Reaction of a Palladium(II) Complex Chelated by a Tridentate *PNC* Ligand with Water to Produce a $[(PN)Pd(\mu\text{-}OH)]_2^{2+}$ Dimer: A Rare Observation of a Well-Defined Hydrolysis of a Pd(II)−Aryl Compound

April D. Getty and Karen I. Goldberg*

Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

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The potentially tridenate ligand *o*,*o*′-$Ph_2PC_6H_4C{=}NCH_2C_6H_4Br$ (*PNC*-Br, **1**), prepared by a Schiff base condensation of 2-(diphenylphosphino)benzaldehyde and 2-bromobenzylamine, reacts with $Pd_2(dba)_3$ (dba = dibenzylideneacetone) to form the (*PNC*)PdBr complex (**2**). Abstraction of the bromide ligand from **2** with $AgBF_4$ in acetone-d_6 results in formation of the acetone adduct $[(PNC)Pd(OC(CD_3)_2)][BF_4]$ (**3**). Reaction of **3** with water lead to formation of the Pd(II) dimer $[(PN)Pd(\mu\text{-}OH)]_2[BF_4]_2$ (**4**). That formation of dimer **4** occurs by protonation of the metal-bound aryl group of the *PNC* ligand by water was verified by a deuterium-labeling experiment. This is a rare example of protonation of a hydrocarbyl group from a d^8 square planar metal by water. **4** has been characterized by NMR, elemental analysis, and X-ray crystallography. Reaction of **4** with 2−10 equiv of aniline or *p*-toluidine results in the formation of the mixed dimer *syn*-$[((PN)Pd)_2(\mu\text{-}NHAr)(\mu\text{-}OH)][BF_4]_2$ (**5**).

Introduction

Many catalytic processes involve transition metal complexes of groups 9−11. Of these late metal complexes, those containing hydroxo or amido groups have received considerable attention over the past two decades due to their high reactivity and potential as new catalysts.[1] The majority of reported platinum and palladium hydroxo complexes are formed by the reaction of hydroxide with a metal-halide species by a simple metathesis reaction.[1a] Direct observation of protonation of a hydrocarbyl ligand (M−R) on a d^8 square planar metal by water to form R−H and a M−OH species is extremely rare.[2] However, this type of protonation reaction with water has been proposed as the product release step in catalytic reactions that involve d^8 square planar hydroxo complexes.[3]

We report here the preparation of a new potentially tridentate ligand, *o*,*o*′-$Ph_2PC_6H_4C{=}NCH_2C_6H_4Br$ (*PNC*-Br, **1**), and a Pd(II)−Br complex, (*PNC*)PdBr (**2**), of this new ligand. Abstraction of a bromide ion from **2** with $AgBF_4$ in the presence of H_2O leads to protonation of the benzyl group of the *PNC* ligand, resulting in formation of a palladium bis-μ-hydroxo dimer, $[(PN)Pd(\mu\text{-}OH)]_2[BF_4]_2$ (**4**). Details of this unusual and reversible reactivity are presented.

Results

Synthesis of the *PNC*−Br Ligand (1). *PNC*−Br (**1**) was prepared by a Schiff base condensation of 2-(diphenylphosphino)benzaldehyde and 2-bromobenzylamine (Scheme 1).[4]

Compound **1** is a pale yellow crystalline solid that is stable to air and moisture. However, in solution, **1** is sensitive to the atmosphere and decomposes within a day. Compound **1** was characterized by NMR spectroscopy and elemental analysis. A 5.0 Hz phosphorus-proton coupling ($^4J_{P-H}$) of the imino-proton (H^7) is observed in the ^1H NMR of **1**. Such a four-bond coupling is likely to be a through-space interaction between the phosphorus and H^7.[5] This would involve rotation around the C^6-C^7 bond (as shown in Scheme 1) to bring the phosphorus and H^7 in close proximity. As observed with a similar *PNN*′ ligand, this coupling is lost upon complexation of the ligand to palladium.[5]

Synthesis of the (*PNC*)PdBr Complex (2). The dark red $Pd_2(dba)_3$ (dba = dibenzylideneacetone) was combined with **1** in benzene and heated at 40 °C for several days to generate yellow-green (*PNC*)PdBr (**2**), which precipitated from the solution (Scheme 2). Following recrystallization, **2** was isolated as a yellow crystalline solid and has been characterized by NMR spectroscopy and elemental analysis. Once the triden-

(1) Reviews: (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (c) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (d) Bergman, R. G. *Polyhedron* **1995**, *14*, 3227.

(2) (a) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1848. (b) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028. (c) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (d) Bennett, M. A.; Rokicki, A. *Aust. J. Chem.* **1985**, *38*, 1307. (e) Paterniti, D. P.; Atwood, J. D. *Chem. Commun.* **1997**, 1665. (f) Paterniti, D. P.; Atwood, J. D. *Polyhedron* **1998**, *17*, 1177.

(3) (a) Ganguly, S.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1991**, 639. (b) Ganguly, S.; Roundhill, D. M. *Organometallics* **1993**, *12*, 4825.

(4) For preparation of phosphine-containing ligands by Schiff base condensation see: Lavery, A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1984**, 615.

(5) Rülke, R. E.; Kaasjager, V. E.; Wehman, P.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1996**, *15*, 3022.

