Highly Air-Stable Anionic Mononuclear and Neutral Binuclear Palladium(II) Complexes for C–C and C–N Bond-Forming Reactions

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The short-bite aminobis(phosphonite), PhN{P(–OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O–)}$_2$ (**2**), containing a mesocyclic thioether backbone is synthesized by either treating PhN(PCl$_2$)$_2$ with 2 equiv of thiobis(2,2′-naphthol) or reacting chlorophosphite (–OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O–)PCl (**1**) with aniline in the presence of a base. Treatment of **2** with an equimolar amount of Pd(COD)Cl$_2$ in the presence of H$_2$O affords a P–N–P-bridged and P,S-metalated binuclear complex, [PhN(P(–OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O–)-κP)$_2$Pd$_2$Cl$_2${P(–OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O–)(O)-$\kappa P,\kappa S$}$_2$] (**3**), whereas the same reaction with 2 equiv of Pd(COD)Cl$_2$ in the presence of H$_2$O and Et$_3$N produces the mononuclear anionic complex [{(–OC$_{10}$H$_6$-(μ-S)C$_{10}$H$_6$O–)P(O)-$\kappa P,\kappa S$}PdCl$_2$](Et$_3$NH) (**5**). By contrast, reaction of **2** with 2 equiv of Pd(COD)Cl$_2$ and H$_2$O in the absence of Et$_3$N gives the hydrogen phosphonate coordinated complex [{(–OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O–)P(OH)}-PdCl$_2$] (**4**) which converts to the anionic complex in solution or in the presence of a base. Compound **2** on treatment with Pt(COD)X$_2$ (X = Cl or I) afforded P-coordinated four-membered chelate complexes [PhN(P(–OC$_{10}$H$_6$(μ-S)-C$_{10}$H$_6$O–)-κP)$_2$PtX$_2$] (**6** X = Cl, **7** X = I). The crystal structures of compounds **2**, **3**, **5**, and **7** are reported. Compound **3** is the first example of a crystallographically characterized binuclear palladium complex containing a bidentate bridging ligand and its hydrolyzed fragments forming metallacycles containing a palladium–phosphorus σ bond. All palladium complexes proved to be very good catalysts for the Suzuki–Miyaura and Mizoroki–Heck cross-coupling and amination reactions with excellent turnover numbers (TON up to 1.46 $\times$ 10^5 in the case of the Suzuki–Miyaura reaction).

Introduction

Despite a plethora of phosphorus ligands available,[1] the enthusiasm to generate new ones is remarkable mainly due to the demand from industry for economical and robust ligands that can be handled under normal atmospheric conditions. Complexes such as Pd(PPh$_3$)$_4$ are highly air and moisture sensitive and often form phosphido-bridged dimers which are catalytically inactive. Further, the dissociated phosphines in solution can be readily oxidized to give Ph$_3$P=O, which prevents regeneration of the catalyst, thereby reducing the catalytic efficiency. In order to overcome these challenges, the following strategies are considered: (i) Protecting the P(III) center as a BH$_3$ adduct until in situ generation of the active catalytic species and (ii) stabilizing the P(III) center in the form of a suitable P(V) species which can undergo tautomerism in the presence of a transition metal to give a phosphinous acid type derivative as pointed out by Chatt and Heaton (Scheme 1).[2] Since the R$_3$P:BH$_3$ adduct is unstable toward the routinely used catalytic reaction condi-

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(1) For examples, see: (a) *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983. (b) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. H., Eds.; VCH: Weinheim, 1996. (c) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27−110. (d) Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Nixon, J. F.; St. Laurent, J. C. T. R. B. *Coord. Chem. Rev.* **1994**, *129*, 1−90. (e) Dilworth, J. R.; Wheatley, N. *Coord. Chem. Rev.* **2000**, *199*, 89−158. (f) Appleby, T.; Woollins, J. D. *Coord. Chem. Rev.* **2002**, *235*, 121−140. (g) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627−681. (h) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (i) Suzuki, A. In *Metal Catalysed Cross Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; pp 49−97 and references therein. (j) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633−9695.

(2) (a) Chatt, J.; Heaton, B. T. *J. Chem. Soc. A* **1968**, 2745−2757. See also: (b) Dixon, K. R.; Rattray, A. D. *Can. J. Chem.* **1971**, *49*, 3997−4004. (c) Lindner, E.; Schilling, B. *Chem. Ber.* **1977**, *110*, 3266−3271.
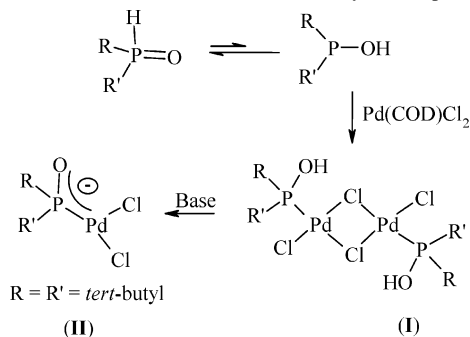
Scheme 1
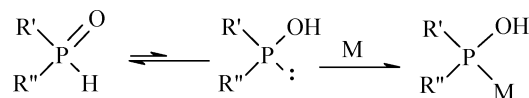
Scheme 2
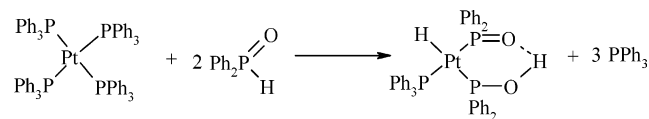
Scheme 3. Formation of Active Anionic Catalytic Complex

R = R' = *tert*-butyl

(II)   **(I)**

tions (especially toward acids and Lewis bases), the second option looks reasonable and also is supported by the following reaction of $Pt(PPh_3)_4$ with phosphinous acid (Scheme 2).[3]

Li and others employed phosphinous acid complexes of type **I** for palladium-catalyzed cross-coupling reactions (Scheme 3).[4] These dimers can be readily deprotonated in the presence of a base to yield an electron-rich anionic species (**II**) which was thought to be a catalyst for carbon–carbon coupling reactions. It is speculated that the anionic species facilitates the oxidative addition reaction and also stabilizes the Pd^0 species in the catalytic cycle.[5] Although this strategy has been explored in homogeneous catalysis of these coupling reactions, the active species involved in the catalytic process have not been fully identified and the mechanistic details are not yet clear. Tertiary phosphines with sterically bulky groups are often employed for cross-coupling reactions in organic synthesis with excellent results. After scanning several substituted aromatic derivatives we found that biphenyl groups showed good activity and are easy to make. The donor atoms such as sulfur can be readily incorporated into the framework. Further, compounds with biphenyl groups are known for their excellent photophysical

activity in addition to catalysis. The P–O bonds present in phosphonites derived from naphthyl derivatives are resistant to hydrolytic cleavage but can readily form phosphonate anion if they contain a P–N or P–halogen bond as they are prone to hydrolysis. Further, the anionic complexes mentioned above have never been isolated and characterized. In this context, we report the first examples of fully characterized, readily accessible, and air stable anionic mononuclear as well as neutral binuclear Pd^{II} complexes and their catalytic utility in C–C and C–N cross-coupling reactions.

Experimental Section

All experimental manipulations were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques unless otherwise stated. Solvents were dried and distilled prior to use by conventional methods. Bis(2-hydroxy-1-naphthyl)sulfide,[6] chlorophosphite (**1**),[7] $PhN(PCl_2)_2$,[8] $M(COD)Cl_2$ (M = Pd, Pt),[9] and $Pt(COD)I_2$[10] were prepared according to the published procedures. Other reagents were obtained from commercial sources and used after purification. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were obtained on a Varian VRX 400 spectrometer operating at frequencies of 400 and 162 MHz, respectively. The spectra were recorded in CDCl$_3$ (or DMSO-d_6) solutions with CDCl$_3$ (or DMSO-d_6) as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. Positive shifts lie downfield of the standard in all cases. Infrared spectra were recorded on a Nicolet Impact 400 FT IR instrument as a KBr disk. Microanalyses were carried out on a Carlo Erba (model 1106) elemental analyzer. Electrospray ionization (EI) mass spectrometry experiments were carried out using Waters Q-Tof micro(YA-105). Melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected. GC analyses were performed on a Perkin-Elmer Clarus 500 GC fitted with a FID detector and packed column.

