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Synthesis of Neutral (Pd^{II}, Pt^{II}), Cationic (Pd^{II}), and Water-Induced Anionic (Pd^{II}) Complexes Containing New Mesocyclic[§] Thioether–Aminophosphonite Ligands and Their Application in the Suzuki Cross-Coupling Reaction

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Mesocyclic thioether–aminophosphonite ligands, {–$OC_{10}H_6$(μ-S)$C_{10}H_6O$–}PNC_4H_8O (**2a**, 4-(dinaphtho[2,1-*d*:1′,2′-*g*][1,3,6,2]dioxathiaphosphocin-4-yl)morpholine) and {–$OC_{10}H_6$(μ-S)$C_{10}H_6O$–}$PNC_4H_8NCH_3$ (**2b**, 1-(dinaphtho[2,1-*d*:1′,2′-*g*][1,3,6,2]dioxathiaphosphocin-4-yl)-4-methylpiperazine) are obtained by reacting {–$OC_{10}H_6$(μ-S)$C_{10}H_6O$–}PCl (**1**) with corresponding nucleophiles. The ligands **2a** and **2b** react with $(PhCN)_2PdCl_2$ or $M(COD)Cl_2$ (M = Pd^{II} or Pt^{II}) to afford P-coordinated cis-complexes, [{(–$OC_{10}H_6$(μ-S)$C_{10}H_6O$–)PNC_4H_8X-κP}$_2MCl_2$] (**3a**, M = Pd^{II}, X = O; **3b**, M = Pd^{II}, X = NMe; **4a**, M = Pt^{II}, X = O; **4b**, M = Pt^{II}, X = NMe). Compounds **2a** and **2b**, upon treatment with [Pd(η^3-C_3H_5)Cl]$_2$ in the presence of AgOTf, produce the P,S-chelated cationic complexes, [{(–$OC_{10}H_6$(μ-S)-$C_{10}H_6O$–)PNC_4H_8X-$\kappa P,\kappa S$}Pd(η^3-C_3H_5)](CF_3SO_3) (**5a**, X = O and **5b**, X = NMe). Treatment of **2a** and **2b** with $(PhCN)_2PdCl_2$ in the presence of trace amount of H_2O affords P,S-chelated anionic complexes, [{(–$OC_{10}H_6$(μ-S)-$C_{10}H_6O$–)P(O)-$\kappa P,\kappa S$}$PdCl_2$]($H_2NC_4H_8X$) (**6a**, X = O and **6b**, X = NMe), via P–N bond cleavage. The crystal structures of compounds **1**, **2a**, **2b**, **4a**, and **6a** are reported. Compound **6a** is a rare example of crystallographically characterized anionic transition metal complex containing a thioether–phosphonate ligand. Most of these palladium complexes proved to be very active catalysts for the Suzuki–Miyaura reaction with excellent turnover number ((TON), up to 9.2×10^4 using complex **6a** as a catalyst).

Introduction

The application of transition metal complexes for homogeneous catalysis has been established for a wide variety of chelating phosphorus-, nitrogen-, and carbon-based ligands.[1] In terms of greater catalytic activity and selectivity, these ligands continue to be the primary focus of academic and industrial research. Initially, diphosphine ligands predominated; however, in recent years mixed-donor ligands have shown excellent activity in organic transformations.[2] In principle, mixed-donor ligands containing one strongly and one weakly binding center (i.e., hemilabile ligands) can be used to protect an active site at a metal center via chelation until it is required to effect the transformation of a substrate. Specifically, the development of mixed-donor ligands such as P,O-,[3] P,N-,[4] and P,S-compounds[5] led to high activity in several catalytic processes, and their reactivity offers interest-

§ The "small ring macrocycle" (alternatively "mesocycle"[5f]) refers to cyclic ligands that have a ring too small to fit completely around a metal atom, that is a ring of less than about 14 atoms. These ligands have properties intermediate between those of true macrocycles and those of acyclic multidentate ligands.

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ing structural possibilities. Ligands combining phosphorus centers and sulfur centers are especially interesting. Both phosphorus and sulfur are excellent donor atoms for a wide range of metals, and the low ionization energy of sulfur and the existence of several lone pairs of electrons (three in the case of a thiolate anion) offer the possibility of rich sulfur-based chemistry of the complexes. The P,S-donor ligands have been least explored and have been used with limited success in catalysis, possibly due to the well-known tendency of sulfur to act as a "catalyst poison".[6] However, the recent results have been very promising.[2b,7]

Among the mixed P,S-ligands used in coordination chemistry and catalysis, thioether−phosphines,[8] thioether−phosphinites,[9] and thioether−phosphites[10] have been well studied and have achieved greater success. Despite the considerable current interest in the chemistry of P,S-type functional ligands and the catalytic properties of their metal complexes, other types of P,S-donor ligands are rarely given much attention. To the best of our knowledge, there are no reports on cyclic thioether−aminophosphonite types of ligands, either in coordination chemistry or in catalysis. Holmes and co-workers have reported several eight-membered cyclic P,S-type ligands where sulfur shows a coordinative interaction toward phosphorus.[11] They have shown that the donor action provided by sulfur leads to an increase in coordination at phosphorus from tricoordinate to pseudopentacoordinate. However, they have not studied any coordination behavior or catalytic activity of such ligands. It will be interesting to see the coordination chemistry of such ligands as sulfur shows a coordinative tendency toward phosphorus. In view of this and as a part of our interest in designing new, inexpensive ligands and studying their coordination behavior[12] and catalytic applications,[13] we report herein on the synthesis and characterization of a new class of mixed P,S-mesocyclic ligands and their Pd(II) and Pt(II) complexes. As will be seen, we also show that the palladium-

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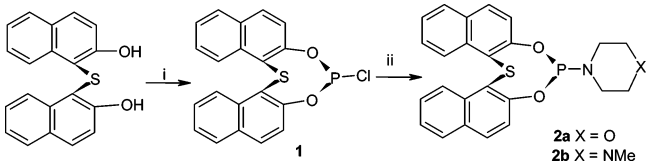
Scheme 1. (i) PCl_3, Et_3N, DMAP, −20 °C, THF; (ii) Morpholine or *N*-Methyl Piperazine, 0 °C, THF



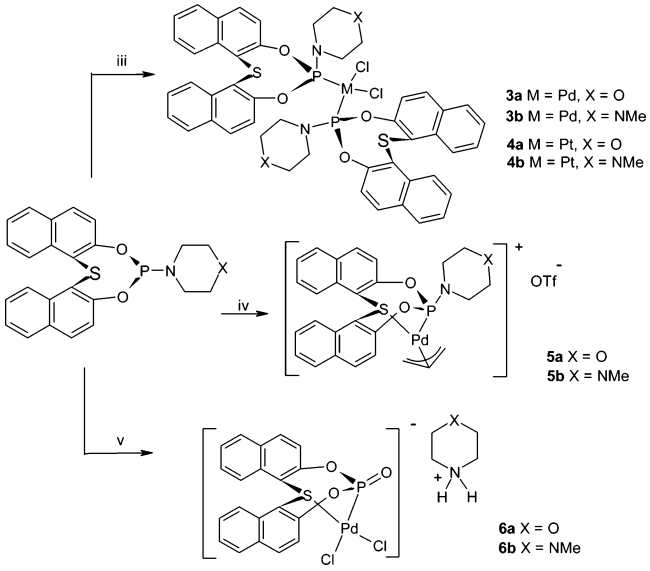
(II) complexes of these new ligands exhibit a significant catalytic activity in the Suzuki−Miyaura cross-coupling reaction.