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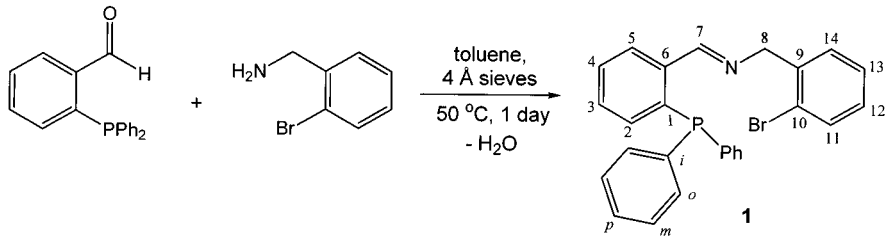
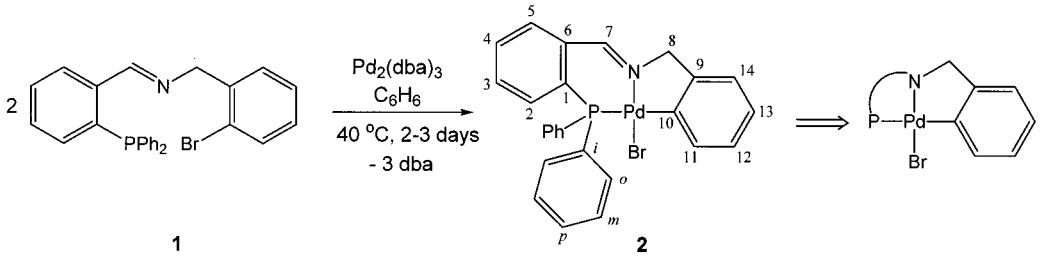
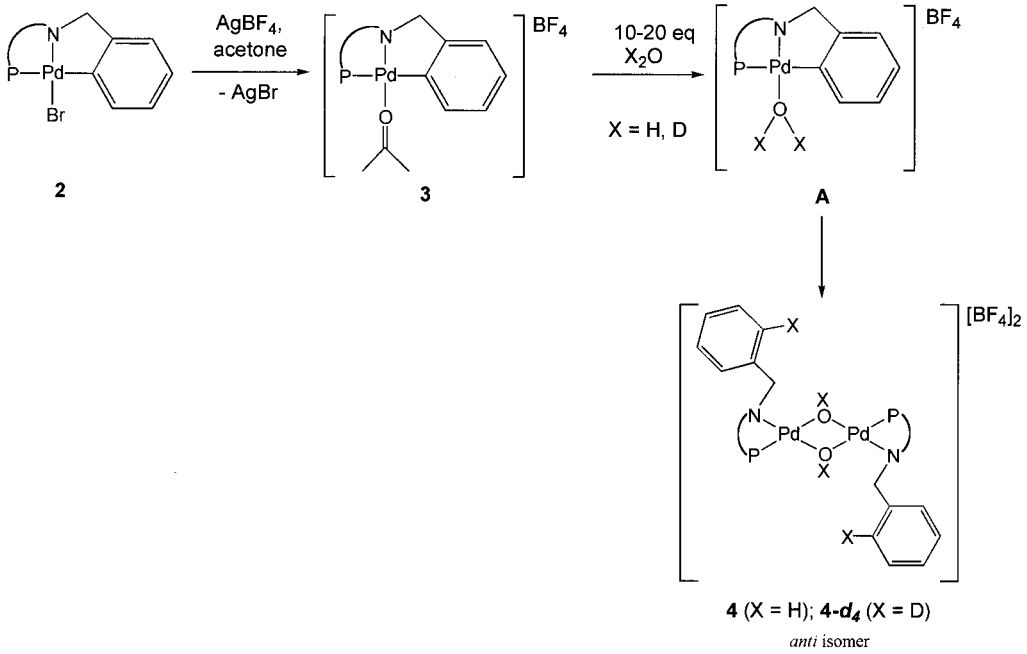
Scheme 1



Scheme 2



Scheme 3



tate ligand is attached to the metal, the $^{31}P\{^1H\}$ NMR signal shifts from −13.6 to 14.9 ppm and the ^1H NMR signal for the imine (H^7) shifts from 9.04 to 8.36 ppm. The phosphorus coupling to this imine proton is lost upon coordination. The large downfield shift of C^{10} in **2** from 124.0 to 159.0 ppm, and a $^2J_{P-C}$ of 144 Hz for this carbon is consistent with coordination of C^{10} to the metal and with the *trans* arrangement of the aryl and phosphine groups.

Synthesis of the [(*PN*)Pd(*μ*-OH)]$_2$[BF$_4$]$_2$ Dimer (4). Upon combination of **2** with $AgBF_4$ in acetone-d_6, a precipitate (AgBr) formed and the yellow solution became orange. The $^{31}P\{^1H\}$ and ^1H NMR spectra of the reaction solution showed only slight chemical shift variations as compared to **2**. This orange species is assigned as the acetone adduct [(*PNC*)Pd(OC(CD$_3$)$_2$)][BF$_4$] (**3**) (Scheme 3).

The reaction mixture containing **3** was filtered to remove the AgBr, and then 10−20 equiv of water was added (Scheme 3). Addition of water to **3** resulted in the appearance of a signal in the $^{31}P\{^1H\}$ NMR at 32.5 ppm, ca. 17 ppm downfield of the signal for **3**. This new signal grew in over 2 h, after which time no signal for the starting material remained. A yellow air-stable solid ([(*PN*)Pd(*μ*-OH)]$_2$[BF$_4$]$_2$ (**4**)) was isolated from the reaction solution by the addition of Et_2O. **4** is insoluble in nonpolar organic solvents and only sparingly soluble in CH_2Cl_2.

X-ray quality crystals of **4**·2CH_2Cl_2 were obtained by slow evaporation of a CH_2Cl_2 solution under atmospheric conditions. The ORTEP drawing is shown in Figure 1, selected bond lengths and angles are listed in Table 1, and the summary of crystal data and details of structure refinement are shown in Table 2.[6] The molecule has a center of symmetry with a Pd1···Pd1A

(6) Details of the X-ray crystal structure determination are provided in the Supporting Information.

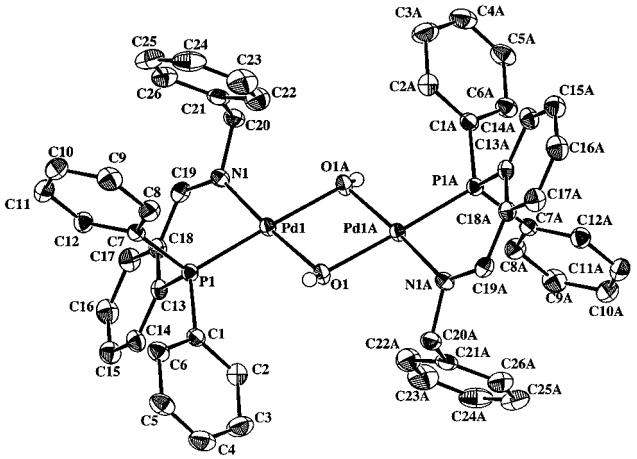


Figure 1. Figure 1. ORTEP drawing of the cation in **4**·$2CH_2Cl_2$. Ellipsoids are shown at 50% probablility level. Hydrogens (except on μ-OH), BF_4 anions, and CH_2Cl_2 molecules are not shown.

