61.46; H, 8.18. ^1H NMR ($CDCl_3$, 25 °C): δ 8.77 (d, 1H, $^3J_{HH} = 5.4$, H6′), 8.26 (d, 1H, $^3J_{HH} = 5.8$, H6), 7.83 (s, 1H, H3), 7.76 (s, 1H, H3′), 7.17 (d, 1H, $^3J_{HH} = 5.8$, H5), 7.12 (d, 1H, $^3J_{HH} = 5.4$, H5′), 2.67 (m, 4H, $-CH_2-$), 1.62 (m, 4H, $-CH_2-$), 1.16 (m, 24H, $-CH_2-$), 0.77 (t, 6H, $^3J_{HH} = 7.1$, $-CH_2CH_3$), 0.77 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 156.7 (s, quat), 155.4 (s, quat), 155.1 (s, quat), 152.8 (s, quat), 148.4 (s, C6′), 148.0 (s, C6), 126.2 (s, C5 or C5′), 126.1 (s, C5 or C5′), 122.9 (s, C3), 121.6 (s, C3′), 35.8 (s, $-CH_2$), 35.7 (s, $-CH_2-$), 31.9 (s, $-CH_2-$), 31.8 (s, $-CH_2-$), 30.4 (s, $-CH_2-$),

(25) Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2080.

30.1 (s, −*C*H$_2$−), 29.5 (s, −*C*H$_2$−), 29.4 (s, −*C*H$_2$−), 29.3 (s, −*C*H$_2$−), 29.2 (s, −*C*H$_2$−), 28.1 (s, −*C*H$_2$−), 22.7 (s, −*C*H$_2$−), 14.2 (s, −CH$_2$*C*H$_3$), −1.1 (s, Pd*Me*).