Results and Discussion

Ligand Synthesis. The reaction of thiobis(2,2′-naphthol) with an excess of PCl_3 in the presence of an excess of triethylamine and a catalytic amount of DMAP (4-*N*,*N*-(dimethylamino)pyridine) afford the cyclic chlorophosphite $\{-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-\}PCl$ (**1**) in quantitative yield. Compound **1** is a white crystalline solid soluble in most of the polar organic solvents. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a single resonance peak at 172.3 ppm, and the mass spectrum shows the base peak at (*m*/*z*) 347.2 for the ion corresponding to $M^+ - Cl$. The aminophosphonite ligands $\{-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-\}PNC_4H_8O$ (**2a**) and $\{-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-\}PNC_4H_8NCH_3$ (**2b**) were prepared by reacting the chlorophosphite (**1**) with 2 equiv of morpholine or *N*-methylpiperazine (Scheme 1). Both compounds **2a** and **2b** are white crystalline solids whose $^{31}P\{^1H\}$ NMR spectra show single resonance peaks at 134.9 and 135.1 ppm, respectively. The ^1H NMR spectrum of compound **2a** shows two triplets at 3.41 and 3.79 ppm for the ethylene protons of morpholine, whereas those of *N*-methylpiperazine in compound **2b** show two resonance peaks at 2.55 and 3.46 ppm, with an additional singlet at 2.39 ppm for the *N*-methyl protons. Further, the structure and composition of compounds **1**, **2a**, and **2b** were confirmed by analytical data and X-ray diffraction studies.

Metal Complexes. The reactions of **2a** and **2b** with $(PhCN)_2PdCl_2$ are independent of stoichiometry and produce exclusively the phosphorus-coordinated complexes, *cis*-$[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)PNC_4H_8O\text{-}\kappa P\}_2PdCl_2]$ (**3a**) and *cis*-$[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)PNC_4H_8NCH_3\text{-}\kappa P\}_2PdCl_2]$ (**3b**), respectively, with the ligands exhibiting a monodentate mode of coordination. Similarly, the thioether−aminophosphonites **2a** and **2b** react with $Pt(COD)Cl_2$ to afford the complexes *cis*-$[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)PNC_4H_8O\text{-}\kappa P\}_2PtCl_2]$ (**4a**) and *cis*-$[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)PNC_4H_8NCH_3\text{-}\kappa P\}_2PtCl_2]$ (**4b**), respectively. The ^{31}P NMR spectra of **3a** and **3b** exhibit single resonance peaks at 93.9 and 94.1 ppm, respectively. The ^{31}P NMR spectra of complexes **4a** and **4b** also show single resonance peaks at 69.4 and 69.9 ppm with very large $^1J_{PtP}$ values of 5835 and 5842 Hz, respectively. This high value of the Pt−P coupling constant indicates the strong σ-donor capabilities of the aminophosphonite ligands **2a** and **2b**, which are comparable to those observed for *cis*-$PtCl_2\{P(OPh)_3\}_2$ ($^1J_{PtP} = 5770$ Hz).[14] The structure of complex **4a** has been confirmed by a single-crystal X-ray diffraction study.

Scheme 2. (iii) $(PhCN)_2PdCl_2$ or $Pt(COD)Cl_2$, CH_2Cl_2, Room Temperature; (iv) $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/AgOTf, CH_2Cl_2 or Acetone, Room Temperature; (v) $(PhCN)_2PdCl_2$, H_2O(trace), Toluene, 90 °C



Surprisingly, in the above complexes, ligands **2a** and **2b** did not form the chelate rings via P- and S-centers, despite phosphorus and sulfur centers being in close proximity (P···S nonbonded distances in **2a** and **2b** are 3.089(1) and 3.040(1) Å, respectively), which can facilitate the formation of a strain-free six-membered chelate ring with either palladium or platinum centers. However, the P,S-chelated cationic complexes $[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)PNC_4H_8O\text{-}\kappa P,\kappa S\}Pd(\eta^3\text{-}C_3H_5)](CF_3SO_3)$ (**5a**) and $[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)PNC_4H_8NCH_3\text{-}\kappa P,\kappa S\}Pd(\eta^3\text{-}C_3H_5)](CF_3SO_3)$ (**5b**) are formed when ligands **2a** or **2b** are treated with 0.5 equiv of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in the presence of AgOTf, as shown in Scheme 2. Complexes **5a** and **5b** are moderately stable in the solid state, whereas they decompose slowly in solution. The $^{31}P\{^1H\}$ NMR spectra of complexes **5a** and **5b** show single resonance peaks at 123.8 and 125.1 ppm, respectively. The ^1H NMR spectrum of complex **5a** shows two broad singlets at 4.88 and 4.28 ppm and a multiplet in the region 5.75−5.79 ppm for the protons on the allylic group. The mass spectrum of complex **5a** shows a peak at (*m*/*z*) 580.1 that corresponds to the cation ($M^+ - OTf$).

Amino−phosphonites or phosphinites containing a P−N bond(s) are known to undergo hydrolytic cleavage when they are exposed to moisture or acid impurities during the complexation reactions.[15] This kind of P−N bond cleavage either can generate hydrogen−phosphonates of the type $X_2P(O)H$, which can be excellent sources of catalyst precursors, or can covalently bind to the metal center via HCl elimination to produce neutral or anionic complexes.[16] From the catalytic point of view, neutral complexes are not useful because oxidation of the metal center must occur. Anionic complexes

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are very useful as potential catalysts because they can retain the low oxidation state of the metal center. With this in mind, it was anticipated that the reactions of **2a** and **2b** with palladium(II) or platinum(II) derivatives in the presence of moisture would furnish the catalytically active anionic complexes. As expected, the reactions of **2a** and **2b** with $(PhCN)_2PdCl_2$ in the presence of H_2O in toluene at 90 °C afforded the P,S-chelated anionic complexes $[\{(-OC_{10}H_6-(\mu\text{-}S)C_{10}H_6O-)P(O)\text{-}\kappa P,\kappa S\}PdCl_2](H_2NC_4H_8O)$ (**6a**) and $[\{(-OC_{10}H_6(\mu\text{-}S)C_{10}H_6O-)P(O)\text{-}\kappa P,\kappa S\}PdCl_2](H_2NC_4H_8\text{-}NCH_3)$ (**6b**), respectively. The anionic complexes **6a** and **6b** are formed as a result of the fission of the P−N bond followed by the oxidation of the P-center on the aminophosphonite ligands **2a** and **2b**. The broken amine fragment gets protonated to form the countercation, as shown in Scheme 2. The $^{31}P\{^1H\}$ NMR spectra of **6a** and **6b** show single resonance peaks at 44.5 and 44.7 ppm, respectively. In the IR spectrum, bands at 3302 and 3309 cm^{-1} confirm the presence of N−H bonds (ammonium cation) for the complexes **6a** and **6b**, respectively, whereas a band at 1112 cm^{-1} is assigned to υ(P═O) in both the complexes. Further, the structural compositions of both the complexes were confirmed by elemental analysis and the single-crystal X-ray diffraction study in the case of complex **6a**.

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.[16g−i] The palladium complexes **6a** and **6b** are very unique, as the ligands bind to the metal through both phosphonate and sulfur moieties via σ-bonds and coordinate bonds, respectively, to form anionic complexes. These types of anionic palladium complexes with chelating thioether−phosphonates are not seen in the literature.

Crystal and Molecular Structures of Compounds 1, 2a, 2b, 4a, and 6a. Perspective views of the molecular structures of compounds **1**, **2a**, **2b**, **4a** and **6a** with the atom numbering schemes are shown in Figures 1−5, respectively. The crystallographic data and the details of the structure determination are given in Table 1, whereas the selected bond lengths and bond angles are given in Tables 2 and 3.