Table 1. Selected Bond Lengths and Angles for the Cation in 4·2CH_2Cl_2

bond lengths (Å)		bond angles (deg)	
N1−Pd1	2.020(3)	N1−Pd1−P1	86.59(8)
P1−Pd1	2.1946(9)	N1−Pd1−O1A	94.84(10)
Pd1−O1	2.015(2)	P1−Pd1−O1	98.14(7)
Pd1−O1A	2.096(2)	Pd1−O1−Pd1A	99.59(10)
C19−C18	1.475(5)	C18−C13−P1	118.8(3)
C18−C13	1.408(5)	O1A-Pd1−O1	80.41(10)
C13−P1	1.819(3)	C13−P1−Pd1	105.06(11)
C19−N1	1.280(4)	C18−C19−N1	125.8(3)

Table 2. Crystallographic Data for 4·2CH_2Cl_2

	$[(PN)Pd(\mu\text{-}OH)]_2[BF_4]_2\cdot 2CH_2Cl_2$
empirical formula	$C_{54}H_{50}B_2Cl_4F_8N_2O_2P_2Pd_2$
fw	1349.12
temp (K)	161(2)
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell dimens (Å, deg)	$a = 10.6096(2)$, $\alpha = 65.085(1)$ $b = 12.4309(5)$, $\beta = 66.503(2)$ $c = 12.6585(5)$, $\gamma = 84.356(2)$
volume (Å^3)	1383.70(8)
Z	1
$F(000)$	676
D_{calc} (g/cm^3)	1.619
μ (mm^{-1})	0.971
radiation, λ (Å)	Mo Kα, 0.71070
cryst size (mm)	0.31 × 0.25 × 0.18
θ range (deg)	2.10−30.53
index ranges	$-11 \le h \le 14$, $-17 \le k \le 16$, $-17 \le l \le 18$
no. of reflns collected	29 515
no. of unique reflns	7672 ($R_{int} = 0.041$)
no. of params refined	353
final R, R_w [$I > 4\sigma(I)$]	0.0533, 0.1401
R indices (all data)	0.0745, 0.1473
goodness-of-fit	1.074
largest diff peak and hole (e Å^{-3})	1.056 and −1.253

nonbonding distance of 3.142(1) Å. The four donor atoms (i.e., P1, N1, O1, and O1A) form an exact plane (mean plane deviation = 0.000 Å), and Pd1 is 0.024(4) Å from the plane. The nearest nonbonded neighbor to Pd is a chlorine from one of the CH_2Cl_2 molecules in the crystal (3.633(5) Å). There appears to be a hydrogen bond interaction between the proton of the bridging hydroxo group and a fluorine from the tetrafluoroborate counterion. The H···F distance is 1.90 Å and the O···F nonbonding distance is 2.828(3) Å with an O−H−F angle of 147.8°. The Pd1−O1 distance is 2.015(2) Å, which is ca. 0.08 Å shorter than the Pd1−O1A distance due to the greater *trans* effect of phosphorus compared to nitrogen. The Pd−O bond lengths of **4** are similar to those of other Pd−μ-OH dimers reported in the literature.[7]

The spectroscopic features of **4** are also similar to those of reported Pd−μ-OH dimers.[3b,7,8] The ^{1}H NMR signal for the μ-OH group is at −1.34 ppm (CD_2Cl_2), and the O−H stretch (ν(OH)) in the IR spectrum is at 3480 cm^{-1} (br, Nujol). The C^{10} signal of **4** is shifted upfield relative to its position in **2** to a value similar to C^{10} in the free ligand (**1**). The C^{10} signal of **4** no longer shows coupling to phosphorus, consistent with this carbon no longer being bound to the metal.

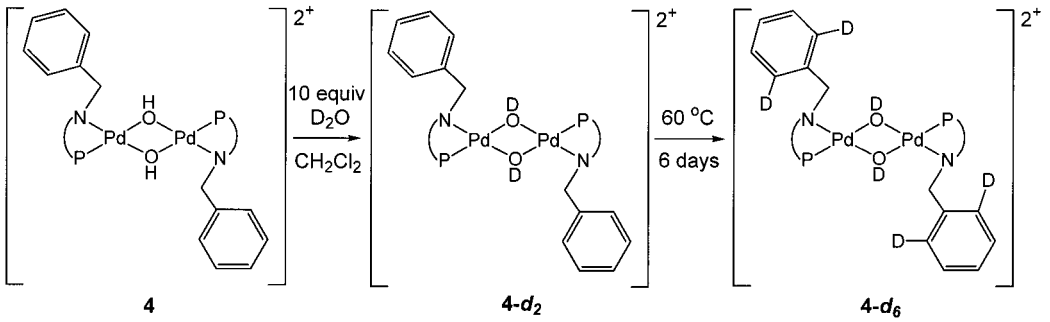
The ^{1}H NMR spectrum also shows low-intensity signals of similar multiplicities near the major signals, and in the ^{31}P{^{1}H} NMR spectrum there is a signal at 29.5 ppm, which is ca. 1/6 the height of the major signal at 31.9 ppm. These smaller signals can be assigned to a minor product in which the phosphines are *syn*, rather than *anti*, as seen in the X-ray structure (Figure 1). The μ-OH signals in the ^{1}H and ^{1}H{^{31}P} NMR spectra are particularly diagnostic in assigning the major and minor isomers. For the *anti* (major) isomer, there is only one OH signal in the ^{1}H NMR spectrum, which integrates 1:2 relative to the corresponding benzyl protons (H^8). This signal is a doublet at δ −1.34 ($^3J_{P-H}$ = 2.2 Hz) and reduces to a singlet in the ^{1}H{^{31}P} spectrum, consistent with coupling of the OH hydrogens to one *trans* phosphorus atom. In contrast, there are two OH signals (δ 0.41 (t, $^3J_{P-H}$ = 3.4 Hz) and δ −2.84 (s)) in the ^{1}H NMR spectrum for the inequivalent hydroxyl groups in the the *syn* (minor) isomer. These OH signals integrate relative to the corresponding benzyl protons (H^8) as 0.5: 0.5:2. In the ^{1}H{^{31}P} spectrum, the triplet OH signal at δ 0.41 becomes a singlet, consistent with that OH being *trans* to two phoshorus atoms and the other *trans* to only nitrogens. The *syn* isomer is more sterically crowded, which likely accounts for its lower concentration.