Synthesis of $PhN\{P(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)\}_2$ (2). Method I. A solution of $PhN(PCl_2)_2$ (0.69 g, 2.36 mmol) in THF (20 mL) was added dropwise to a solution of bis(2-hydroxy-1-naphthyl)-sulfide (1.5 g, 4.71 mmol), Et$_3$N (1.37 mL, 9.89 mmol), and a catalytic amount of DMAP (4-*N,N*-dimethylaminopyridine) in THF (60 mL) at −15 °C. The reaction mixture was warmed to room temperature and stirred for an additional 20 h. The solvent was removed under reduced pressure, and the white residue obtained was dissolved in 40 mL of toluene and filtered through celite to remove the Et$_3$N·HCl salt. The filtrate obtained was concentrated under reduced pressure and stored at −25 °C to give white crystalline product of **2**. Yield: 83% (1.54 g).

Method II. A mixture of aniline (0.24 mL, 2.63 mmol) and Et$_3$N (2.67 mL, 19.2 mmol) in toluene (30 mL) was added dropwise to a solution of chlorophosphite (2 g, 5.26 mmol) also in toluene (50 mL) at −15 °C. The reaction mixture was warmed to room temperature and stirred for an additional 12 h. The suspension obtained was filtered through celite to remove amine hydrochloride; the filtrate was concentrated to 20 mL under reduced pressure and on storing at −25 °C gave product **2** as colorless crystals. Yield:

(3) Beaulieu, W. B.; Rauchfuss, T. B.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 1732−1734.

(4) (a) Li, G. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1513−1516. (b) Li, G. Y. *J. Org. Chem.* **2002**, *67*, 3643−3650. (c) Li, G. Y.; Zheng, G.; Noonan, A. F. *J. Org. Chem.* **2001**, *66*, 8677−8681. (d) Arif, A. M.; Bright, T. A.; Jones, R. A. *J. Coord. Chem.* **1987**, *16*, 45−50. (e) Cobley, C. J.; van den Heuvel, M.; Abbadi, A.; de Vries, J. G. *Tetrahedron Lett.* **2000**, *41*, 2467−2470. (f) Ghaffar, T.; Parkins, A. W. *Tetrahedron Lett.* **1995**, *36*, 8657−8660. (g) Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. Z. *Z. Naturforsch. B* **1994**, *49*, 801−811.

(5) (a) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314−321. (b) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047−1062. (c) Grushin, V. V.; Alper, H. *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer: New York, 1999; Vol. 3, pp 193−226 and references there in.

(6) Mercado, R. M. L.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1999**, *18*, 906−914.

(7) Punji, B.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2006**, *45*, 9454−9464.

(8) Davies, A. R.; Dronsfield, A. T.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc., Perkin Trans.* **1973**, *1*, 379−385.

(9) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346−349.

(10) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411−428.

90% (1.86 g). Mp: 168−170 °C. Anal. Calcd for $C_{46}H_{29}NO_4P_2S_2$: C, 70.31; H, 3.72; N, 1.78; S, 8.16. Found: C, 70.29; H, 3.71; N, 1.75; S, 8.12. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.76 (d, 4H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.65−7.79 (m, 8H, *Ar*, 5H, *Ph*), 7.61 (t, 4H, *Ar*, $^3J_{HH}$ = 6.8 Hz), 7.59 (t, 4H, *Ar*, $^3J_{HH}$ = 6.8 Hz), 7.30 (d, 4H, *Ar*, $^3J_{HH}$ = 8.8 Hz). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 127.5 (s). MS (EI): M$^+$, 786.2.

Synthesis of [PhN(P(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)-κP)$_2$Pd$_2$Cl$_2$-{P(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−) (O)-$\kappa P,\kappa S$}$_2$] (3). A solution of Pd-(COD)Cl$_2$ (0.05 g, 0.175 mmol) in dichloromethane (6 mL) was added dropwise to a dichloromethane (10 mL) solution of **2** (0.137 g, 0.175 mmol) followed by addition of H$_2$O (3.15 μL, 0.175 mmol). The reaction mixture was stirred for 1 h at room temperature. The solution was concentrated under vacuum, and diethyl ether was added to precipitate a yellowish solid which was filtered off and dried. Recrystallization from a CH$_2$Cl$_2$/diethyl ether mixture (1:1) gave analytically pure crystals of **3**. Yield: 68% (0.112 g). Mp: 220−222 °C. Anal. Calcd for $C_{86}H_{53}NO_{10}P_4S_4Pd_2Cl_2 \cdot CH_2Cl_2$: C, 55.55; H, 2.95; N, 0.74; S, 6.82. Found: C, 55.52; H, 2.93; N, 0.72; S, 6.78. IR (KBr disk, cm^{-1}): v(P=O), 1212 s. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.64 (d, 4H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.07−8.63 (m, 40H, *Ar*, 5H, *Ph*), 6.01 (d, 4H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 5.29 (s, 2H, C*H*$_2$Cl$_2$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 100.8 (d, 2P, N−P), 47.0 (d, 2P, P(O)), $^2J_{PP}$ = 104 Hz.

Synthesis of [{(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)P(OH)}PdCl$_2$] (4). A solution of Pd(COD)Cl$_2$ (0.06 g, 0.21 mmol) in dichloromethane (8 mL) was added dropwise to a dichloromethane (8 mL) solution of **2** (0.083 g, 0.105 mmol) followed by addition of H$_2$O (3.8 μL, 0.21 mmol). The reaction mixture was stirred for 1 h at room temperature and filtered through celite. The filtrate was concentrated under vacuum and diluted with diethyl ether (5 mL) to give analytically pure product of **4** as yellow crystals. Yield: 82% (0.093 g). Mp: 216−218 °C. Anal. Calcd for $C_{20}H_{13}Cl_2O_3$PSPd: C, 44.35; H, 2.42; S, 5.92. Found: C, 44.52; H, 2.48; S, 5.81. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.93 (d, 2H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 8.04 (d, 2H, *Ar*, $^3J_{HH}$ = 9.2 Hz), 7.88 (d, 2H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.28−7.85 (m, 6H, *Ar*). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 85.1 (s).

Synthesis of [{(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)P(O)-$\kappa P,\kappa S$}PdCl$_2$] (Et$_3$NH) (5). This was synthesized similar to that of **4** by reacting **2** (0.083 g, 0.105 mmol) with Pd(COD)Cl$_2$ (0.06 g, 0.21 mmol), H$_2$O (3.8 μL, 0.21 mmol), and Et$_3$N (29 μL, 0.21 mmol) in THF (20 mL). Yield: 68% (0.092 g). Mp: 230 °C (dec). Anal. Calcd for $C_{26}H_{28}Cl_2NO_3$PSPd: C, 48.57; H, 4.39; N, 2.18; S, 4.99. Found: C, 48.51; H, 4.34; N, 2.15; S, 4.94. IR (KBr disk, cm^{-1}): v(P=O), 1206 s. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 9.98 (br s, 1H, N*H*), 8.84 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.88 (d, 2H, *Ar*, $^3J_{HH}$ = 9.2 Hz), 7.76 (d, 2H, *Ar*, $^3J_{HH}$ = 8.0 Hz), 7.69 (t, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.46 (t, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.31 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 3.18 (quartet, 6H, C*H*$_2$, $^3J_{HH}$ = 5.2 Hz), 1.33 (t, 9H, C*H*$_3$, $^3J_{HH}$ = 7.2 Hz). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 48.7 (s).

Synthesis of [PhN(P(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)-κP)$_2$PtCl$_2$] (6). A solution of Pt(COD)Cl$_2$ (0.03 g, 0.08 mmol) in dichloromethane (6 mL) was added dropwise to a solution of **2** (0.063 g, 0.08 mmol) also in dichloromethane (8 mL) at room temperature, and the reaction mixture was stirred for 6 h. The solution was concentrated under vacuum and layered with petroleum ether to give crystalline product **6**. Yield: 87% (0.073 g). Mp: 260 °C (dec). Anal. Calcd for $C_{46}H_{29}Cl_2NO_4P_2S_2Pt$: C, 52.53; H, 2.78; N, 1.33; S, 6.08. Found: C, 52.49; H, 2.76; N, 1.31; S, 6.05. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.62 (d, 4H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.23−7.69 (m, 20H, *Ar*, 5H, *Ph*). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 71.9 (s), $^1J_{PtP}$ = 6525 Hz.