Similar to the P−S-containing eight-membered cyclic phosphite structures reported by Sherlock et al.,[11] the geometries of the phosphites **1**−**2b** are considered as pseudotrigonal bipyramids (TBP). In all of these cyclic derivatives, the eight-membered ring containing phosphorus and sulfur is in a *syn* boat-like conformation, where the sulfur atom shows coordinative tendencies toward phosphorus, as expressed by the P−S distances. The effect of the sulfur−phosphorus interaction leads to a structural displacement with varying degrees, from pyramidal toward a pseudo trigonal bipyramid. The P−S distance ranges from 2.887(1) for **1** to 3.089(1) Å for **2a**, which compares well with the similar structures reported (see Table 4). This range also compares well with the sum of the van der Waals radii for phosphorus and sulfur (3.65 Å)[17] and the sum of the covalent radii (2.12 Å).[18]

In the proposed TBP geometries for compounds **1**−**2b**, the sulfur atom is located in an axial position, with the lone electron pair and two oxygen atoms occupying the equatorial

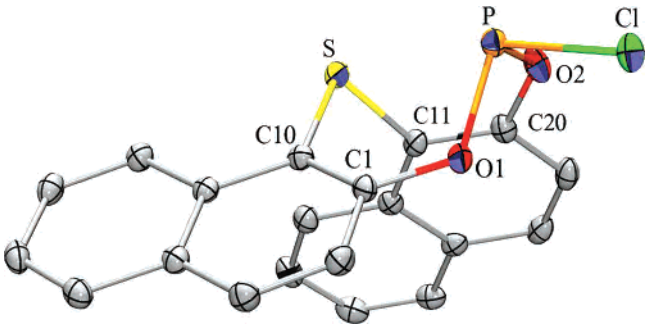

Figure 1. Molecular structure of **1**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

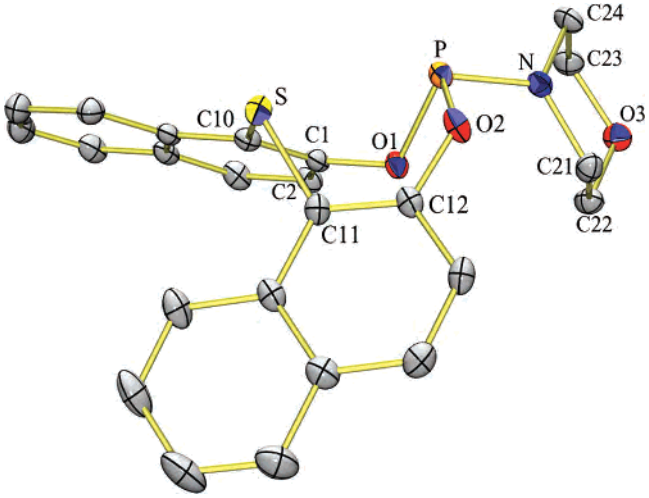

Figure 2. Molecular structure of **2a**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

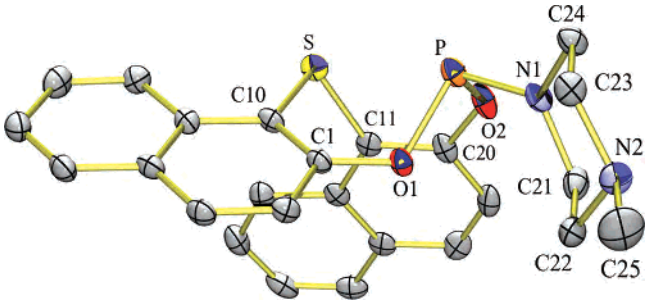

Figure 3. Molecular structure of **2b**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

(16) (a) Dubrovina, N. V.; Borner, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5883−5886. (b) Li, G. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1513−1516. (c) Han, L. B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571−1572. (d) Han, L. B.; Mirzaei, F.; Zhao, C. Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407−5408. (e) Zhao, C. Q.; Han, L. B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196−4198. (f) Ackermann, L.; Born, R.; Spatz, J. H.; Meyer, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7216−7219. (g) Levine, A. M.; Stockland, R. A.; Clark, R.; Guzei, I. *Organometallics* **2002**, *21*, 3278−3284. (h) Stockland, R. A.; Levine, A. M.; Giovine, M. T.; Guzei, I. A.; Cannistra, J. C. *Organometallics* **2004**, *23*, 647−656. (i) Pryjomska, I.; Bartosz-Bechowski, H.; Ciunik, Z.; Trzeciak, A. M.; Ziòlkowski, J. J. *Dalton Trans.* **2006**, 213−220.

(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(18) 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.

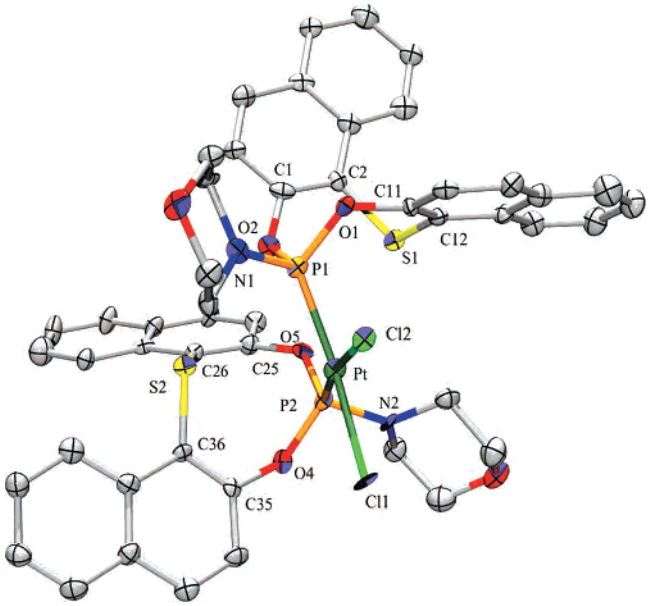

Figure 4. Molecular structure of **4a**. For clarity, all the hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

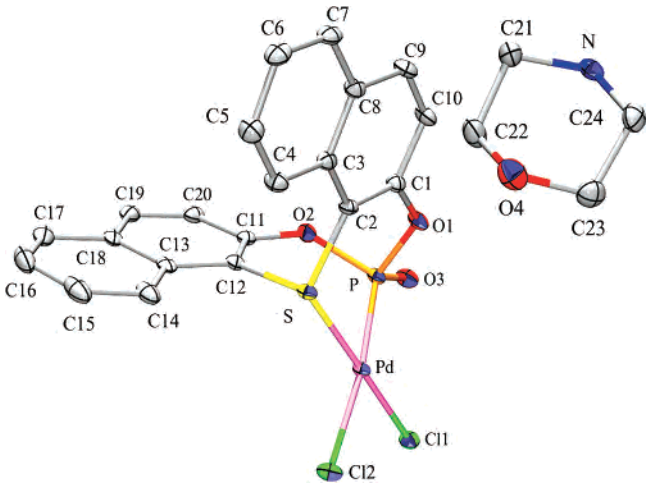

Figure 5. Molecular structure of **6a**·CH_2Cl_2. For clarity, solvent and all the hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

site. The degree to which the TBP is approached can be seen from the axial S−P−R angles for this series, which range from 164.47° for **2a** to 166.68° for **2b**. The degree of displacement toward TBP can be measured following the procedure of Holmes and co-workers.[19] In this procedure, the degree of displacement from pyramidal toward TBP can be calculated by noting how far the P−S distance has displaced from the van der Waals sum (3.65 Å) toward the sum of the covalent radii (2.12 Å). The results are presented in Table 4 as % TBP in increasing order along with other parameters. A similar type of sulfur−phosphorus coordinative interaction is also observed in our previously reported P−S−P ten-member heterocyclic diphosphane.[12a] All these results again compare well with that observed for the similar structures reported by Holmes and co-workers.[11] The naphthyl-based chlorophosphite (**1**) shows more structural displacement toward TBP (49.9%) next to the 2,2′-[thiobis(4-methyl-6-*tert*-butylphenyl)] chlorophosphite (54.5%).[11a] The P−S distance observed for **1** is shorter than those for **2a** and **2b**, because of the same reason the geometry of **1** displaced more toward a TBP (49.9%), as compared to **2a** and **2b**.