Synthesis of the $[(d_1\text{-}PN)Pd(\mu\text{-}OD)]_2[BF_4]_2$ Dimer (4-d_4). When the reaction of (*PNC*)PdBr (**2**) with $AgBF_4$ was carried out in the presence of D_2O, formation of the $[(d_1\text{-}PN)Pd(\mu\text{-}OD)]_2[BF_4]_2$ dimer (**4-d_4**) was observed (Scheme 3). The ^{1}H NMR signal for the μ-OH proton in **4** is absent in the spectrum of **4-d_4**. The signal for H^{11} should appear as a doublet of 1:1:1 triplets due to coupling with H^{12} and the deuterium which replaced H.[10] However, the pattern is more complex as the signal for H^{11} overlaps with the expected triplet signal for H^{13}. The ^{2}H NMR spectrum has two broad signals, −1.3 and

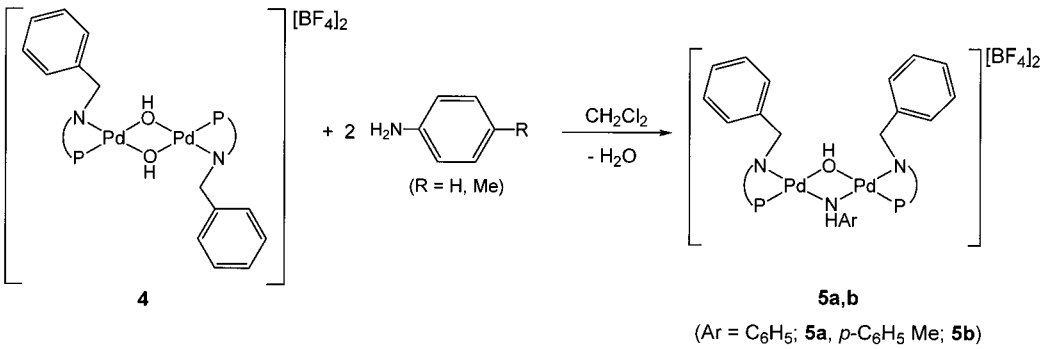
(7) Examples of Pd−μ-OH dimers that contain phosphine or nitrogen ligands in which the crystal structure has been determined: (a) Pisano, C.; Consiglio, G.; Sironi, A.; Moret, M. *J. Chem. Soc., Chem. Commun.* **1991**, 421. (b) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890. (c) Pieri, G.; Pasquali, M.; Leoni, P.; Engleert, U. *J. Organomet. Chem.* **1995**, *491*, 27. (d) Ruiz, J.; Cutillas, N.; Sampedro, J.; López, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1996**, *526*, 67. (e) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450.

(8) (a) Bushnell, G. W.; Dixon, K. R.; Hunter, R. G.; McFarland, J. J. *Can. J. Chem.* **1972**, *50*, 3694. (b) Wimmer, S.; Castan, P.; Wimmer, F. L.; Johnson, N. P. *J. Chem. Soc., Dalton Trans.* **1989**, 403. (c) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Santana, M. D. *J. Orgamomet. Chem.* **1990**, *393*, C53. (d) López, G.; Ruiz, J.; García, G.; Martí, J. M.; Sánchez, G.; García, J. *J. Organomet. Chem.* **1991**, *412*, 435. (e) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabo, J.; Molins, E.; Miravitlles, C. *Inorg. Chem.* **1991**, *30*, 2605. (f) Strukul, G.; Varagnolo, A.; Pinna, F. *J. Mol. Catal. A* **1997**, *117*, 413. (g) Gavagnin, R.; Catalodo, M.; Pinna, F.; Strukul, G. *Organometallics* **1998**, *17*, 661.

Scheme 4



Scheme 5



7.2 ppm, which correspond to the chemical shifts of the μ-OH and H^{10} protons, respectively, in the ^{1}H NMR spectrum of **4**. The $^{31}P\{^1H\}$ spectrum of **4-*d*$_4$** is identical to that of **4**, showing signals for both the major and minor isomers. The IR spectrum of **4-*d*$_4$** shows bands at 2570 cm^{-1} (ν(OD)) and 2356 cm^{-1} (ν(C^{10}−D)).