Synthesis of [PhN(P(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)-κP)$_2$PtI$_2$] (7). This was synthesized by a procedure similar to that of **6** using aminobis(phosphonite) **2** (0.056 g, 0.072 mmol) and Pt(COD)I$_2$ (0.04 g, 0.072 mmol). Yield: 78% (0.069 g). Mp: 250 °C (dec). Anal. Calcd for $C_{46}H_{29}I_2NO_4P_2S_2Pt$: C, 44.75; H, 2.37; N, 1.13; S, 5.19. Found: C, 44.71; H, 2.35; N, 1.09; S, 5.17. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.65 (d, 4H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.21−8.17 (m, 20H, *Ar*, 5H, *Ph*). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, δ): 76.9 (s), $^1J_{PtP}$ = 6334 Hz.

Catalysis. In a two-necked round-bottom flask under an atmosphere of nitrogen were placed the appropriate amount of catalyst solution and 5 mL of solvent (methanol or toluene). The correct amount of catalyst was added as a methanol solution made up by multiple volumetric dilutions of stock solutions. After stirring for 5 min, aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), and K$_2$CO$_3$ (0.138 g, 1 mmol) for Suzuki reaction, aryl bromide (0.5 mmol), *tert*-butylacrylate (0.088 mL, 0.6 mmol), and K$_2$CO$_3$ (0.138 g, 1 mmol) for Heck coupling reaction, and aryl bromide (0.5 mmol), morpholine (0.052 mL, 0.6 mmol), and NaO^{t}Bu (0.058 g, 0.6 mmol) for amination reaction were introduced into the reaction flask. The mixture was heated at 60 or 80 or 100 °C for the required time under an atmosphere of nitrogen (the course of the reaction was monitored by GC analysis), and the solvent was removed under reduced pressure. The residual mixture was diluted with H$_2$O (8 mL) and Et$_2$O (8 mL) followed by extraction with Et$_2$O (2 × 6 mL). The combined organic fractions were dried (MgSO$_4$) and stripped of the solvent under vacuum, and the residue obtained was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated versus aryl bromides or dodecane as an internal standard.

X-ray Crystallography. Crystals of **2**, **5**, and **7** were mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker Smart APEX CCD diffractometer. A full sphere of data was collected for each using three sets of 400 scans in ω (0.5° per scan) at φ = 0°, 90°, and 180° plus two sets of 800 scans in φ (0.45° per scan) at ω = −30° and 210° using the SMART software package.[11] The raw data were reduced to F^2 values using the SAINT+ software,[12] and a global refinement of unit cell parameters using 6790−8770 reflections chosen from the full data sets was performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during data collection (SADABS[13]). The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.[14] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms with the exception of **5** where the hydrogen attached to nitrogen in the cation was refined. The crystal of **3** was mounted on a, Oxford Diffraction XCALI-BUR-S CCD system equipped with graphite-monochromated Mo Kα radiation (0.71073 Å). Data was collected by the $\omega-2\theta$ scan mode, and absorption correction was applied using multiscan. The structure was solved by direct methods SHELXS 97 and refined by full-matrix least-squares against F^2 using SHELXL 97 software.[14b] Non-hydrogen atoms were refined with anisotropic thermal param-

(11) *SMART*, Version 5.625; Bruker-AXS: Madison, WI, 2000.
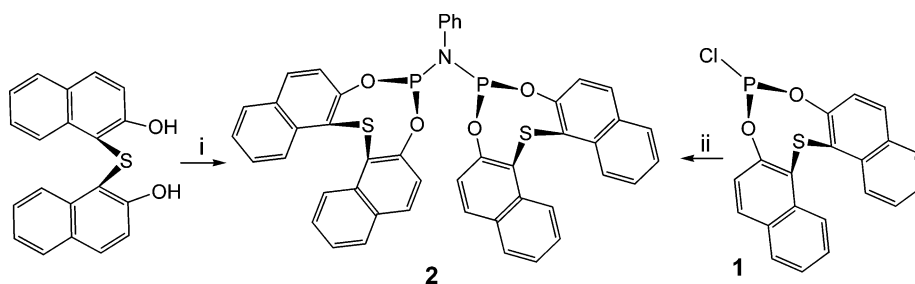(12) *SAINT+*, Version 6.35A; Bruker-AXS: Madison, WI, 2002.
(13) Sheldrick, G. M. *SADABS*, Version 2.05; University of Göttingen: Göttingen, Germany, 2002.
(14) (a) *SHELXTL*, Version 6.10; Bruker-AXS: Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXS97 and SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for Compounds **2**, **3**, **5**, and **7**

	2	**3**	**5**	**7**
formula	$C_{46}H_{29}NO_4P_2S_2 \cdot CH_2Cl_2$	$C_{87}H_{55}Cl_4NO_{11}P_4Pd_2S_4$	$C_{26}H_{28}Cl_2NO_3PSPd \cdot CH_2Cl_2$	$C_{46}H_{29}I_2NO_4P_2PtS_2$
mol wt	870.71	1897.04	727.75	1234.7
cryst syst	monoclinic	triclinic	triclinic	monoclinic
cryst size (mm)	$0.07 \times 0.09 \times 0.22$	$0.25 \times 0.20 \times 0.15$	$0.13 \times 0.25 \times 0.29$	$0.11 \times 0.15 \times 0.16$
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2/n$ (No. 13)
a (Å)	10.105(1)	13.854(1)	8.207(7)	18.068(2)
b (Å)	20.162(1)	17.168(2)	12.610(1)	11.882(1)
c (Å)	20.186(1)	21.344(3)	15.004(1)	23.402(2)
α (deg)	90	80.239(1)	101.169(1)	90
β (deg)	102.732(1)	72.418(1)	101.788(1)	111.127(1)
γ (deg)	90	74.730(1)	97.862(1)	90
V (Å^3)	4011.5(4)	4646.1(1)	1465.9(2)	4686.3(8)
Z	4	2	2	2
$\rho_{calcd} \cdot g\ cm^{-3}$	1.442	1.356	1.649	1.773
μ (Mo Kα), mm^{-1}	0.394	0.714	1.154	4.512
F (000)	1792	1912	736	2392
temp. (K)	100(2)	293(2)	100(2)	100(2)
θ (min, max) (deg)	2.1, 28.3	2.97, 25.00	2.4, 28.3	2.1, 28.3
GOF (F^2)	1.03	0.889	1.04	1.14
R$_1$^{a}	0.0563	0.0747	0.0278	0.0414
wR$_2$^{b}	0.1451	0.1842	0.0694	0.0957

^{a} R$_1$ = $\sum|F_o| - |F_c|/\sum|F_o|$. ^{b} wR$_2$ = $\{\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Scheme 4^a

^{a} (i) PhN(PCl$_2$)$_2$, Et$_3$N, DMAP, THF, -15 °C; (ii) PhNH$_2$, Et$_3$N, toluene, -15 °C.

eters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Crystallographic data are summarized in Table 1.

Results and Discussion

Ligand Synthesis. Recently we reported the synthesis of a novel 10-membered heterocycle PhN(PCl)$_2${($-OC_6H_2$(^{t}-Bu)$_2$)(μ-S)((^{t}Bu)$_2$C$_6$H$_2$O$-$)} by reacting phenylaminobis-(dichlorophosphine), PhN(PCl$_2$)$_2$, with 2,2′-thiobis(4,6-di-*tert*-butylphenol) in a 1:1 ratio.[15] A similar reaction between thiobis(2,2′-naphthol) and PhN(PCl)$_2$ resulted in formation of a mixture of the 10-membered heterocycle PhN(PCl)$_2${$-$OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O$-$} and the aminobis(phosphonite) PhN-{P($-$OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O$-$)}$_2$ (**2**) as indicated by ^{31}P NMR data. Attempts to separate them from the reaction mixture have been unsuccessful; however, **2** was synthesized in good yield by treatment of PhN(PCl$_2$)$_2$ with 2 equiv of thiobis-(2,2′-naphthol) in the presence of Et$_3$N and a catalytic amount of DMAP (4-*N,N*-dimethylaminopyridine) (Scheme 4). In another straightforward method reaction of aniline with 2 equiv of chlorophosphite ($-$OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O$-$)PCl (**1**) in the presence of an excess of Et$_3$N at -15 °C also afforded **2** in good yield. The second method is more convenient as it gives comparatively pure product in excellent yield. The

^{31}P NMR spectrum of **2** shows a single resonance at 127.5 ppm. In the mass spectrum a peak is observed at m/z 786.2 for the molecular ion. The structure and molecular composition of the ligand **2** were further confirmed by ^{1}H NMR data, elemental analysis, and single-crystal X-ray structure determination.