In the molecular structure of **4a**, the platinum center is coordinated through two phosphorus centers and two chlorine atoms in a square planar fashion with cis angles varying from 98.55(15)° (P1−Pt−P2) to 86.21(14)° (Cl1−Pt−P2). The bond angles at sulfur, C2−S1−C12 (103.7(7)°) and C26−S2−C36 (105.7(7)°), have increased, as compared to the same in the free ligand. This may be due to the decrease in the coordinative interaction of sulfur (S1−P1, 3.342(6) Å; S2−P2, 3.156(6) Å) toward phosphorus that makes the sulfur center more relaxed in complex **4a**. The Pt−P1 (2.202(4) Å) and Pt−P2 (2.218(4) Å) bond lengths are comparable with those found in the somewhat similar mesocyclic chelate complex, (5-phenyl-1-thia-5-phosphacyclooctane)$PtCl_2$ (Pt−P, 2.207(3) Å).[20] However, complex **4a** exhibited a higher $^1J_{PtP}$ value (5835 Hz) compared with the above-mentioned platinum(II) complex, which shows a $^1J_{PtP}$ of 3424 Hz.[20] This is somewhat surprising, because a correlation is not observed between bond lengths and $^1J_{PtP}$ values. Maybe the additional coordination supplied by sulfur to phosphorus in **4a** is responsible for such a high Pt−P coupling constant. Also, a number of factors affect the values of one-bond metal−phosphorus coupling constants;[21] therefore, the apparent contradiction between the Pt−P bond length and the $^1J_{PtP}$ values for the above complexes is not easily accounted for.

Suitable crystals of **6a** were obtained by slow diffusion of petroleum ether into a dichloromethane solution of the complex at room temperature. The molecular structure of **6a** is shown in Figure 5. While numerous structures of transition metal complexes bearing simple monodentate phosphonate ligands are known,[16g,22] the molecular structure of **6a** is a rare example of a transition metal complex with a thioether group chelating cis to a phosphonate and forming an anionic complex. The arrangement of the ligand about palladium is slightly distorted from the expected square-planar geometry. The Pd−P bond length of 2.1836(4) Å is around 0.104 Å shorter than that found in the phosphonate complex, [(dppe)PdCl{$P(O)(OPh)_2$}] (P−Pd = 2.2871(7) Å).[16h] This is suggestive of the significant π-accepting nature of the aminophosphonite ligand in complex **6a**. The Pd−S bond distance of 2.3047(4) Å is comparable to that of the thioether−phosphine palladium complex [$PdCl_2$($MeSC_6H_4$-

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(20) Toto, S. D.; Olmstead, M. M.; Arbuckle, B. W.; Bharadwaj, P. K.; Musker, W. K. *Inorg. Chem.* **1990**, *29*, 691−699.

(21) (a) Pregosin, P. S.; Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979. (b) Diehl, P.; Fluck, E.; Kosfeld, R. *NMR Basic Principles and Progress 16*; Springer-Verlag: New York, 1979.

(22) (a) Chang, C.; Lin, Y.; Lee, G.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 4223−4230. (b) Leung, W.; Chan, E. Y. Y.; Wong, W. *Inorg. Chem.* **1999**, *38*, 136−143. (c) Chang, C.; Lin, Y.; Lee, G.; Huang, S.; Wang, Y. *Organometallics* **1998**, *17*, 2534−2542. (d) Leung, W.; Chan, E. Y. Y.; Williams, I. D.; Wong, W. *Organometallics* **1997**, *16*, 3234−3240.

Table 1. Crystallographic Data for Compounds **1**, **2a**, **2b**, **4a**, and **6a**

	1	**2a**	**2b**	**4a**	**6a**
formula	$C_{20}H_{12}ClO_2PS$	$C_{24}H_{20}NO_3PS$	$C_{25}H_{23}N_2O_2PS$	$C_{48}H_{40}Cl_2N_2O_6P_2PtS_2$	$C_{20}H_{12}Cl_2O_3PPdS\cdot C_4H_{10}NO.CH_2Cl_2$
mol wt	382.79	433.45	446.49	1132.88	713.71
crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
crystal size (mm)	0.16 × 0.21 × 0.23	0.13 × 0.21 × 0.26	0.20 × 0.21 × 0.26	0.08 × 0.07 × 0.12	0.09 × 0.19 × 0.23
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	8.787(1)	6.928(1)	9.947(2)	12.735(3)	8.873(1)
b (Å)	8.878(1)	9.220(1)	11.663(3)	9.856(2)	12.452(1)
c (Å)	11.361(1)	17.083(2)	11.860(3)	35.707(8)	12.801(1)
α (deg)	74.211(1)	82.065(1)	60.967(3)	90	106.318(1)
β (deg)	88.421(1)	85.694(1)	86.534(3)	94.646(3)	95.263(1)
γ (deg)	75.960(1)	70.673(1)	66.273(3)	90	93.850(1)
V (Å ^{3})	826.63(1)	1019.35(1)	1085.6(5)	4467.2(1)	1345.22(1)
Z	2	2	2	4	2
ρ_{calcd} (g cm^{-3})	1.538	1.412	1.366	1.684	1.762
μ (Mo Kα) (mm^{-1})	0.465	0.264	0.248	3.479	1.259
F(000)	392	452	468	2256	716
temp (K)	100	100	100	100	100
$\theta_{min-max}$ (deg)	1.9, 28.3	1.2, 27.7	2.0, 28.3	1.1, 26.5	2.0, 29.2
GOF (F^2)	1.03	1.05	1.04	1.14	1.05
R_1 [a]	0.0305	0.0350	0.0587	0.1064	0.0223
wR_2 [b]	0.0842	0.0950	0.1454	0.2419	0.0569

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds **1**, **2a**, and **2b**

1		**2a**		**2b**	
Cl−P	2.1044(5)	S−C10	1.7769(14)	S−C10	1.785(3)
S−C10	1.7778(14)	S−C11	1.7691(15)	S−C11	1.777(3)
S−C11	1.7771(14)	P−O1	1.6843(10)	P−O1	1.680(2)
P−O1	1.6480(11)	P−O2	1.6686(11)	P−O2	1.676(2)
P−O2	1.6335(11)	P−N	1.6534(13)	P−N1	1.646(2)
C10−S−C11	101.95(7)	C10−S−C11	102.98(7)	C10−S−C11	101.93(13)
Cl−P−O1	93.69(4)	O1−P−O2	96.53(5)	O1−P−O2	95.29(11)
Cl−P−O2	93.66(4)	O1−P−N	100.75(6)	O1−P−N1	99.08(10)
O1−P−O2	100.99(6)	O2−P−N	96.33(6)	O2−P−N1	96.37(12)

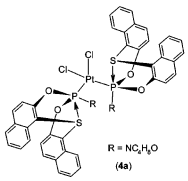
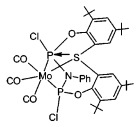
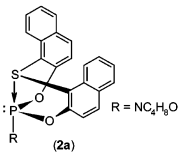
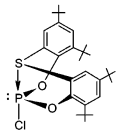
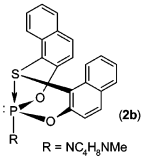
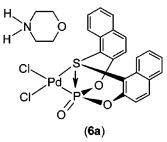
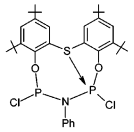
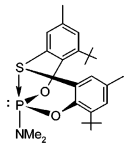
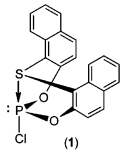
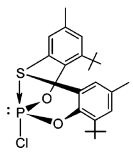
Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes **4a** and **6a**