Synthesis of (Nbipy)PdMe(P(O)(OPh)$_2$) (3). A round-bottom flask was charged with (Nbipy)PdMeCl (0.11 g, 0.195 mmol), Ag(P(O)(OPh)$_2$) (0.066 g 0.195 mmol), CH_2Cl_2 (20 mL), and THF (10 mL). The mixture was stirred (25 °C, 1 h) in the absence of light. After filtration the volatiles were removed under vacuum. The resulting dark yellow solid was washed with diethyl ether and dried in vacuo to afford 0.131 g (88.5%) of a dark yellow solid. Anal. Calcd for $C_{41}H_{57}N_2O_3PPd$: C, 64.53; H, 7.48. Found: C, 64.18; H, 7.60. ^{1}H NMR ($CDCl_3$): δ 9.90 (d, 1H, $^3J_{HH}$ = 5.5, H6′), 8.31 (dd, 1H, $^3J_{HH}$ = 5.5, $^3J_{PH}$ = 5.5, H6), 7.77 (s, 1H, H3), 7.71 (s, 1H, H3′), 7.29 (d, 4H, $^3J_{HH}$ = 8.5, *o*-C$_6$*H*$_5$), 7.24 (d, 2H, $^3J_{HH}$ = 5.6, H5 and H5′), 7.15 (t, 4H, $^3J_{HH}$ = 8.2, *m*-C$_6$*H*$_5$), 6.91 (t, 2H, $^3J_{HH}$ = 8.2, *p*-C$_6$*H*$_5$), 2.67 (q, 4H, $^3J_{HH}$ = 7.6, −CH$_2$−), 1.60 (m, 4H, −CH$_2$−), 1.20 (m, 24H, −CH$_2$−), 0.80 (t, 6H, $^3J_{HH}$ = 6.6 −CH$_2$*Me*), 0.79 (s, 3H, Pd*Me*). ^{1}H NMR (acetone-d_6, 25 °C): δ 10.14 (d, 1H, $^3J_{HH}$ = 5.5, H6′), 8.45 (m, H6), 8.45 (s, 1H, H3), 8.38 (s, 1H, H3′), 7.57 (d, 1H, $^3J_{HH}$ = 5.5, H5), 7.47 (d, 1H, $^3J_{HH}$ = 5.5, H5′), 7.33 (d, 4H, $^3J_{HH}$ = 8.2, *o*-C$_6$*H*$_5$), 7.20 (d, 4H, $^3J_{HH}$ = 8.2, *m*-C$_6$*H*$_5$), 6.95 (d, 2H, $^3J_{HH}$ = 8.2, *p*-C$_6$*H*$_5$), 2.65 (m, 4H, −CH$_2$−), 1.72 (m, 4H, −CH$_2$−), 1.26 (m, 24H, −CH$_2$−), 0.85 (t, 6H, $^3J_{HH}$ = 7.2, CH$_2$*Me*), 0.65 (s, 3H, Pd*Me*). ^{1}H NMR (C_6D_6): δ 10.45 (d, 1H, $^3J_{HH}$ = 5.5, H6′), 8.07 (dd, 1H, $^3J_{HH}$ = 5.5, $^4J_{PH}$ = 3.0, H6), 8.03 (d, 4H, $^3J_{HH}$ = 8.2, *o*-C$_6$*H*$_5$), 7.87 (s, 1H, H3), 7.78 (s, 1H, H3′), 7.29 (t, 4H, $^3J_{HH}$ = 8.2, *m*-C$_6$*H*$_5$), 6.98 (t, 2H, $^3J_{HH}$ = 8.2, *p*-C$_6$*H*$_5$), 6.64 (d, 1H, $^3J_{HH}$ = 5.6, H5′), 6.56 (d, 1H, $^3J_{HH}$ = 5.7, H5), 2.52 (q, 4H, $^3J_{HH}$ = 7.2, −CH$_2$), 1.45 (m, 31H, −CH$_2$− and PdMe), 1.05 (t, 6H, $^3J_{HH}$ = 6.6 −CH$_2$*Me*). ^{13}C NMR ($CDCl_3$, 25 °C): δ 156.0 (s, quat), 155.9 (s, quat), 154.7 (s, quat), 153.5 (s, quat), 153.3 (s, C6′), 152.9 (d, $^2J_{PC}$ = 7.2, *ipso*-*C*$_6$H$_5$), 147.0 (s, C6), 128.9 (s, *m*-*C*$_6$H$_5$), 126.6 (s, C5 or C5′), 125.7 (s, C5 or C5′), 122.5 (s, *p*-*C*$_6$H$_5$), 121.6 (s, C3), 121.5 (d, $^3J_{PC}$ = 5.43, *o*-*C*$_6$H$_5$), 121.2 (s, C3′), 35.7 (s, −CH$_2$−), 35.6 (s, −CH$_2$−), 31.8 (s, −CH$_2$−), 30.2 (s, −CH$_2$−), 29.5 (s, −CH$_2$−), 29.4 (s, −CH$_2$−), 29.36 (s, −CH$_2$−), 29.33 (s, −CH$_2$−), 29.25 (s, −CH$_2$−), 29.24 (s, −CH$_2$−), 29.16 (s, −CH$_2$−), 22.6 (s, −CH$_2$−), 14.1 (s, CH$_2$*C*H$_3$), −0.16 (d, $^2J_{PC}$ = 4.81, PdMe). ^{13}C NMR (acetone-d_6): δ 157.8 (s, quat), 156.7 (s, quat), 156.5 (s, quat), 155.0 (s, quat), 154.4 (d, $^2J_{PC}$ = 6.2, *ipso*-*C*$_6$H$_5$), 153.6 (s, C6′), 147.8 (s, C6), 129.7 (s, *m*-*C*$_6$H$_5$), 127.2 (s, C5 or C5′), 127.1 (s, C5 or C5′), 123.8 (s, C3), 123.4 (s, C3′), 123.2 (s, *p*-*C*$_6$H$_5$), 122.3 (d, $^3J_{PC}$ = 5.5, *o*-*C*$_6$H$_5$), 36.1 (s, −CH$_2$−), 32.7 (s, −CH$_2$−), 31.0 (s, −CH$_2$−), 30.3 (s, −CH$_2$−), 30.2 (s, −CH$_2$−), 30.1 (s, −CH$_2$−), 30.09 (s, −CH$_2$−), 30.04 (s, −CH$_2$−), 29.99 (s, −CH$_2$−), 23.3 (s, −CH$_2$−), 14.4 (s, −CH$_2$*C*H$_3$), −0.2 (d, $^2J_{PC}$ = 4.7, Pd*Me*). ^{13}C NMR (C_6D_6, 25 °C): δ 156.2 (s, quat), 156.1 (s, quat), 154.8 (s, quat), 154.7 (s, quat), 153.9 (s, quat), 153.8 (s, C6′), 146.7 (s, C6), 129.7 (s, *m*-*C*$_6$H$_5$), 126.2 (s, C5′), 125.5 (s, C5), 123.2 (s, C3), 123.2 (s, *p*-*C*$_6$H$_5$) 122.5 (s, C3′), 122.5 (d, $^3J_{PC}$ = 5.4, *o*-*C*$_6$H$_5$), 36.0 (s, −CH$_2$−), 35.9 (s, −CH$_2$−), 32.7 (s, −CH$_2$−), 30.7 (s, −CH$_2$−), 30.5 (s, −CH$_2$−), 30.4 (s, −CH$_2$−), 30.3 (s, −CH$_2$−), 30.2 (s, −CH$_2$−), 30.1 (s, −CH$_2$−), 30.03, (s, −CH$_2$−), 30.0 (s, −CH$_2$−), 23.5, (s, −CH$_2$−), 14.7 (s, −CH$_2$*C*H$_3$), 0.83 (d, $^2J_{PC}$ = 4.81, PdMe). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 79.1. ^{31}P{^{1}H} NMR (acetone -d_6, 25 °C): δ 80.6. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ 75.3.