Metal Complexes. Aminophosphines containing P$-$N bond(s) are known to undergo hydrolytic cleavage when they are exposed to moisture, acid, or base impurities during the complexation reactions.[16] This type of P$-$N bond cleavage resulted in air-stable phosphine oxides (RR′P(O)H) which in the presence transition metals can undergo tautomerization to the less stable phosphinous acid (RR′POH) and subsequently coordinate to the metal centers to form metal

(15) Balakrishna, M. S.; Panda, R.; Mague, J. T. *Inorg. Chem.* **2001**, *40*, 5620−5625.

(16) (a) Balakrishna, M. S.; Krishnamurthy, S. S. *Ind. J. Chem.* **1991**, *30A*, 536−537. (b) Burrows, A. D.; Mahon, M. F.; Palmer, M. T.; Varrone, M. *Inorg. Chem.* **2002**, *41*, 1695−1697. (c) Priya, S.; Balakrishna, M. S.; Mague, J. T. *J. Organomet. Chem.* **2003**, *679*, 116−124.

(17) (a) Dubrovina, N. V.; Borner, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5883−5886. (b) Han, L.-B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407−5408. (c) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571−1572. (d) Zhao, C.-Q.; Han, L.-B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196−4198. (e) Ackermann, L.; Born, R.; Spatz, J. H.; Meyer, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7216−7219. (f) Levine, A. M.; Stockland, R. A.; Clark, R.; Guzei, I. *Organometallics* **2002**, *21*, 3278−3284. (g) Stockland, R. A.; Levine, A. M.; Giovine, M. T.; Guzei, I. A.; Cannistra, J. C. *Organometallics* **2004**, *23*, 647−656. (h) Pryjomska, I.; Bartosz-Bechowski, H.; Ciunik, Z.; Trzeciak, A. M.; Ziòłkowski, J. J. *Dalton Trans.* **2006**, 213−220.

Scheme 5[a]
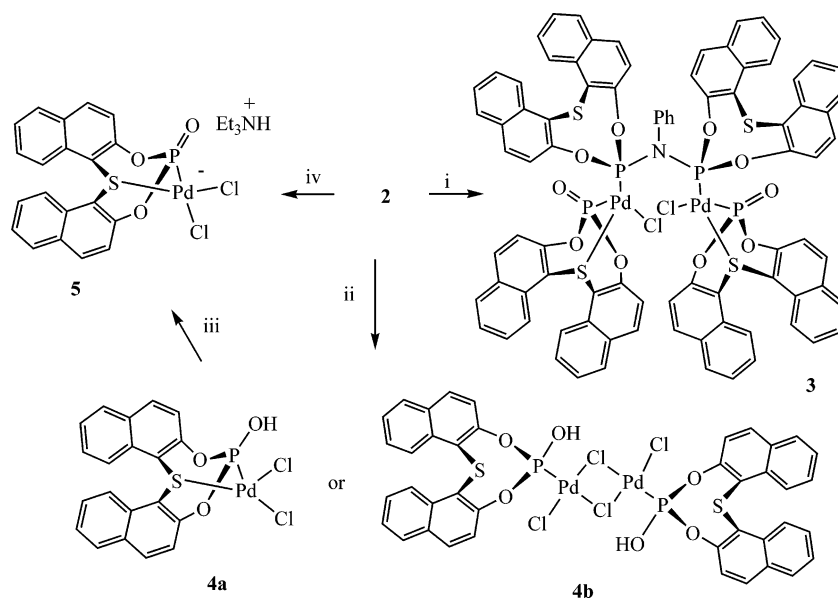
[a] (i) Pd(COD)Cl₂, H₂O, CH₂Cl₂; (ii) 2Pd(COD)Cl₂, H₂O, CH₂Cl₂; (iii) Et₃N, THF; (iv) 2Pd(COD)Cl₂, H₂O, Et₃N, THF.

**Scheme 6.** Probable Pathway for Formation of Complex **3**
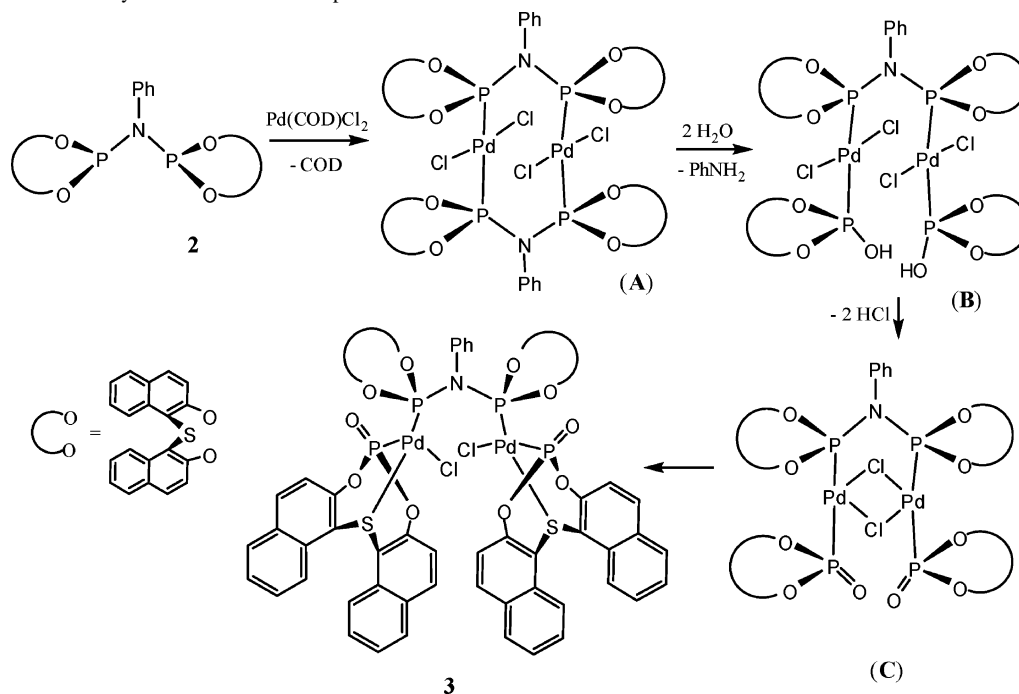
phosphinous acid complexes (Scheme 3). These phosphinous acid metal complexes can produce neutral or anionic complexes via HCl elimination which are excellent sources of catalyst precursors.[4c,17] With this in mind, the aminobis-(phosphonite) **2** was treated with 1 equiv of Pd(COD)Cl₂ in the presence of H₂O at room temperature which resulted in formation of a P–N–P (ligand **2**) bridged and thioether–phosphonate–cyclometalated binuclear complex [PhN(P(–OC₁₀H₆(μ-S)C₁₀H₆O–)-κP)₂Pd₂Cl₂{P(–OC₁₀H₆(μ-S)C₁₀H₆O–)(O)-$\kappa P,\kappa$ S}₂] (**3**). However, the 1:2 reaction of **2** with Pd(COD)Cl₂ in the presence of H₂O and Et₃N gave the anionic mononuclear complex [{(–OC₁₀H₆(μ-S)C₁₀H₆O–)P-(O)-$\kappa P,\kappa S$}PdCl₂] (Et₃NH) (**5**) in moderate yield. The bi-

nuclear complex **3** formed as a result of the fission of the P–N bond followed by oxidation of the P center on 0.5 equiv of **2**, whereas the remaining 0.5 equiv of the ligand **2** anchors the two cyclometalated Pd^{II} centers in a bridged bidentate mode of coordination (Scheme 5). Similarly, P–N bond fission of the whole aminobis(phosphonite) resulted in the hydrogen phosphonate which subsequently forms the anionic complex **5**. The complex [{(–OC₁₀H₆(μ-S)C₁₀H₆O–)P-(OH)}PdCl₂] (**4**) was obtained in the reaction of **2** with 2 equiv of Pd(COD)Cl₂ and H₂O in the absence of Et₃N. Complex **4** can be readily converted into the anionic complex **5** by treating it with Et₃N. Complex **4** can be either in the cyclometalated monomeric [{(–OC₁₀H₆(μ-S)C₁₀H₆O–)P-