4a		**6a**	
Pt−Cl1	2.339(4)	Pd−Cl1	2.3450(4)
Pt−Cl2	2.356(3)	Pd−Cl2	2.4024(4)
Pt−P1	2.202(4)	Pd−S	2.3047(4)
Pt−P2	2.218(4)	Pd−P	2.1836(4)
P2−O4	1.604(11)	P−O1	1.5717(12)
P2−O5	1.599(11)	P−O2	1.6770(13)
		P−O3	1.4798(13)
Cl1−Pt−Cl2	89.45(13)	Cl1−Pd−Cl2	92.62(1)
Cl1−Pt−P1	172.34(14)	Cl1−Pd−S	175.85(1)
Cl1−Pt−P2	86.21(14)	Cl1−Pd−P	93.04(1)
P1−Pt−P2	98.55(15)	Cl2−Pd−S	89.99(1)
C2−S1−C12	103.7(7)	Cl2−Pd−P	172.53(2)
C26−S2−C36	105.7(7)	S−Pd−P	84.09(1)
O4−P2−O5	101.7(6)	C2−S−C12	98.35(8)
		O1−P−O2	99.92(7)

CH_2PPh_2)] (2.295(1) Å).[8c] The P═O bond length of 1.4798(13) Å and the P−O bond lengths of 1.5717(12) and 1.6770(13) Å are typical of other metal complexes containing phosphonate groups.[16g,22a] The Pd−Cl2 bond length of 2.4024(4) Å (trans to phosphorus) is slightly longer than the Pd−Cl1 bond length (trans to sulfur), which is 2.3450(4) Å. This reflects the difference between the σ-donor strengths of phosphorus and sulfur (trans influence), which is not unusual. For example, in [$PdCl_2$(^{t}BuS$C_6H_4CH_2PPh_2$)], the Pd−Cl bond trans to the phosphorus center is longer (2.3686(9) Å) than the one located trans to the sulfur (2.3157(9) Å).[8c] Comparison of these data with that for complex **6a** indicates the better σ-donor strength of the phosphonate ligand in **6a** than the above-mentioned phosphine. The S−Pd−P bite angle of 84.09(1)° is significantly smaller compared to the same (88.51(4)°) in the six-membered thioether−phosphine complex [$PdCl_2$(Me$SC_6H_4CH_2PPh_2$)].[8c] The bond angle at sulfur (C2−S−C12, 98.35(8)°) has decreased approximately by 5°, compared to that of the free ligand **2a** (C10−S−C11, 102.98(7)°), whereas the angle at phosphorus has increased from 96.53(5)° (O1−P−O2) to 99.92(7)° (O1−P−O2) after complex formation. These signify that the P−S mesocyclic ring becomes more bent at sulfur and straightens at the phosphorus upon chelation to the palladium center. Interestingly, NH_2 shows a hydrogen bonding interaction (NH2···O3, 1.7600 Å and N−H2N···O3, 162.38°) with the oxygen of P═O, which may give extra stability to the anionic complex **6a**.

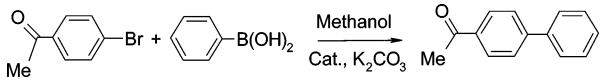
Suzuki Cross-Coupling Reactions. The application of all the palladium complexes **3a**, **3b**, **5a**, **5b**, **6a**, and **6b** and related complexes formed in-situ as catalysts in the Suzuki coupling reaction was investigated. In all cases, the initial coupling studied was that of phenylboronic acid with the "easy-to-couple" substrate 4-bromoacetophenone. The results were encouraging, with most of the catalysts showing excellent activity using 0.01% mol at 60 °C, except for the complexes **3a** and **3b,** which displayed low reactivity even

Table 4. 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
 (4a)	3.342(6) 3.156(6)	20.1 32.2	156.99 169.28	69.4 $^1J_{PtP}$ = 5835 Hz	This Work
	3.152(1)	32.5	166.35	138.1	12a
 (2a)	3.089(1)	36.7	164.47	134.9	This Work
	3.043(2)	39.7	172.22(8)	170.4	11b
 (2b)	3.040(1)	39.8	166.68	135.1	This Work
 (6a)	3.007	42.0	172.64	44.5	This Work
	2.998(2)	42.6	167.56	145.7	12a
	2.952(9)	47.1	173.3(9)	132.5	11b
 (1)	2.887(1)	49.9	165.55	172.3	This Work
	2.816(2)	54.5	169.24(7)	168.4	11a

[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 5. Influence of Different Catalysts and Catalyst Loading on the Coupling Reaction[a]



entry	catalyst	amount of cat. (mol %)	time (h)	conv (%)[b]	TON
1	**6a**	0.01	2	100	10 000
2	**6a**	0.001	12	72	72 000
3	**6a**	0.0005	12	46	92 000
4	**6b**	0.01	5	97	9700
5	**6b**	0.001	5	46	46 000
6	**5a**	0.01	2	99	9900
7	**5a**	0.001	5	29	29 000
8	**5b**	0.01	2	88	8800
9	**5b**	0.001	2	28	28 000
10	$Pd(OAc)_2$/**2a**	0.01	3	96	9600
11	$Pd(OAc)_2$/**2a**	0.001	18	92	92 000
12	$Pd(OAc)_2$/**2a**	0.0005	18	28	56 000
13	$Pd(OAc)_2$/**2b**	0.01	12	93	9300
14	$Pd(OAc)_2$/**2b**	0.001	12	20	20 000
15	**3a**	0.5	12	70	140
16	**3a**	1	12	99	99
17	**3b**	0.5	12	67	134
18	$Pd(OAc)_2$	0.01	6	31	3100

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.75 mmol of phenylboronic acid, 1 mmol of K_2CO_3, 5 mL of methanol, at 60 °C. [b] Conversion to coupled product determined by GC, based on aryl halides (or dodecane); average of two runs.

with a high mole percent (Table 5). The best results were obtained with all of the four precatalysts (**5a**,**b** and **6a**,**b**). Use of other palladium precursors such as $Pd(OAc)_2$/**2a**,**b** also gave good yields, but reactions were carried out for a prolonged period (18 or 12 h). From a comparison of the activities of the P,S-chelated complexes **5a**,**b** and **6a**,**b** with that of the nonchelated complexes **3a**,**b** in the coupling of 4-bromoacetophenone, two conclusions can be drawn: (i) the P−S-chelated complexes show greatly enhanced activity and (ii) the P−S chelated complexes are atom-economic (i.e., 1 equiv of ligand was used compared to 2 equiv in the case of complexes **3a** and **3b**. The high activities of P−S-chelated complexes demonstrate the importance of heterofunctional coordination in the coupling reaction.

Next, we examined the effect of catalyst loading on this convenient coupling between 4-bromoacetophenone and phenylboronic acid. High yields are maintained from normal catalyst loads (0.01 mol %) down to a level of 0.001 mol % for the catalyst **6a** and $Pd(OAc)_2$/**2a**. A moderate yield (>46%) is achieved even at catalyst loading as low as 0.0005 mol % with a turnover number (TON) of 92 000 (Table 5, entry 3). The overall activity of the complexes **6a**,**b** and $Pd(OAc)_2$/**2a** follows the order **6a** > $Pd(OAc)_2$/**2a** > **6b**, with anionic complexes predominating over all the precatalysts. Although **6a** and **6b** have the same metal environments, the former shows better activity than the latter.