Synthesis of (MePh$_2$P)$_2$PdMe(P(O)(OPh)$_2$) (4). A round-bottom flask was charged with **3** (0.04 g, 0.052 mmol), MePPh$_2$ (19.5 μL, 0.105 mmol), and hexane (5 mL). The reaction was stirred for 10 min and filtered. The resulting solid was dried under vacuum to afford 0.029 g (73%) of a colorless solid. Anal. Calcd for $C_{39}H_{39}O_3P_3Pd$: C, 62.04; H, 5.17. Found: C, 61.98; H, 5.42. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.45−6.66 (m, 30H, C$_6$*H*$_5$), 2.07 (d, 3H, $^2J_{HP}$ = 7.1, PC*H*$_3$), 1.04 (m, 3H, PC*H*$_3$), 0.56 (m, 3H, Pd*Me*). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 88.5 (dd, $^2J_{PP}$ = 595.9, $^2J_{PP}$ = 62.4, −*P*(O)(OPh)$_2$), 8.2 (dd, $^2J_{PP}$ = 595.9, $^2J_{PP}$ = 33.3, −*P*MePh$_2$, trans to P(O)(OPh)$_2$), 2.9 (dd, $^2J_{PP}$ = 62.4, $^2J_{PP}$ = 33.1, cis-*P*MePh$_2$).

Synthesis of (dppe)PdMe(P(O)(OPh)$_2$) (5). A round-bottom flask was charged with **3** (0.04 g, 0.052 mmol), dppe (0.021 g, 0.052 mmol), ether (5 mL), and hexane (5 mL). The reaction mixture was stirred for 10 min and filtered. The resulting solid was dried under vacuum to afford 0.038 g (90%) of a colorless solid. Anal. Calcd for $C_{39}H_{37}O_3P_3Pd$: C, 62.20; H, 4.92. Found: C, 62.00; H, 5.37. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.60−6.75 (m, 30H, −C$_6$*H*$_5$), 2.26−2.05 (m, 4H, −C*H*$_2$−), 0.615 (m, 3H, $^3J_{HP}$ = 4.6, $^3J_{HP}$ = 6.7, $^3J_{HP}$ = 7.0, PdMe). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 92.9 (dd, $^2J_{PP}$ = 564.3, $^2J_{PP}$ = 44.5, −*P*(O)(OPh)$_2$), 48.3 (dd, $^2J_{PP}$ = 564.3, $^2J_{PP}$ = 22.5, trans-Ph$_2$*P*(CH$_2$)$_2$PPh$_2$), 40.1 (dd, $^2J_{PP}$ = 44.5, $^2J_{PP}$ = 22.5, cis-Ph$_2$*P*(CH$_2$)$_2$PPh$_2$).