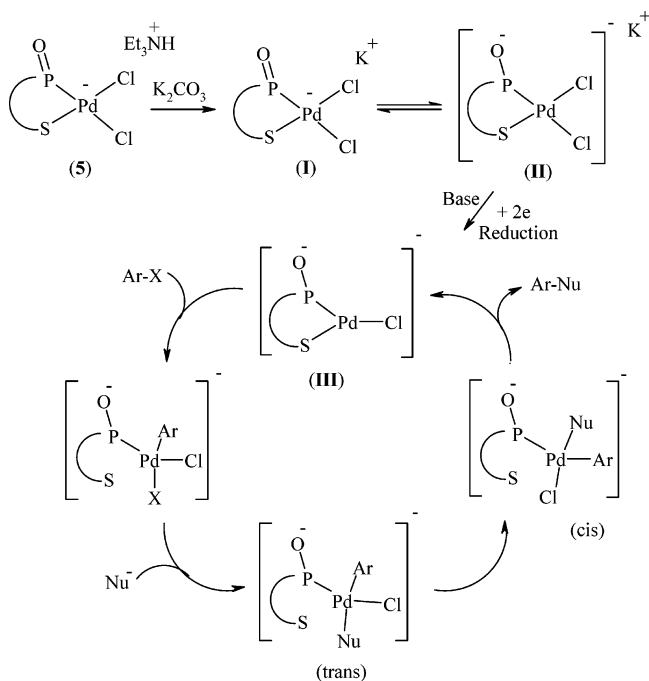**Scheme 7.** Probable Pathway for Formation of Complexes **4** and **5**
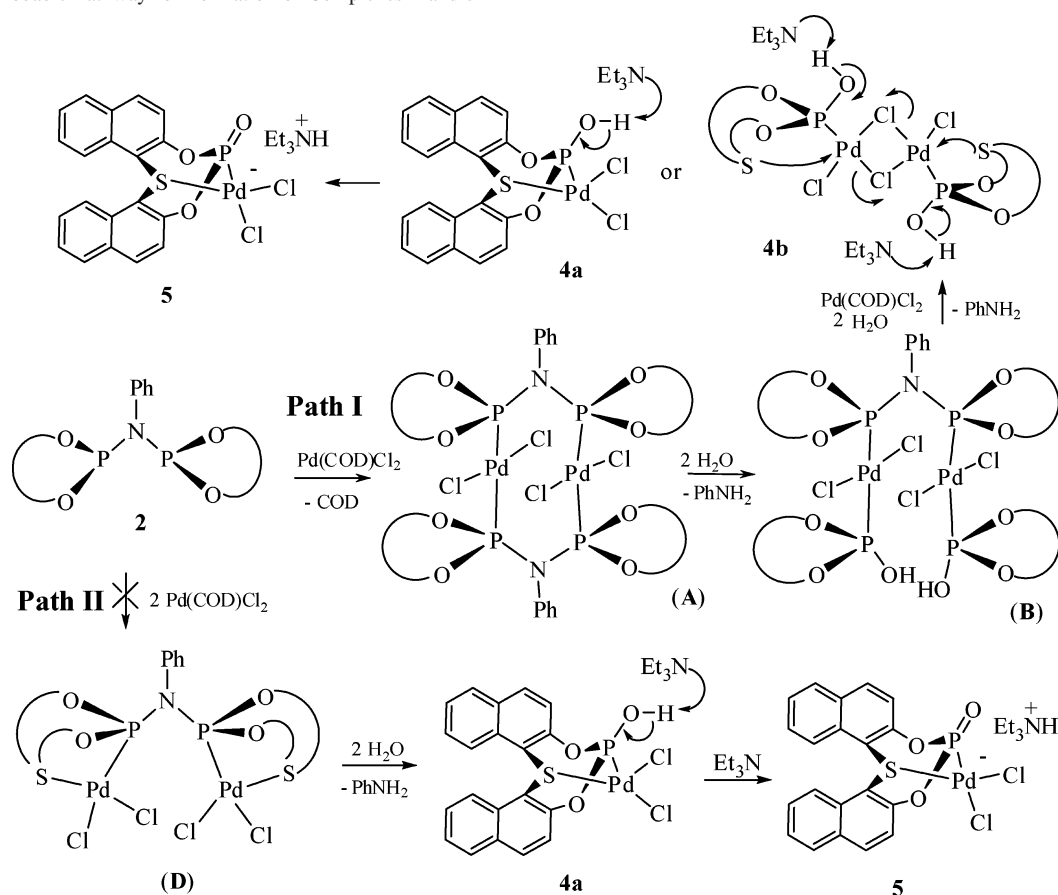
Scheme 8
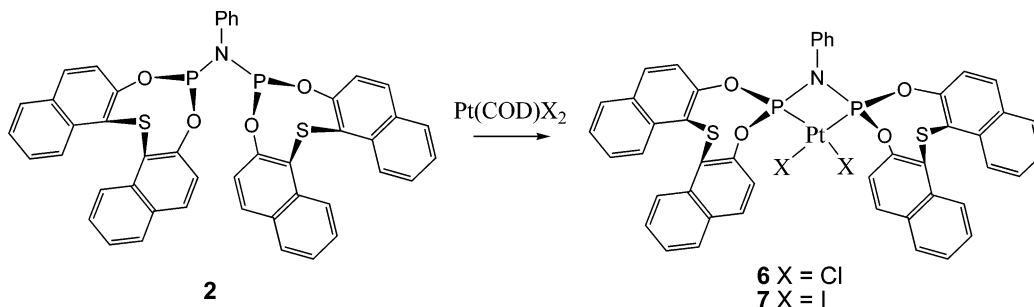
(OH)-$\kappa P,\kappa S$}PdCl$_2$ (**4a**) or in the chloro-bridged dimeric form [{($-$OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O$-$)P(OH)-κP}Pd(μ-Cl)Cl]$_2$ (**4b**). Although palladium complexes of simple monodentate phosphonate ligands such as HP(O)(OR)$_2$ (R = alkyl, aryl) are known, only a few of them are well characterized.[17f−h] Palladium complexes **3** and **5** are unique as similar types of palladium complexes containing metalated thioether−phosphonates do not appear in the literature.

The phosphorus-31 NMR spectrum of complex **3** shows two doublets centered at 100.8 and 47.0 ppm for the P^{III} and P(O) phosphorus centers, respectively, with a $^2J_{PP}$ coupling of 104 Hz, while for complex **4** a sharp singlet is observed at 85.1 ppm. In the IR spectrum of **3** v(P=O) appears at 1212 cm^{-1}. The ^{31}P NMR spectrum of complex **5** consists of a singlet at 48.7 ppm, and the IR spectrum shows v(P=O) at 1206 cm^{-1}. The ^{1}H NMR spectrum of complex **5** shows a broad singlet at 9.98 ppm for the NH proton, a quartet
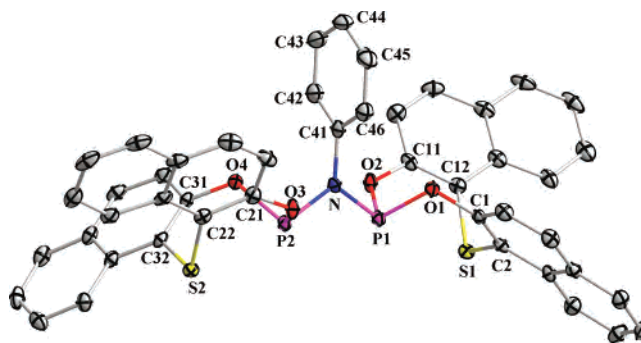
(3.18 ppm) and triplet (1.33 ppm) for the Et$_3$NH$^+$ cation. The structures of **3** and **5** were determined by single-crystal X-ray diffraction studies.

A plausible pathway for formation of complex **3** is given in Scheme 6. The aminobis(phosphonite) reacts with Pd-(COD)Cl$_2$ to form a binuclear complex **A**, which on reaction with H$_2$O cleaves the P−N bonds of one of the ligands to form **B** with elimination of aniline. Complex **B** then eliminates 2 mol of HCl to form the chloro-bridged complex **C**, which on further rearrangement involves sulfur coordination to form complex **3**. Further addition of an excess of water to **3** did not give complexes of the type **4** or **5**. However, addition of another mole of Pd(COD)Cl$_2$ to complex **3** in the presence of Et$_3$N resulted in formation of complex **5** as ascertained from phosphorus-31 NMR data. The most plausible pathways for formation of complexes **4** and **5** are depicted in Scheme 7 (Path I). Formation of these

Scheme 9. Plausible Catalytic Cycle for the Cross-Coupling Reactions

Figure 1. Molecular structure of **2**. For clarity, solvent (CH_2Cl_2) and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

and 6334 Hz, respectively. These coupling constants are significantly larger than in platinum complexes of similar ligands reported in the literature[7,18] and indicate a strong σ-donor capability for the aminobis(phosphonite) which may arise due to the coordinative tendencies of sulfur toward the phosphorus atoms (vide infra).