Recently, Li and co-workers demonstrated that the similar anionic adduct formed under Suzuki reaction conditions is responsible for the high activity of the catalyst.[16b,23] It was observed that the palladium−dialkylhydroxyphosphine com-

(23) (a) Li, G. Y.; Zheng, G.; Noonan, A. F. *J. Org. Chem.* **2001**, *66*, 8677−8681. (b) Li, G. Y. *J. Org. Chem.* **2002**, *67*, 3643−3650.

plexes of the type Pd−PR_2(OH) readily undergo base-promoted deprotonation of the hydroxyl group to give anionic species that are proposed to act as the true catalysts. However, in the present study, the isolated anionic complex (**6a** or **6b**) during catalysis can exchange cation with the base (i.e., K_2CO_3) to form K^+-Pd^-, which is likely to act as the true catalyst. The rate at which these anionic complexes catalyze the Suzuki coupling reaction may be due to the interaction of the metal cation (K^+) with the halide anion ligated to the palladium, affording a more reactive palladium-(0) complex, as proposed by Jutand and co-workers.[24] However, it warrants further investigations to understand the effect of such interactions on active catalyst formation and also on the catalytic performance of such anionic species.

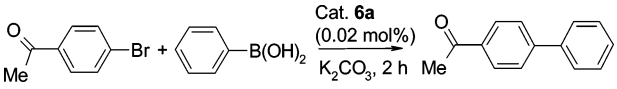
The activity of **5a**,**b** and **6a**,**b** is found to be superior to that of the commonly used catalysts $PdCl_2$(dppf) and Pd_2-$(dba)_3$/(dppf), which catalyzes the reaction between 4-bromoacetophenone and phenylboronic acid in toluene at 70 °C in 94% and 86% yield, respectively.[25] In comparison with other P,S-chelated palladium catalysts, the catalytic activity of **5a**,**b** and **6a**,**b** is similar to that of the analogous Pd^{II} complexes of the 1-phosphabarrelene phosphine sulfide system, whose reactions were carried out in toluene at 110 °C.[5a]

One run was performed on coupling of 4-bromoacetophenone with phenylboronic acid at 60 °C using 0.01 mol % of $Pd(OAc)_2$ (in the absence of ligand), which showed only 31% conversion after 6 h, which could be significantly improved to 96% within 3 h once **2a** was introduced (Table 5, entry 10). The homogeneous nature of the catalysis was checked by the classical mercury test.[26] 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.

To examine the solvent capability, the coupling between 4-bromoacetophenone and phenylboronic acid catalyzed by **6a** (0.02 mol %) was examined in different solvents (Table 6) at 60 °C. Polar solvents such as MeOH and DMF as well as nonpolar solvents like xylene and toluene were found to be most productive. However, solvents like THF and acetonitrile generally resulted in poor yields.

Investigation into the optimal base showed that the common and less expensive inorganic bases such as K_2CO_3, Na_2CO_3, KOH, K_3PO_4, and K^{t}BuO are the reagents of choice (Table 7). The organic base Et_3N is less effective. Surprisingly, Cs_2CO_3 and KF, the most common and effective base for phosphite-based palladacycles[27] and the $Pd_2(dba)_3$/phosphine[28] Suzuki-type catalytic reaction, respectively, proved to be less effective in the present system.

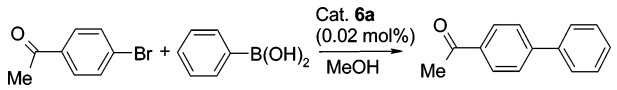
Table 6. Effect of the Solvent on the Coupling Reaction[a]



entry	solvent	conv (%)[b]
1	methanol	100
2	THF	58
3	acetone	63
4	dioxane	63
5	MeCN	52
6	DMF	94
7	xylene	96
8	toluene	98

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.75 mmol of phenylboronic acid, 1 mmol of K_2CO_3, at refluxing temperature of solvent. [b] Conversion to coupled product determined by GC, based on aryl halides (or dodecane); average of two runs.

Table 7. Effect of the Base on the Coupling Reaction[a]



entry	base	conv (%)[b]
1	K_2CO_3	100
2	Na_2CO_3	>99
3	Cs_2CO_3	79
4	Et_3N	85
5	KOH	>99
6	KF	77
7	K_3PO_4	99
8	K^{t}BuO	99

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.75 mmol of phenylboronic acid, 1 mmol of base, 5 mL of MeOH, at 60 °C, 2 h. [b] Conversion to coupled product determined by GC, based on aryl halides (or dodecane); average of two runs.

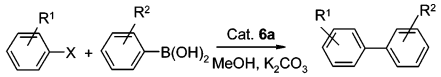
Under the optimized reaction conditions, a wide array of aryl halides can react with arylboronic acid in the presence of **6a** to provide cross-coupling products in good yields (Table 8). For example, in a methanol solution of **6a** (0.02 mol %) and K_2CO_3 (2 equiv), 4-bromoacetophenone couples with phenylboronic acid to give 4-acetylbiphenyl with 100% conversion at 60 °C (entry 1). It is notable that the use of deactivated, electron-rich aryl bromides (e.g., entry 7) as well as activated and electron-poor ones (e.g., entry 1) also resulted in high yields. We have studied the coupling of some substituted boronic acids with aryl bromides, which also resulted in good yields (entries 8, 9). However, the coupling of deactivated 2,4-dimethoxybromobenzene with phenylboronic acid resulted in coupling with poor yield (entry 13).

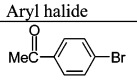
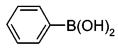
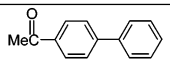
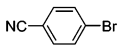
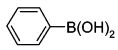
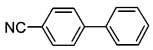
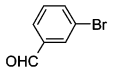
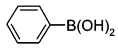
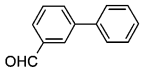
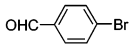
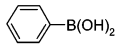
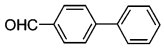
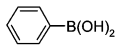
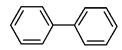
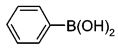
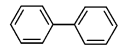
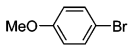
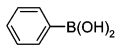
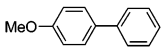
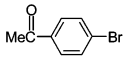
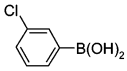
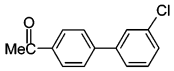
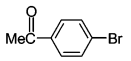
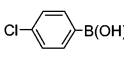
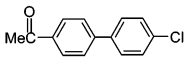
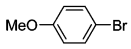
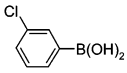
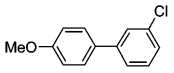
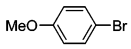
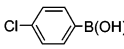
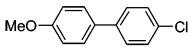
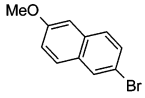
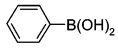
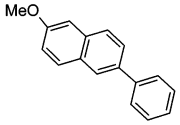
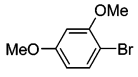
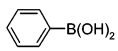
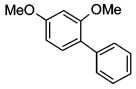
Conclusion

The mesocyclic thioether−aminophosphonites show sulfur → phosphorus coordination due to the flexible nature of the eight-membered ring system; as a consequence, the tricoordinated geometry is displaced toward a TBP. The aminophosphonites **2a** and **2b** containing the hemilabile thioether functionality show versatile coordination properties. By choosing appropriate metal reagents and reaction conditions, we can achieve both mono- and chelating bidentate modes of coordination. These ligands form neutral, cationic, and

(24) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314−321.
(25) Colacot, T. J.; Qian, H.; Cea-Olivares, R.; Hernandez-Ortega, S. *J. Organomet. Chem.* **2001**, *637*−*639*, 691−697.
(26) (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.
(27) Bedford, R. B.; Coles, S. J.; Hursthouse, M. B.; Scordia, V. J. M. *Dalton Trans.* **2005**, 991−995.
(28) (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020−4028. (b) Pramick, M. R.; Rosemeier, S. M.; Beranek, M. T.; Nickse, S. B.; Stone, J. J.; Stockland, R. A.; Baldwin, S. M.; Kastner, M. E. *Organometallics* **2003**, *22*, 523−528.