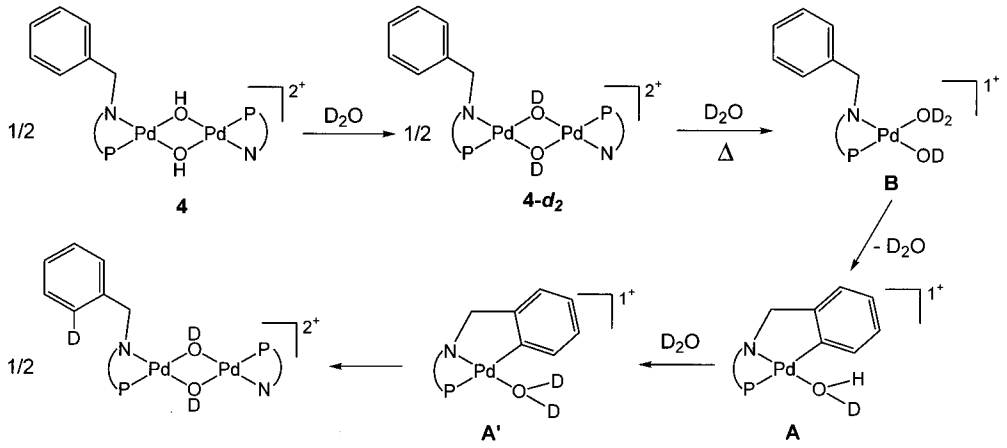
Syntheses of [(*PN*)Pd(μ-OD)]$_2$[BF$_4$]$_2$ (4-*d*$_2$) and [(*d*$_2$-*PN*)Pd(μ-OD)]$_2$[BF$_4$]$_2$ (4-*d*$_6$) Dimers. The deuterated dimer **4-*d*$_2$** can be easily prepared by reaction of **4** with D_2O in CH_2Cl_2. Upon addition of 10−20 equiv of D_2O to the solution of **4**, the signal for the OH proton of **4** at −1.34 ppm in the ^{1}H NMR spectrum disappears and the ^{2}H NMR spectrum shows a signal for the OD proton of **4-*d*$_2$** at −1.3 ppm. Heating this solution at 60 °C for several days results in formation of the further deuterated dimer **4-*d*$_6$** (Scheme 4). Deuterium incorporation into the *ortho* positions of the benzyl rings is noted by the appearance of a signal at 7.2 ppm in the ^{2}H NMR. The ^{1}H NMR signal for $H^{11,13}$ (δ 7.28) in **4-*d*$_6$** appears as a doublet of 1:1:1 triplets. The signal for $H^{10,14}$ (δ 7.16) eventually disappears from the ^{1}H NMR spectrum of **4-*d*$_6$** as deuterium incorporates into those sites. The $^{31}P\{^1H\}$ NMR spectrum remains unchanged.

Syntheses of *syn*-[((*PN*)Pd)$_2$(μ-NHAr)(μ-OH)][BF$_4$]$_2$ Dimers (5a,b). The addition of 2−10 equiv of aniline or *p*-toluidine to a CD_2Cl_2 solution of **4** resulted in the rapid formation of the mixed hydroxo-amido dimers **5a** or **b**, respectively, as observed by ^{1}H and $^{31}P\{^1H\}$ NMR (Scheme 5). A signal appeared at the chemical shift for H_2O (δ 1.60) when the formation of **5** was monitored by ^{1}H NMR. The IR spectrum for **5a** shows bands for ν(NH) and ν(OH) at 3290 and 3520 cm^{-1} (br, Nujol), respectively. Upon completion of the reaction, the $^{31}P\{^1H\}$ NMR showed a single peak at 25.1 ppm (CD_2Cl_2) and the ^{1}H NMR indicated that only one product was present. The ^{1}H NMR data are consistent with this one product being the *syn* isomer. For **5a**, the NH proton gives rise to a broad singlet in the ^{1}H NMR at 0.53 ppm and the signal for the OH proton appears as a triplet due to phosphorus coupling at 0.09 ppm ($^3J_{P-H}$ = 3 Hz). The benzyl protons (H^8) are inequivalent, and the signals for each appear as doublets at 4.54 and 5.78 ppm with a 12.5 Hz H−H coupling. Similar signals are observed for **5b**. Integration of the ^{1}H NMR of **5b** showed the ratio of imine (H^7):*p*-Me:OH signals as 2:3:1, which is consistent with the dimer containing one μ-OH bridge and one μ-NHAr bridge. Attempts to produce the bis-μ-amido dimer by using more than 10 equiv of aniline or *p*-toluidine were unsuccessful, even when the solution was heated and 4 Å sieves were added to remove the water from the anticipated equilibrium.

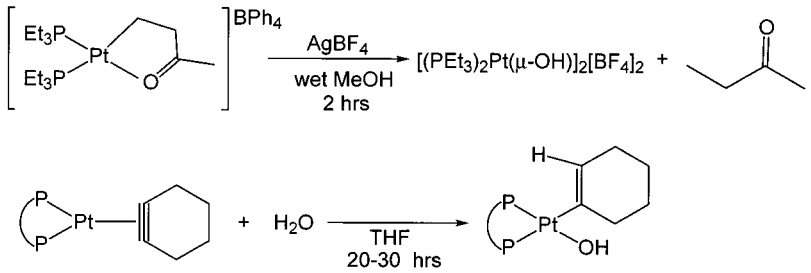
Discussion

A novel, potentially tridentate *PNC*−Br ligand (**1**) has been prepared by a Schiff base condensation reaction. Reaction of **1** with the Pd(0) precursor complex $Pd_2(dba)_3$ resulted in oxidative addition of the aryl−bromide bond of **1** to the Pd(0) center. The Pd(II) product (*PNC*)PdBr (**2**) was formed with *PNC* acting as a tridentate ligand bearing a formal negative charge. Removal of the bromide ligand from **2** with $AgBF_4$ followed by addition of H_2O produced the dimeric species [(*PN*)Pd(μ-OH)]$_2$[BF$_4$]$_2$ (**4**). Formation of **4** resulted from protonation of the benzyl ring of the tridentate *PNC* ligand by the added water. This was confirmed by a deuterium-labeling experiment; reaction of **2** with $AgBF_4$ in the presence of D_2O led to the deuterated dimer [(*d*$_1$-*PN*)-Pd(μ-OD)]$_2$[BF$_4$]$_2$ (**4-*d*$_4$**). The deuterium atoms in **4-*d*$_4$** are located in the μ-hydroxo positions and in the *ortho* position of the benzyl ring. A reasonable mechanism for this reaction is shown in Scheme 3. An acetone molecule occupies the site that was left vacant by the departed bromide anion (**3**). Then, the acetone is replaced by an aquo ligand to form intermediate **A**. Either direct

Scheme 6



Scheme 7



protonation by the water of the *ortho* benzyl carbon (C^{10}) takes place freeing the aryl ring from the palladium or the palladium itself is protonated, followed by rapid C−H reductive elimination.