Crystal and Molecular Structures of Compounds 2, 3, 5, and 7. The molecular structures of compounds **2**, **3**, **5**, and **7** with atom numbering schemes are depicted in Figures 1−4, and selected bond parameters are summarized in Table 2.

Compound **2** has approximate 2-fold rotation symmetry following the classification of similar PNP compounds.[19] Similar to the P−S containing eight-membered cyclic monophosphite structures reported by Holmes and co-workers,[20] the aminobis(phosphonite) **2** contains two such cyclic phosphite units in which the geometries around the phosphorus atoms can be considered as pseudo trigonal bipyramidal (TBP). Both eight-membered rings contain phosphorus and sulfur atoms in a boat-like syn conformation. The sulfur atom in the ring shows coordinative tendencies toward phosphorus so that the geometry about the latter departs from pyramidal toward a pseudo TBP. The P−S distances 2.993(1) and 2.967(1) Å are comparable with those in similar structures (see Table 3) and considerably less than the sum of the van der Waals' radii for phosphorus and sulfur (3.65 Å)[21] but noticeably longer than the sum of their covalent radii (2.12 Å).[22] Following the procedure of Day et al., the percent of displacement from pyramidal toward TBP is found to be 42.9% and 44.7% for the P1 and P2 centers, respectively.[23] The axial S−P−N angles are 166.46° and 167.99° for S1−

(18) (a) Slawin, A. M. Z.; Wainwright, M.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 513−519. (b) Calabrò, G.; Drommi, D.; Graiff, C.; Faraone, F.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2004**, 1447−1453. (c) Balakrishna, M. S.; George, P. P.; Mague, J. T. *J. Organomet. Chem.* **2004**, *689*, 3388−3394.
(19) Calabrò, G.; Drommi, D.; Bruno, G.; Faraone, F. *Dalton Trans.* **2004**, 81−89.
(20) (a) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5082−5089. (b) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 1317−1322.
(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.
(22) Sutton, L. *Tables of Interatomic Distances and Configuration in Molecules and Ions;* Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.
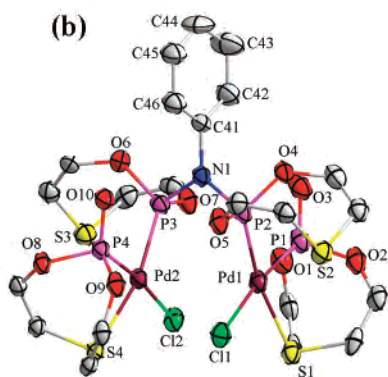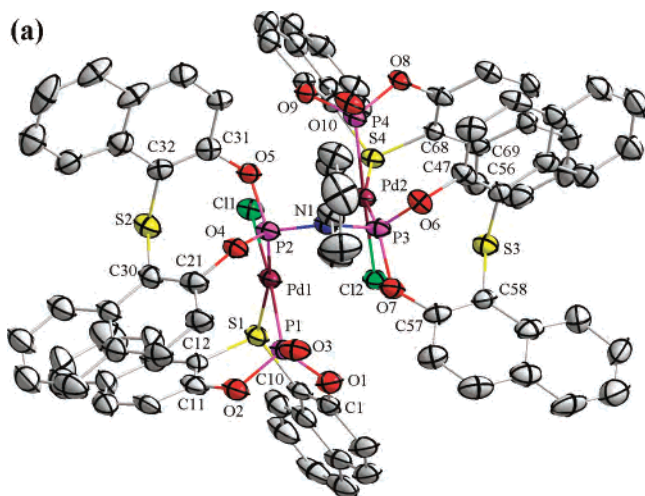(23) Day, R. O.; Prakasha, T. K.; Holmes, R. R.; Eckert, H. *Organometallics* **1994**, *13*, 1285−1293.

complexes follows a pathway similar to that described above until generation of **B**, which can liberate another molecule of aniline via P−N bond cleavage and undergo a disproportionation reaction with the unreacted Pd(COD)Cl$_2$ present in solution. Deprotonation of complex **4** in the presence of a base can form the metallacyclic complex **5**. Formation of complex **5** can also follow path II (Scheme 7) by initial formation of a P,S-chelated binuclear complex (**D**) followed by hydrolysis and abstraction of a proton. However, recent investigations have shown that compound **2** does not form a P,S-chelate complex with palladium unless it undergoes P−N bond hydrolysis.[7] Hence, path II can be ruled out for formation of anionic complex **5**. The 1:1 reaction between **2** and Pd(COD)Cl$_2$ produces complex **3**, whereas the 1:2 reaction affords either **4** or **5**. Hence, from both reaction profiles it is concluded that the palladium precursor plays a major role in the P−N bond cleavage to form complexes **3** or **5**, although an H$_2$O molecule evidently assists in the P−N bond cleavage. Attempts to isolate the binuclear complex [PhN(P(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)-κP)$_2$PdCl$_2$]$_2$ (**A**) was unsuccessful as it readily cleaves one of the bridging ligands and rearranges to give complex **3**. In contrast, platinum forms (complexes **6** and **7**) moderately stable four-membered chelate complexes with ligand **2** which are resistant to hydrolytic cleavage of P−N bonds. Generally, palladium-(II) complexes are more reactive in terms of both thermodynamic and kinetic aspects, whereas the platinum(II) analogues show kinetic inertness.

Treatment of aminobis(phosphonite) **2** with Pt(COD)X$_2$ (X = Cl and I) in dichloromethane produces the four-membered chelate complexes [PhN(P(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)-κP)$_2$PtX$_2$], (**6**, X = Cl; **7**, X = I) in good yield (Scheme 8). The ^{31}P NMR spectra of complexes **6** and **7** show single resonances at 71.9 and 76.9 ppm with $^1J_{PtP}$ couplings of 6525

Figure 2. (a) Molecular structure of **3**. For clarity, solvent (CH₂Cl₂) and all hydrogen atoms have been omitted. (b) Core view of complex **3**. Thermal ellipsoids are drawn at the 30% probability level.
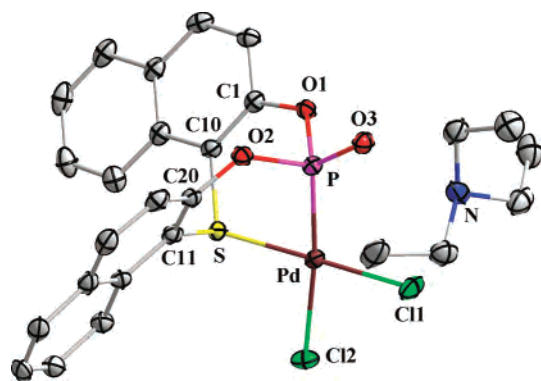

Figure 3. Molecular structure of complex **5**. For clarity, solvent (CH₂-Cl₂) and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

P1−N and S2−P2−N, respectively. The P−N−P bond angle is 113.66(1)°, and the geometry around the nitrogen center is planar with the sum of the angles around nitrogen close to 360°. The four donor atoms (two P and two S) are oriented in the same direction with a S−P−P−S torsion angle of 8.49°.

In the structure of **3** two palladium atoms are bridged by the aminobis(phosphonite) ligand to form a binuclear complex. The thioether−phosphonate groups are in approximately eclipsed conformations and facing in opposite directions. Both palladium centers are slightly distorted from the expected square-planar geometry. Each palladium center
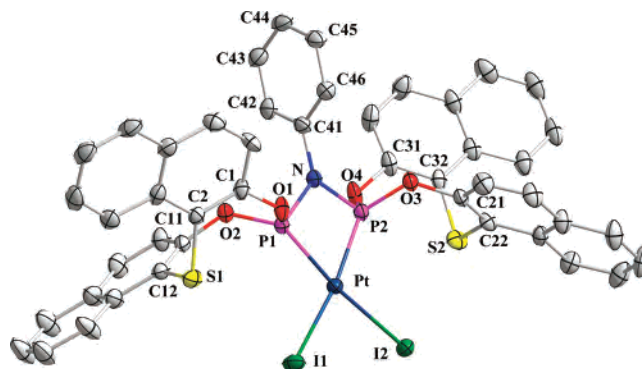

Figure 4. Molecular structure of **7**. For clarity, solvent (THF) and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

is coordinated to P, S, and one chloride ligand with the fourth coordination site being occupied by the phosphonate phosphorus via a σ bond. Each sulfur atom is syn to the nearest palladium atom with S···Pd distances of 3.464(3) (Pd2··· S3) and 3.688(3) Å (Pd1···S2) which are too long for there to be any significant interaction. The Pd−P bond distances are 2.221(3) (P1−Pd1) and 2.224(2) Å (P4−Pd2). The two palladium atoms are separated by 3.253(1) Å, which is essentially the same as the sum of their van der Waals' radii (3.26 Å) and is therefore not considered to indicate a bonding interaction. The P−N−P angle (P(2)−N(1)−P(3) = 117.5-(4)°) in the aminobis(phosphonite) ligand in complex **3** has increased upon complexation approximately 5° compared to that in the free ligand (P1−N−P2 = 113.66(1)°).