Table 8. Suzuki Cross-Coupling of Aryl Halides with Arylboronic Acids Catalyzed by **6a**[a]



Entry	Aryl halide	Arylboronic acid	Product	Conv. (%)[b]
1				100
2				99
3				83
4				91
5				99
6				96
7				92
8				98
9				97
10				54
11				37
12				78
13				19

[a] Reaction conditions: ArX (0.5 mmol), $ArB(OH)_2$ (0.75 mmol), K_2CO_3 (1 mmol), catalyst (0.02 mol %), MeOH (5 mL), at 60 °C. Time: 2 h. [b] Conversion to coupled product determined by GC, based on aryl halides (or dodecane); average of two runs.

anionic complexes with palladium(II) derivatives. Catalytically useful anionic complexes **6a** and **6b** are synthesized by oxidizing the phosphorus center with a trace amount of water, establishing a metal−phosphorus σ-bond. These complexes are the first examples of thioether−aminophosphonites forming anionic complexes with palladium metal. The reactions of thioether−aminophosphonites with Pt(COD)Cl_2 gave exclusively phosphorus-coordinated cis-complexes with high σ-donor strength. All the palladium complexes present a promising catalytic activity (TON up to 92 000) toward Suzuki cross-coupling reaction for a series of aryl halides. Further utility of these complexes toward various other organic transformations are under investigation in our laboratory.

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,[29] $(PhCN)_2PdCl_2$,[30] $[(\eta^3\text{-}C_3H_5)PdCl]_2$,[31] and Pt(COD)$Cl_2$ [32] were prepared according to the published procedures. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were obtained on a Varian VXR 300 or VRX 400 spectrometer operating at frequencies of 300 or 400 and 121 or 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 of the cases. Infrared spectra were recorded on a Nicolet Impact 400 Fourier transform (FT) IR instrument as a KBr disk. Microanalyses were carried out on a Carlo Erba model 1106 elemental analyzer. Q-Tof Micromass 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 were uncorrected. Gas chromatography (GC) analyses were performed on a Perkin-Elmer Clarus 500 GC fitted with a flame ionization detector (FID) and a packed column.

Synthesis of Thionaphthalatochlorophosphite {−$OC_{10}H_6$(μ-S)$C_{10}H_6O$−}PCl (1). A solution of PCl_3 (0.65 mL, 7.5 mmol) in 15 mL of THF was added dropwise to a solution of thiobis(2,2′-naphthol) (1.5 g, 4.7 mmol) in THF (40 mL) at −20 °C, followed by the addition of Et_3N (1.96 mL, 14.1 mmol) and a catalytic amount of DMAP in THF (15 mL). The reaction mixture was warmed to room temperature and stirred for 14 h. The solvent was removed under reduced pressure, and the white residue obtained was dissolved in 30 mL of toluene; the resulting mixture was filtered through Celite to remove the $Et_3N{\cdot}HCl$ salt. The filtrate obtained was concentrated under reduced pressure and kept at −25 °C to give a white crystalline product (**1**). It was recrystallized from a mixture of CH_2Cl_2/petroleum ether (bp 60−80 °C) to give colorless crystals of X-ray quality at −25 °C. Yield: 90% (1.62 g). Mp: 138−140 °C. Anal. Calcd for $C_{20}H_{12}ClO_2SP$: C, 62.75; H, 3.16; S, 8.38. Found: C, 62.55; H, 3.08; S, 8.29. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.72 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.75 (t, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.54−7.58 (m, 4H, *Ar*), 7.41 (t, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.25 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 172.3 (s). Electrospray ionization mass spectrometry (ESIMS), *m*/*z*: (M^+−Cl), 347.2.

Synthesis of {−$OC_{10}H_6$(μ-S)$C_{10}H_6O$−}PNC_4H_8O (2a). A solution of the chlorophosphite **1** (2 g, 5.22 mmol) in THF (40 mL) was added dropwise to a solution of morpholine (0.96 mL, 10.97 mmol) in THF (20 mL) at 0 °C. After the completion of addition, the solution was warmed to room temperature and stirred for 12 h. The solvent was removed under reduced pressure, the white residue obtained was dissolved in 40 mL of toluene, and the morpholine hydrochloride salt was removed by filtration. The clear solution was concentrated and cooled to −25 °C to give analytically pure product (**2a**) as colorless crystals. Yield: 95% (2.16 g). Mp: 178−180 °C. Anal. Calcd for $C_{24}H_{20}NO_3PS$: C, 66.50; H, 4.65; N, 3.23; S, 7.39. Found: C, 66.39; H, 4.61; N, 3.19; S, 7.36. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.73 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.72−7.75 (m, 4H, *Ar*), 7.55 (t, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.37 (t, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.20 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 3.79 (t, 4H, CH_2, $^3J_{HH}$ = 4.4 Hz), 3.41 (t, 4H, CH_2, $^3J_{HH}$ = 4.8 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, δ): 134.9 (s).

Synthesis of {−$OC_{10}H_6$(μ-S)$C_{10}H_6O$−}$PNC_4H_8NCH_3$ (2b). This was synthesized by the procedure similar to that for **2a**, using

(29) Mercado, R. M. L.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1999**, *18*, 906−914.
(30) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60−63.
(31) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342−343.
(32) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 48−49.

the chlorophosphite **1** (1.5 g, 3.92 mmol) and *N*-methylpiperazine (0.91 mL, 8.23 mmol). Yield: 93% (1.63 g). Mp: 172−174 °C. Anal. Calcd for $C_{25}H_{23}N_2O_2PS$: C, 67.25; H, 5.19; N, 6.27; S, 7.18. Found: C, 67.19; H, 5.16; N, 6.23; S, 7.14. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.73 (d, 2H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.73 (t, 2H, *Ar*, $^3J_{HH}$ = 6.8 Hz), 7.53−7.57 (m, 4H, *Ar*), 7.37 (t, 2H, *Ar*, $^3J_{HH}$ = 6.8 Hz), 7.19 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 3.46 (br s, 4H, CH_2), 2.55 (br s, 4H, CH_2), 2.39 (s, 3H, CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): 135.1 (s).

Synthesis of {(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)PNC$_4$H$_8$O-κ*P*}$_2$PdCl$_2$ (3a). A solution of $(PhCN)_2PdCl_2$ (0.03 g, 0.078 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a solution of **2a** (0.069 g, 0.16 mmol) in 8 mL of dichloromethane at room temperature. The resulting yellowish-green solution was stirred for 3 h. The solution was then concentrated to 3 mL and layered with petroleum ether, which on cooling to −25 °C gave a yellow crystalline product (**3a**). Yield: 94% (0.076 g). Mp: 198 °C (dec). Anal. Calcd for $C_{48}H_{40}Cl_2N_2O_6P_2S_2Pd$: C, 55.21; H, 3.86; N, 2.68; S, 6.14. Found: C, 55.09; H, 3.82; N, 2.65; S, 6.09. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.83 (d, 4H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.15−8.04 (m, 20H, *Ar*), 3.96 (t, 8H, CH_2, $^3J_{HH}$ = 4.4 Hz), 3.49 (t, 8H, CH_2, $^3J_{HH}$ = 4.4 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): 93.9 (s).

Synthesis of {(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)PNC$_4$H$_8$NCH$_3$-κ*P*}$_2$PdCl$_2$ (3b). This was synthesized by the procedure similar to that for **3a**, using $(PhCN)_2PdCl_2$ (0.03 g, 0.078 mmol) and **2b** (0.072 g, 0.16 mmol). Yield: 90% (0.075 g). Mp: 186 °C (dec). Anal. Calcd for $C_{50}H_{46}Cl_2N_4O_4P_2S_2Pd$: C, 56.11; H, 4.33; N, 5.23; S, 5.99. Found: C, 56.09; H, 4.29; N, 5.16; S, 5.89. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.72 (d, 4H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.11−8.61 (m, 20H, *Ar*), 3.73 (br s, 8H, CH_2), 2.61 (br s, 8H, CH_2), 2.43 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): 94.1 (s).