Exposure of a methylene chloride solution of **4** to 10−20 equiv of D_2O resulted in formation of the deuterated dimer **4-*d*$_2$** within 10 min. Such exchange of hydroxyl protons is expected. However, when this solution was heated for several days at 60 °C, exchange of deuterium into the *ortho* positions of the benzyl ring was found. The formation of **4-*d*$_6$** implies that release of the coordinated benzyl ring is reversible. The most reasonable mechanism for such an exchange process would involve cleavage of the dimer as shown in Scheme 6. Cleavage of the **4-*d*$_2$** dimer by water would form the mononuclear complex **B**. The *ortho* C−H bond of the benzyl group can displace the water in either an associative or dissociative exchange reaction. Direct protonation of the hydroxide ligand or oxidative addition of the C−H bond followed by deprotonation of the Pd generates the aquo intermediate **A**. Protons of the aquo ligand can exchange with deuterium from the D_2O, or alternatively D_2O can displace H_2O. The deuterated aquo complex (intermediate **A′**) could then undergo transfer of a deuterium to the benzyl ring to ultimately produce the **4-*d*$_6$** dimer.

While protonation of d^8 square planar hydrocarbyls by strong acids[9] and even phenols[10] is common, reactions that involve protonation by water are rare.[2] However, such a reaction with water can represent a powerful product release step in palladium-catalyzed reactions. The unusual factor in the formation of **4** via such a hydrolysis reaction is that an open coordination site within the square plane was available for the water to bind prior to the protonation. The formation of the aquo complex (intermediate **A**) results in a higher acidity for the coordinated water[11] and brings the hydrogen within close proximity to the bound carbon.

Two previous examples of protonation reactions with water may also allow such H_2O precoordination within the square planar geometry (Scheme 7).[2a,b] The carbonyl oxygen can be displaced by water in the first example in Scheme 7 to form an intermediate similar to **A** in Scheme 3, and the coordinatively unsaturated platinum center in the second example may also accommodate a water molecule. This concept of an open coordination site in the square plane of the d^8 metal center to promote hydrocarbyl protonation by water should certainly be considered in catalyst design.

Cleavage of the Pd−μ-OH dimer **4** is implicated by the reactivity of **4** with both D_2O and anilines. As shown in Scheme 4, reaction of **4** with D_2O at elevated temperatures yielded the $[(d_2\text{-}PN)Pd(\mu\text{-OD})]_2^{2+}$ (**4-*d*$_6$**) dimer with deuterium incorporation into the *ortho* positions of the benzyl group. The most reasonable mechanism for this deuterium exchange reaction (Scheme 6) involves cleavage of the dimer followed by C−H bond activation of the benzyl group. Subsequent release of the deuterated benzyl ring from intermediate **A** or **A′** would generate the deuterated dimer by a path analo-

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gous to that used in the synthesis of **4** (Scheme 3). The reaction of **4** with anilines also provides strong evidence for dimer bridge cleavage. Complex **4** exists in solution as a mixture of *syn* and *anti* isomers, with the majority present as the *anti* isomer. Reaction of **4** with aniline or *p*-toluidine leads to formation of exclusively the *syn* isomer of the mixed hydroxo-amido dimer (**5**, Scheme 5). There are several other reports of the reaction of Pd(II)−μ-OH dimers with primary amines to form bridging bis-amido or mixed amido-hydroxo dimers,[12] and mechanistic evidence has been provided to support cleavage of the dimer bridges in one of these systems.[12a,b] The mechanisms proposed for a variety of catalytic reactions involving Pd(II)−μ-OH dimers (e.g., the hydration of diethyl maleate, the Mannich reaction, and the Baeyer−Villiger oxidation of ketones) involve initial cleavage of the μ-hydroxo bridges.[3,7e,8f,g] Our results for the reaction of **4** with D_2O and aniline point to the viability of such dimer cleavage.

Conclusions

A new tridentate *PNC* ligand has been prepared and attached to palladium, generating the novel Pd(II) complex (*PNC*)PdBr (**2**). Opening up a coordination site at the Pd by abstraction of the bromide anion allows coordination of water to the metal center. Protonation by the coordinated water of the Pd-bound benzyl ring results in the formation of the Pd(II)−μ-OH dimer, $[(PN)Pd(\mu\text{-}OH)]_2[BF_4]_2$ (**4**). This is a rare observation of protonation of a d^8 square planar hydrocarbyl by water. It models an important proposed product release step in Pd(II)-catalyzed reactions, and the open coordination site within the square plane is likely a key component in facilitating this reaction. Strong evidence for cleavage of the hydroxo bridges of **4** is provided by the selective deuterium incorporation into the benzyl group upon heating **4** in the presence of D_2O and by formation of the exclusively *syn* isomer of the hydroxo-amido dimer **5** upon reaction of primarily *anti* isomer of **4** with anilines. Cleavage of Pd−hydroxo dimers are proposed as an initial step in catalytic reactions involving these species.

Experimental Section

General Comments. All manipulations were carried out under N_2 or by using standard high-vacuum techniques, unless otherwise noted. Benzene, toluene, and diethyl ether were dried over sodium benzophenone ketyl. Methylene chloride and pentane were dried over CaH_2. Acetone was predried over $CaSO_4$ and then stored over activated 4 Å sieves. Aniline was distilled from CaH_2 under reduced pressure, and *p*-toluidine was recrystallized from Et_2O in the drybox at −33 °C. Elemental analyses were performed by Atlantic Microlab, Inc. NMR spectra were recorded using Bruker DRX499 or WM500 spectrometers, and chemical shifts (δ) are reported in ppm. ^1H NMR spectra were referenced to residual proton peaks in the deuterated solvent and reported relative to TMS. $^{13}C\{^1H\}$ NMR spectra were referenced to solvent peaks relative to TMS, $^{31}P\{^1H\}$ NMR spectra were referenced to 85% H_3PO_4 external capillary, and the ^2H NMR spectra were referenced to CD_2Cl_2 in CH_2Cl_2. Unless otherwise specified, reagents and solvents were used as purchased (from Aldrich Chemical Co. or Strem). Partial listings of NMR data for **1**, **2**, **4**, and **5** are reported here, with full ^1H and $^{13}C\{^1H\}$ assignments provided in Tables 1−4 of the Supporting Information.