In the structure of complex **5** the palladium center is slightly distorted from the expected square-planar geometry. The P=O (1.478(2) Å) and P−O (1.629(1) and 1.641(2) Å) bond lengths are typical of those in similar metal complexes containing phosphonate groups.[17f,24] The Pd−Cl2 bond length of 2.395(6) Å (trans to phosphorus) is slightly longer than Pd−Cl1 (2.308(6) Å). This reflects the difference between the σ-donor strengths of phosphorus and sulfur (trans influence). The S−Pd−P bite angle is 85.48(2)°.

In the molecular structure of **7** the platinum atom adopts a distorted square-planar geometry with the corners occupied by two iodide ligands and two phosphorus atoms. There is a large variation in the cis angles from 71.35(4)° (P1−Pt−P2) to 100.52(3)° (I2−Pt−P2), primarily because of the small "bite angle" of the bis(phosphonite) ligand. The Pt−P1 and Pt−P2 bond lengths are 2.219(1) and 2.230(1) Å, respectively, while the mean P−N bond length is 1.674(4) Å. The P1−N−P2 bond angle (101.6(3) Å) is considerably smaller than either tetrahedral or trigonal angles, but the sum of angles around nitrogen is 359.8(1)°, which clearly indicates that the geometry around the nitrogen is planar. In the crystal packing the molecules show a $\pi-\pi$ stacking interaction between naphthyl rings with a mean interplanar separation of 3.752 Å, which is within the range of $\pi-\pi$ stacking interactions (3.80 Å).[25]

(24) Chang, C.; Lin, Y.; Lee, G.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 4223−4230.
(25) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885−3896.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **2**, **3**, **5**, and **7**

2		3		5		7	
S1–C12	1.769(2)	Pd1–P1	2.221(3)	Pd–Cl1	2.308(6)	Pt–I1	2.636(1)
S1–C2	1.779(2)	Pd1–P2	2.235(2)	Pd–Cl2	2.395(6)	Pt–I2	2.626(1)
P1–O2	1.658(2)	Pd1–S1	2.358(2)	Pd–S	2.261(6)	Pt–P1	2.219(1)
P1–O1	1.655(2)	Pd1–Cl1	2.382(3)	Pd–P	2.189(5)	Pt–P2	2.230(1)
P1–N	1.701(2)	Pd2–P4	2.224(2)	S–C11	1.784(2)	S1–C2	1.767(5)
S2–C22	1.770(2)	Pd2–P3	2.229(2)	S–C10	1.784 (2)	S1–C12	1.770(6)
S2–C32	1.776(2)	Pd2–S4	2.342(2)	P–O3	1.478(2)	P1–O1	1.583(4)
P2–O3	1.659(2)	Pd2–Cl2	2.394(2)	P–O1	1.628(1)	P1–O2	1.594(4)
P2–O4	1.659(2)	P1–O3	1.446(7)	P–O2	1.641(2)	P1–N	1.673(4)
P2–N	1.695(2)	P1–O2	1.624(7)	P2–N	1.675(4)		
		P1–O1	1.637(7)	P2–O3	1.592(4)		
		P2–N1	1.673(7)	P2–O4	1.593(4)		
		P3–N1	1.690(7)				
		Pd1···Pd2	3.253(1)				
C2–S1–C12	104.21(1)	P1–Pd1–P2	90.86(9)	Cl1–Pd–Cl2	92.96(2)	I1–Pt–I2	89.73(1)
C22–S2–C32	103.29(1)	P1–Pd1–S1	84.75(1)	Cl1–Pd–S	176.43(2)	I1–Pt–P1	98.36(3)
O1–P1–O2	98.86(9)	P2–Pd1–S1	168.64(8)	Cl1–Pd–P	93.09(2)	I1–Pt–P2	169.22(3)
O1–P1–N	96.59(9)	P1–Pd1–Cl1	172.37(1)	Cl2–Pd–S	88.37(2)	P1–Pt–P2	71.35(4)
O2–P1–N	96.86(9)	S1–Pd1–Cl1	88.05(9)	Cl2–Pd–P	173.69(2)	C2–S1–C12	104.2(2)
O3–P2–O4	98.26(9)	O3–P1–O2	108.8(4)	S–Pd–P	85.48(2)	C22–S2–C32	101.7(2)
O3–P2–N	96.84(9)	O3–P1–O1	105.6(4)	Pd–S–C10	114.16(7)	Pt–P1–O1	119.02(1)
O4–P2–N	97.35(9)	C12–S1–C10	103.2(4)	Pd–P–O1	108.14(6)	O1–P1–O2	105.24(2)
P1–N–P2	113.66(1)	C32–S2–C30	102.9(4)	Pd–P–O2	109.65(5)	P1–N–P2	101.6(3)
P1–N–C41	123.63(2)	P2–N1–P3	117.4(4)	Pd–P–O3	123.92(6)	P1–N–C41	129.7(3)
P2–N–C41	122.69(2)			P2–N–C41	128.5(3)		

Suzuki−Miyaura, Mizoroki−Heck Cross-Coupling, and Amination Reactions. The heterodifunctionl ligands containing O, N, or S donors along with P are found to be excellent for cross-coupling reactions. The anionic complexes generated with such ligand systems with flexible coordination modes are even better as they enhance the rate of oxidative addition, a vital step in homogeneous catalysis. As a result, the palladium complexes (**3**, **4**, and **5**) were employed for C−C (Suzuki−Miyaura, Mizoroki−Heck cross-coupling) and C−N bond-forming reactions of aryl bromides with the coupling partners such as phenylboronic acid, *tert*-butylacrylate, or morpholine, respectively. The catalytic reactions were carried out in either methanol or toluene using inexpensive inorganic bases (K₂CO₃, NaOᵗBu). Since the palladium complex **4** transforms into complex **5** in the presence of a base, catalytic activities of both the complexes are found to be the same.

The palladium complexes **3** and **5** catalyze the cross-coupling reactions of aryl bromides and phenylboronic acid to yield the desired biaryls in high yields at 60 °C using methanol as solvent (Table 4, entries 1−7). Using these catalysts, high yields are obtained from catalyst loads from 0.05 to 0.005 mol %. A moderate yield (73%) is achieved at a catalyst loading as low as 0.0005 mol % with a TON of 1.46×10^5 (Table 4, entry 5). Entries 3 and 6 illustrate that the deactivated electron-rich 4-bromoanisole could be coupled with phenylboronic acid in good yield. The activity of catalysts **3** and **5** is found to be superior to that of the most commonly used catalysts PdCl₂(dppf) and Pd₂(dba)₃/(dppf) which catalyze reactions between 4-bromoacetophenone and phenylboronic acid in toluene at 70 °C in 94% and 86% yield, respectively.[26] In comparison with other P,S-chelated palladium catalysts, the catalytic activity of **3** and **5** is similar to the monomeric Pdᴵᴵ complexes of the 1-phosphabarrelene

phosphine sulfide system whose reactions were carried out in toluene at 110 °C.[27]

Although very high turnover numbers (TONs) and yields are observed for both catalysts, complex **5** exhibits high turnover rates in Suzuki−Miyaura cross-coupling reactions. Hence, most of the experiments were performed with complex **5**. Entries 8 and 9 reveal that catalyst **5** is also effective in the Mizoroki−Heck cross-coupling reactions of aryl bromides with *tert*-butylacrylate under mild conditions. Also noteworthy is the efficient catalytic activity even at 0.05 mol % of the catalyst (entry 8) in Heck reactions. Entries 10 and 11 show that aryl bromides can couple with morpholine in the amination reaction at 100 °C in excellent yield. Reports on efficient universal catalysts which can be employed for both C−C and C−N bond-forming reactions are limited. Buchwald's[28] and Fu's[29] groups used electron-rich phosphine/palladium systems such as Pd(OAc)₂/(*o*-biphenyl)P(ᵗBu)₂ and Pd₂(dba)₃/P(ᵗBu)₃, respectively, to promote cross-coupling reactions. However, the present catalyst system is found to be very air stable and catalyzes those reactions under mild reaction conditions.