Thermolysis Reactions. Reactivity of 1 or 3 in the Absence of Lewis Bases. An NMR tube was charged with **1** or **3** (0.005 g; 6.55 μmol for **3**, 9.79 μmol for **1**) and $CDCl_3$ (**1** or **3**, 0.5 mL) or C_6D_6 (**3**, 0.5 mL) containing hexamethylbenzene as an internal standard (0.14 g dissolved in 5 mL of solvent). The sample was heated to 70 °C for 48 h. Integration of the resonances for **1** or **3** vs the internal standard from before and after heating revealed no uptake of **1** or **3**.

Reactivity of 3 in the Presence of Lewis Bases. An NMR tube was charged with **3** (0.005 g, 6.5 μmol) and C_6D_6 (0.5 mL) containing hexamethylbenzene as described above. THF (0.53 μL, 6.5 μmol) was then added to the solution. The sample was heated to 70 °C for 24 h. Comparison of the integration of the resonances for **3** and the internal standard from before and after heating revealed no uptake of **3**. After addition of additional THF (0.053 mL, 0.65 mmol; 100 equiv), the solution was heated (70 °C, 24 h). Integration of the resonances for **3** vs the internal standard revealed no uptake of **3**. Similar results were obtained for CH_3CN (0.34 μL, 6.5 μmol) and pyridine (0.53 μL, 6.5 μmol).

Control Reaction between P(O)Ph$_3$ and 3. An NMR tube was charged with **3** (0.005 g, 6.5 μmol), P(O)Ph$_3$ (0.002 g, 7.19 μmol), and C_6D_6 (0.5 mL) containing hexamethylbenzene as described above. The sample was heated (70 °C, 48 h). Integration of the resonances for **3** vs the internal standard from before and after heating revealed no uptake of **3**.

General Procedure for Reaction of 3 with Added Phosphines. An NMR tube was charged with **3** (0.005 g, 6.55 μmol), the appropriate amount of phosphine (e.g. PPh$_3$, 0.0035 g, 13.3 μmol; 2 equiv), a sealed capillary containing 0.002 g of P(C$_6$H$_4$Cl-2)$_2$Ph and C_6D_6 (internal standard), and C_6D_6 (0.5 mL). The alternate internal standard was needed, since the resonances for the P(O)−*Me* group were obscured by the nonyl peaks in the ^{1}H NMR spectrum (in C_6D_6 solution). Upon standing (25 °C, 12 h) integration of the resonances for **3** vs the internal standard from before and after revealed 70% (when PPh$_3$ was used) conversion of **3** into MeP(O)(OPh)$_2$ (characterized by multinuclear NMR and GC/MS). Similar reactions carried out in $CDCl_3$ using **1** or **3** afforded a 50% conversion into MeP(O)(OPh)$_2$.

Molecular Structure Information for (bipy)PdMe(P(O)(OPh)$_2$). A yellow crystal with approximate dimensions 0.4 × 0.3 × 0.3 mm^3 was selected under oil under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.710 73 Å) radiation and a diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with an exposure time of 10 s per frame. A total of 64 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The final cell constants were calculated from a set of 3263 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere

to a resolution of 0.80 Å. A total of 6427 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 45 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface, as sampled by multiple equivalent measurements.[26] The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$.[27] The E statistics suggested the noncentrosymmetric space group $P1$, but only the centrosymmetric space group $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement. A successful solution by direct methods provided most non-hydrogen atoms from the E map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 272 parameters against 3910 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and R_w (based on F^2 for all data) of 0.0329 and 0.0780, respectively. The final difference Fourier map was featureless. The ORTEP diagrams are drawn with 30% probability ellipsoids.

(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(27) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Acknowledgment. Thanks are expressed to Dr. Janet Braddock-Wilking for helpful discussions concerning 2D NMR. This work was supported by a New Faculty Award from the Henry and Camille Dreyfus Foundation and the Bucknell Undergraduate Research Program (A. L. Levine).

Supporting Information Available: Tables giving molecular structure information for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0202118