Synthesis of *N*-(2-(Diphenylphosphino)benzylidene)-(2-bromobenzyl)amine (*PNC*-Br, 1). 2-(Diphenylphosphino)benzaldehyde (2.12 g, 7.29 mmol) and 2-bromobenzylamine (3.13 g, 16.8 mmol) were placed in a glass bomb with 10 g of 4 Å activated molecular sieves and 50 mL of dry toluene. After 1 day at 50 °C the reaction appeared complete by $^{31}P\{^1H\}$ NMR. The pale yellow reaction mixture was filtered through glass wool, and the solvent was removed under vacuum to leave a yellow-orange oil. **1** was purified by dissolving the oil in a ca. 1:4 mixture of CH_2Cl_2/diethyl ether, layering pentane on the solution, and cooling to −33 °C for several days. **1** was isolated as a pale yellow crystalline solid (2.66 g, 80% yield). Anal. Calcd for $C_{26}H_{21}NPBr$: C, 68.13; H, 4.62; N, 3.06. Found: C, 68.39; H, 4.64; N, 3.10. ^1H NMR (CD_2Cl_2): δ 9.04 (d, 1H, H,[7] $^4J_{P-H}$ = 5.0 Hz), 4.74 (s, 2H, H[8]). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 138.5 (C^1, $^1J_{P-C}$ = 20.2 Hz), 140.0 (C^6, $^2J_{P-C}$ = 17.2 Hz), 161.9 (C^7, $^3J_{P-C}$ = 21.4 Hz), 64.8 (C^8), 139.2 (C^9), 124.0 (C^{10}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.6.

Synthesis of (*PNC*)PdBr (2). To 511 mg (1.12 mmol) of **1** in 20 mL of benzene was added 552 mg (0.602 mmol) of $Pd_2(dba)_3$. After a freeze−pump−thaw cycle, the reaction mixture was placed in a 40 °C bath for 1−3 days. Completion of the reaction was determined by $^{31}P\{^1H\}$ NMR. During the reaction, a yellow-green solid precipitated from the orange solution. The volume of benzene was reduced by half, diethyl ether was added to the mixture to aid complete precipitation of the product, and the solid was collected on a fine frit. The product was washed with Et_2O (3 × 2 mL) to remove any remaining dba. **2** can be recrystallized from either CH_2Cl_2/Et_2O or CH_3CN/Et_2O at −33 °C. The yield was 567 mg (90%). Anal. Calcd for $C_{26}H_{21}NPBrPd{\cdot}CH_3CN$: C, 55.51; H, 3.99; N, 4.63. Found: C, 55.52; H, 4.03; N, 4.65. ^1H NMR (CD_2Cl_2): δ 8.36 (s, 1H, H^7), 5.28 (s, 2H, H^8). ^1H NMR (acetone-d_6): δ 8.82 (s, 1H, H^7), 5.38 (s, 2H, H^8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 127.5 (C^1, $^1J_{P-C}$ = 26.6 Hz), 137.5 (C^6, $^2J_{P-C}$ = 20.4 Hz), 164.3 (C^7), 78.4 (C^8), 144.5 (C^9), 159.0 (C^{10}, $^2J_{P-C}$ = 144.0 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.9. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 15.4.

Synthesis of $[(PN)Pd(\mu\text{-}OH)]_2[BF_4]_2$ (4). In an NMR tube, **2** (8.7 mg, 0.015 mmol) was dissolved in acetone-d_6 and 1.3 equiv of $AgBF_4$ (4.0 mg, 0.020 mmol) was added. The solution changed from yellow to orange, and a white precipitate formed (AgBr). The orange product was assigned as the acetone adduct $[(PNC)Pd(OC(CD_3)_2)]BF_4$ (**3**). ^1H NMR (acetone-d_6): δ 8.95 (s, 1H, H^7), 5.61 (s, 2H, H^8). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 15.5. After 1 h the reaction mixture was filtered to remove the AgBr and **4** was formed by adding 20 equiv of H_2O (5.5 μL). The color returned to yellow, and the reaction was determined to be complete by NMR (ca. 3 h). *Anti* isomer of **4**: ^1H NMR (acetone-d_6): δ 8.73 (s, 1H, H^7), 4.71 (s, 2H, H^8). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 32.5.

Preparative scale synthesis of **4** can be performed in wet acetone solvent; however, higher yields were obtained in wet CH_2Cl_2. **2**·Et_2O (185 mg, 0.290 mmol) was dissolved in 8 mL of CH_2Cl_2, and 100 μL (17 equiv) of H_2O was added via a 50 μL syringe. $AgBF_4$ (56.4 mg, 0.290 mmol) was added, and the reaction mixture was stirred very vigorously for 2 h. The solution was yellow with a dark gray precipitate (AgBr), and completion of the reaction was determined by $^{31}P\{^1H\}$ NMR. In air, the reaction was filtered through glass wool layered with Celite to remove the AgBr, and the volume of the filtrate was reduced by half under vacuum. Et_2O was added to precipitate the pale yellow product. The solid was collected on a fine frit and was further purified by recrystallization from CH_2Cl_2/diethyl ether at −23 °C to yield a yellow crystalline solid (135 mg, 79% yield). Anal. Calcd for $C_{52}H_{46}N_2O_2P_2$-

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$Pd_2B_2F_8 \cdot H_2O$: C, 52.16; H, 4.04; N, 2.34. Found: C, 52.18; H, 3.91; N, 2.28. *Anti* isomer of **4**: ^{1}H NMR (CD_2Cl_2): δ −1.34 (d, 1H, O*H*, $^3J_{P-H}$ = 2 Hz), 8.23 (s, 1H, H^7), 4.56 (s, 2H, H^8), 7.16 (d, $H^{10,14}$), $H^{11,13}$ (t, 7.29), H^{12} (t, 7.43). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 168.0 (C^7), 67.0 (C^8), 129.5 ($C^{10,14}$), 130.0 ($C^{11,13}$ + C^{12}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.9. IR (Nujol): ν(OH) 3480 cm^{-1} (br).

X-ray Structure Determination of [(*PN*)Pd(*μ*-OH)]$_2$[BF$_4$]$_2$·2CH$_2$Cl$_2$ (4). The selected crystal was mounted on a glass capillary in oil since solvent evaporation rapidly resulted in loss of crystallinity. All hydrogen atoms were located by difference Fourier synthesis and were refined with a riding model. U_{iso} values were fixed such that they were $1.1U_{eq}$ of their parent atom ($1.5U_{eq}$ for O*H*). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The data were corrected for absorption anisotropy by scaling and averaging using the program SCALEPACK.[6] Details of the crystal data collection and refinement are listed in Table 2.