Recently, Li and co-workers employed binuclear phosphinous acid (RR′POH) metal complexes for a variety of C−C, C−N, and C−S bond-forming process.[4a−c] They demonstrated that the binuclear complex [RR′P(OH)PdCl-(*μ*-Cl)]₂ is subjected to cleavage and deprotonation in the presence of bases and thought to form an electron-rich phosphane-containing mononuclear tricoordinated an-
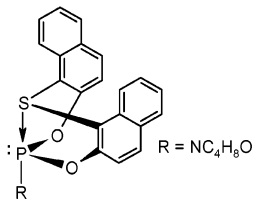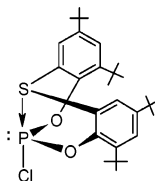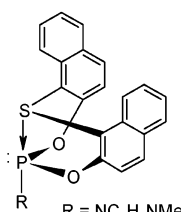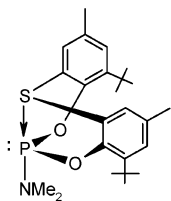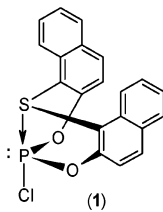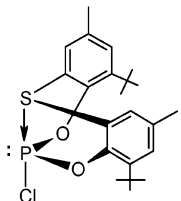
(26) Colacot, T. J.; Qian, H.; Cea-Olivares, R.; Hernandez-Ortega, S. *J. Organomet. Chem.* **2001**, *637−639*, 691−697.

(27) Piechaczyk, O.; Doux, M.; Ricard, L.; Le Floch, P. *Organometallics* **2005**, *24*, 1204−1213.

(28) (a) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2413−2416. (b) Huang, X.; Anderson, K. W.; Zim, J.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653−6655. (c) Aranyos, A.; Old, D. W.; Kiyomori, A.; Wolfe, J. P.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4369−4378.

(29) (a) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989−7000. (b) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4211.

Table 3. Comparison of P−S Bond Parameters, Ring Conformations, and ^{31}P Chemical Shifts for Cyclic Phosphites (in increasing order of % TBP)

Compound	P-S (Å)	% TBP[a]	S-P-R$_{ax}$, (deg)[b]	δ(^{31}P) in ppm	Reference
7	3.263(2)	25.3	158.41	76.9 (s), $^{1}J_{PtP}$	This Work
	3.157(2)	32.2	162.01	= 6334 Hz	
3	3.176(4)	30.9	162.88	100.8(d)	This Work
	3.106(4)	35.6	167.82	47.0(d)	
				$^{2}J_{PP}$ = 104 Hz	
R = NC$_4$H$_8$O	3.089(1)	36.7	164.47	134.9	7
(Cl)	3.043(2)	39.7	172.22(8)	170.4	20a
R = NC$_4$H$_8$NMe	3.040(1)	39.8	166.68	135.1	7
2	2.993(1)	42.9	166.46	127.5 (s)	This Work
	2.967(1)	44.7	167.99		
NMe$_2$	2.952(9)	47.1	173.3(9)	132.5	20a
(1) Cl	2.887(1)	49.9	165.55	172.3	7
Cl	2.816(2)	54.5	169.24(7)	168.4	20b

[a] Percent geometrical displacement from a pyramid toward a TBP. [b] With reference to a TBP with sulfur in an axial position and both ring oxygen atoms in equatorial positions.

Table 4. Palladium Complex-Catalyzed Cross-Coupling of Aryl Bromides with $PhB(OH)_2$, *tert*-Butylacrylate, and Morpholine[a]
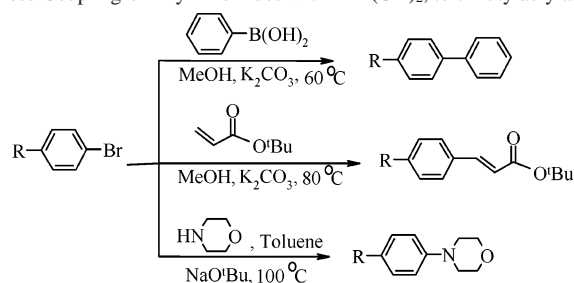
Entry	Cat.	R	Coupling partner	Amount of cat. (mol %)	Time (h)	Product	Conv. (%)[b]	TON
1	**3**	MeC(O)	—B(OH)₂	0.005	2		100	2.0×10^4
2	**3**	MeC(O)	—B(OH)₂	0.0005	14		39	7.8×10^4
3	**3**	MeO	—B(OH)₂	0.05	5		77	1.5×10^3
4	**5**	MeC(O)	—B(OH)₂	0.005	2		100	2.0×10^4
5	**5**	MeC(O)	—B(OH)₂	0.0005	5		73	1.46×10^5
6	**5**	MeO	—B(OH)₂	0.05	5		96	1.92×10^3
7	**5**	MeO	—B(OH)₂	0.005	9		53	1.06×10^4
8	**5**	MeC(O)	O'Bu	0.05	20		77	1.54×10^3
9	**5**	MeC(O)	O'Bu	0.2	20		92	4.6×10^2
10	**5**	MeC(O)	HN—O	0.05	20		91	1.82×10^3
11	**5**	MeC(O)	HN—O	0.2	20		96	4.8×10^2

[a] Reaction conditions: aryl bromide (1.0 equiv), boronic acid (or *tert*-butylacrylate, morpholine) (1.2−1.5 equiv), K_2CO_3 (or NaO'Bu) (1.2−2 equiv), methanol (or toluene) (5 mL). [b] Conversion to coupled product determined by GC, based on aryl halides (or dodecane); average of two runs.

ionic complex which is responsible for the high activity of the catalyst (Scheme 3). However, in the present study the isolated and fully characterized anionic palladium complex **5** was employed for C−C and C−N cross-coupling reactions. With regard to the involvement of anionic species in catalysis,[5a] a plausible catalytic cycle for the cross-coupling reactions of aryl halides is given in Scheme 9. During catalysis the anionic complex **5** can exchange cation with the base (i.e., K_2CO_3) to form $[Pd]^-[K]^+$ (**I**) as the oxidative addition is faster in the presence of metal cations.[30] The metal cation interacts with the halide anions ligated to palladium by ion pairing to afford more reactive Pd(0) complex (**III**). In this complex the sulfur coordination provides a temporary platform for the active catalytic species during an oxidative addition step and also extra stability to the catalyst precursor. Although several hemilabile phosphorus ligands containing thioether sulfur have been used

in catalysis, well-characterized palladium complexes containing a hemilabile motif of this type are rare in catalytic reactions. In the case of complex **3**, the catalytic cycle would be similar to any other palladium(II) complex which in the presence of a base gives the catalytically active palladium-(0) species.[1]

The homogeneous nature of the catalysis was checked by the classical mercury test. Addition of a drop of mercury to the reaction mixtures did not affect the activity of the catalyst, thus showing them to be truly homogeneous systems.[31]

Conclusion

Catalytically active Pd^{II} complexes **3** and **5** are synthesized by oxidizing the phosphorus centers with an appropriate amount of water from the 1:1 and 1:2 reactions of aminobis-

(30) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375−8384.

(31) (a) Widegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10301−10310. (b) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317−341.

(phosphonite) and palladium precursor, respectively, where the thioether−phosphonate moiety forms a metallacycle containing a metal−phosphorus σ bond. These are the first examples of any thioether-based phosphorus ligands which form anionic mononuclear and neutral binuclear complexes. The bridged binuclear Pd[II] complex of aminobis-(phosphonite) is highly unstable essentially due to the steric bulk of the ligand. However, Pt[II] forms moderately stable chelate complexes which are found to be resistant to moisture-induced P−N bond cleavage reactions. The sulfur atom present in the eight-membered aminobis(phosphonite) ring shows coordinative interaction toward phosphorus; as a result, the tricoordinated geometry around phosphorus is displaced toward TBP. The anionic and neutral binuclear palladium complexes show excellent catalytic activity toward Suzuki−Miyaura cross-coupling (TON up to 1.46×10^5) and Mizoroki−Heck coupling reactions as well as amination reactions under mild conditions. Interestingly, P−O bonds in phosphonites are quite stable toward aerial oxidation and hydrolytic cleavage. They also survive rigorous conditions employed during catalytic reactions. Further studies on the utilization of these complexes toward cross coupling of unactivated aryl chlorides with arylboronic acids, amines, and thiols are currently under investigation.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**, **3**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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