Synthesis of [(*d*$_1$-*PN*)Pd(*μ*-OD)]$_2$[BF$_4$]$_2$ (4-*d*$_4$). To 93.0 mg (0.165 mmol) of **2** in 6 mL of CH_2Cl_2 was added 41.7 mg (0.214 mmol) of $AgBF_4$. The reaction was stirred for 3 h, after which time the solution was filtered through glass wool layered with Celite. D_2O (30 μL, 1.66 mmol) was added. After another 3 h the reaction appeared complete by $^{31}P\{^1H\}$ NMR. **4-*d*$_4$** was purified in a drybox using the same procedure as **4** (25.0 mg, 25.6% yield). *Anti* isomer of **4-*d*$_4$**: ^{1}H NMR (CD_2Cl_2): δ 8.23 (s, 1H, H^7), 4.54 (s, 2H, H^8). ^{2}H NMR (CH_2Cl_2): δ −1.3 (br, O*D*), 7.2 (br, D^{10}). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 31.9. IR (Nujol): ν(OD) 2570 cm^{-1} (br), ν(C^{10}−D) 2356 cm^{-1}.

Syntheses of [(*PN*)Pd(*μ*-OD)]$_2$[BF$_4$]$_2$ (4-*d*$_2$) and [(*d*$_2$-*PN*)Pd(*μ*-OD)]$_2$[BF$_4$]$_2$ (4-*d*$_6$) Dimers. 4 (5 mg, 0.0042 mmol) was dissolved in CH_2Cl_2 in a J-Young type NMR tube. D_2O (10−20 equiv) was added to the tube via a 10 μL syringe. After a freeze−pump−thaw cycle, NMR spectra were obtained. A broad signal appears in the ^{2}H NMR at δ −1.3, which corresponds to the chemical shift for the O*H* signal in the ^{1}H NMR spectrum of **4**. This signal is absent in the ^{1}H NMR. This complex is assigned as the **4-*d*$_2$** dimer. The $^{31}P\{^1H\}$ NMR is unchanged (δ 31.9). The tube was then immersed in a 60 °C oil bath, and after 6 days there was significant incorporation of deuterium into the benzyl ring of the ligand (at the $H^{10,14}$ sites, δ 7.16). This complex is assigned as the **4-*d*$_6$** dimer (Scheme 4). After the 6 day period of heating, the solvent was removed from the tube under vacuum and CD_2Cl_2 was transferred into the tube in order to obtain a ^{1}H NMR spectrum. *Anti* isomer of **4-*d*$_6$**: ^{2}H NMR (CH_2Cl_2): δ −1.3 (br, O*D*), 7.2 (br, D^{10}). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 31.9. ^{1}H NMR (CD_2Cl_2): 7.28 (d of 1:1:1 t, $H^{11,13}$).

Synthesis of *syn*-[((*PN*)Pd)$_2$(*μ*-NHAr)(*μ*-OH)][BF$_4$]$_2$ (5a,b). To 63.3 mg (0.0537 mmol) of **4** in 7 mL of CH_2Cl_2 was added 10.8 μL (0.118 mmol) of aniline. Upon addition of the aniline, the solution became a brighter yellow color and all of the solid dissolved. After 1 h the reaction appeared complete by $^{31}P\{^1H\}$ NMR. In air, the volume of the solution was reduced by half and Et_2O was added to precipitate the product. The product was collected on a fine frit and was further purified by recrystallization from CH_2Cl_2/diethyl ether at −23 °C (50.6 mg; 70.9% yield). **5a**: Anal. Calcd for $C_{58}H_{51}N_3P_2OPd_2B_2F_8 \cdot H_2O$: C, 54.74; H, 4.20; N, 3.30. Found: C, 54.50; H, 4.25; N, 3.29. ^{1}H NMR (CD_2Cl_2): δ 8.41 (s, 2H, H^7), 4.54 and 5.78 (d for each signal, 2H each, $H^{8\ a+b}$, $^2J_{H-H}$ = 12.5 Hz), 0.09 (t, 1H, O*H*, $^3J_{P-H}$ = 3 Hz), 0.53 (br, N*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 121.0 (C^1, $^1J_{P-C}$ = 52.5 Hz), 136.9 (C^6, $^2J_{P-C}$ = 12.5), 166.8 (C^7), 66.0 (C^8), 135.5 (C^9). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 25.1. IR (Nujol): ν(NH) 3290 cm^{-1} (br); ν(OH) 3520 cm^{-1} (br). **5b** was prepared on an NMR scale to confirm that the mixed hydroxo-amido dimer, rather than the bis-*μ*-amido dimer, was formed. To 4.5 mg (0.0038 mmol) of **4** in a J-Young type NMR tube was added 1.0 mg (0.0095 mmol, 2.5 equiv) of *p*-toluidine and 0.5 mL of dry CH_2Cl_2. After 2.5 h the reaction was determined to be complete by $^{31}P\{^1H\}$ NMR. The CH_2Cl_2 was removed under vacuum, and the NMR tube was taken into the drybox. The solid was rinsed with 3 × 1 mL of Et_2O to remove the excess *p*-toluidine. Then the J-Young tube was placed under vacuum for several hours, after which time CD_2Cl_2 was vacuum transferred into the tube and NMR spectra were recorded. ^{1}H NMR (CD_2Cl_2): δ 8.37 (s, 2H, H^7), 4.51 and 5.79 (d for each signal, 2H each, $H^{8\ a+b}$, $^2J_{H-H}$ = 13 Hz), 2.26 (s, 3H, *p*-$C_6H_4CH_3$), −0.04 (t, 1H, O*H*, $^3J_{P-H}$ = 3 Hz), 0.52 (br, N*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 24.8. Integration of H^7:*p*-$C_6H_4CH_3$:O*H* is 2:3:1, confirming that **5** is a mixed hydroxo-amido dimer.

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Supporting Information Available: A listing of ^{1}H and $^{13}C\{^1H\}$ NMR assignments for **1**, **2**, **4**, and **5a** and detailed crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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