Synthesis of {(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)PNC$_4$H$_8$O-κ*P*}$_2$PtCl$_2$ (4a). A solution of **2a** (0.071 g, 0.164 mmol) in CH_2Cl_2 (10 mL) was added dropwise to 6 mL of dichloromethane solution of Pt(COD)Cl_2 (0.03 g, 0.08 mmol) at room temperature. After stirring for 1 h, the clear solution was concentrated to 3 mL and layered with petroleum ether (1 mL), which on slow evaporation gave the product **4a** as colorless crystals. Yield: 87% (0.079 g). Mp: 187 °C (dec). Anal. Calcd for $C_{48}H_{40}Cl_2N_2O_6P_2S_2Pt$: C, 50.88; H, 3.56; N, 2.47; S, 5.66. Found: C, 50.68; H, 3.52; N, 2.42; S, 5.59. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.94 (d, 4H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.66−8.42 (m, 20H, *Ar*), 3.81 (t, 8H, CH_2, $^3J_{HH}$ = 4.4 Hz), 3.41 (t, 8H, CH_2, $^3J_{HH}$ = 4.8 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, DMSO-d_6, δ): 69.4 (s, $^1J_{PtP}$ = 5835 Hz).

Synthesis of {(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)PNC$_4$H$_8$NCH$_3$-κ*P*}$_2$PtCl$_2$ (4b). This was synthesized by the procedure similar to that for **4a**, using **2b** (0.073 g, 0.164 mmol) and Pt(COD)Cl_2 (0.03 g, 0.08 mmol). Yield: 90% (0.084 g). Mp: 218 °C (dec). Anal. Calcd for $C_{50}H_{46}Cl_2N_4O_4P_2S_2Pt$: C, 51.82; H, 4.00; N, 4.83; S, 5.53. Found: C, 51.68; H, 3.92; N, 4.72; S, 5.51. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.95 (d, 4H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.63−8.44 (m, 20H, *Ar*), 3.48 (br s, 8H, CH_2), 2.58 (br s, 8H, CH_2), 2.40 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, DMSO-d_6, δ): 69.9 (s, $^1J_{PtP}$ = 5842 Hz).

Synthesis of [{(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)PNC$_4$H$_8$O-κ*P*,κ*S*}Pd(η^3-C$_3$H$_5$)](CF$_3$SO$_3$) (5a). A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.025 g, 0.068 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a dichloromethane (8 mL) solution of **2a** (0.061 g, 0.14 mmol) at room temperature. After 2 h, AgOTf (0.035 g, 0.014 mmol) was added, and the resulting mixture was stirred for an additional 1 h. The suspension obtained was filtered through Celite to remove AgCl salt. The clear solution was concentrated, and petroleum ether (5 mL) was added to precipitate the product, which was then filtered off and dried. Yield: 94% (0.094 g). Mp: 118 °C (dec). Anal. Calcd for $C_{28}H_{25}F_3NO_6PS_2Pd$: C, 46.07; H, 3.45; N, 1.92; S, 8.78. Found: C, 45.97; H, 3.34; N, 1.89; S, 8.66. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.86 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 7.36−7.95 (m, 10H, *Ar*), 5.75−5.79 (m, 1H, *allyl*), 4.88 (br s, 2H, *allyl*), 4.28 (br s, 2H, *allyl*), 3.95 (t, 4H, CH_2, $^3J_{HH}$ = 4.4 Hz), 3.73 (t, 4H, CH_2, $^3J_{HH}$ = 4.6 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): 123.8 (s). ESIMS, *m*/*z*: ($M^+ - CF_3SO_3$), 580.1.

Synthesis of [{(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)PNC$_4$H$_8$NCH$_3$-κ*P*,κ*S*}Pd(η^3-C$_3$H$_5$)](CF$_3$SO$_3$) (5b). To a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.025 g, 0.068 mmol) in acetone (5 mL) was added AgOTf (0.035 g, 0.014 mmol), and the reaction mixture was stirred for 15 min. The AgCl salt was separated from the light yellow mother liquor using a cannula. To the above resulting yellowish solution was added slowly at room temperature a solution of the ligand **2b** (0.063 g, 0.14 mmol) in dichloromethane (8 mL), and this mixture was stirred for 2 h. The orange solution obtained was concentrated to 2 mL, and diethyl ether (5 mL) was added to give **5b** as an orange microcrystalline residue. Yield: 88% (0.089 g). Mp: 148 °C (dec). Anal. Calcd for $C_{29}H_{28}F_3N_2O_5PS_2Pd$: C, 46.87; H, 3.79; N, 3.77; S, 8.63. Found: C, 46.76; H, 3.69; N, 3.72; S, 8.42. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.85 (d, 2H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.29−7.89 (m, 10H, *Ar*), 5.81−5.85 (m, 1H, *allyl*), 4.84 (br s, 2H, *allyl*), 4.04 (br s, 2H, *allyl*), 3.48 (br s, 4H, CH_2), 2.75 (br s, 4H, CH_2), 2.36 (s 3H, CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, δ): 125.1 (s).

Synthesis of [{(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)P(O)-κ*P*,κ*S*}PdCl$_2$](H$_2$NC$_4$H$_8$O) (6a). A mixture of $(PhCN)_2PdCl_2$ (0.04 g, 0.104 mmol), the ligand **2a** (0.047 g, 0.109 mmol), and H_2O (2 μL, 0.11 mmol) in 10 mL of toluene was heated at 90 °C for 3 h. The yellowish-green precipitate formed was filtered off and dried. It was recrystallized from the CH_2Cl_2/petroleum ether mixture to give the product (**6a**) as yellowish crystals at room temperature. Yield: 90% (0.059 g). Mp: 232 °C (dec). Anal. Calcd for $C_{24}H_{22}Cl_2NO_4PPdS$: C, 45.84; H, 3.53; N, 2.23; S, 5.09. Found: C, 45.79; H, 3.49; N, 2.21; S, 4.98. IR (KBr disc, cm^{-1}): ν_{N-H}, 3302 s; ν_{C-H}, 3055 s, 2963, 2920, and 2852 s; ν_{P-O}, 1112 s. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.76 (d, 2H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 8.18 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 8.01 (d, 2H, *Ar*, $^3J_{HH}$ = 7.6 Hz), 7.82 (t, 2H, *Ar*, $^3J_{HH}$ = 7.2 Hz), 7.57 (t, 2H, *Ar*, $^3J_{HH}$ = 6.8 Hz), 7.45 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 3.76 (t, 4H, CH_2, $^3J_{HH}$ = 4.8 Hz), 3.11 (t, 4H, CH_2, $^3J_{HH}$ = 4.4 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, DMSO-d_6, δ): 44.5 (s).

Synthesis of [(−OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O−)P(O)-κ*P*,κ*S*}PdCl$_2$](H$_2$NC$_4$H$_8$NCH$_3$) (6b). This was synthesized by the procedure similar to that for **6a**, using $(PhCN)_2PdCl_2$ (0.04 g, 0.104 mmol), **2b** (0.049 g, 0.109 mmol), and H_2O (2 μL, 0.11 mmol). Yield: 82% (0.055 g). Mp: 156 °C (dec). Anal. Calcd for $C_{25}H_{25}Cl_2N_2O_3PPdS$: C, 46.78; H, 3.93; N, 4.36; S, 4.99. Found: C, 46.69; H, 3.88; N, 4.31; S, 4.89. IR (KBr disc, cm^{-1}): ν_{N-H}, 3309 s; ν_{C-H}, 3054 s, 2970, 2928, and 2720 s; ν_{P-O}, 1112 s. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.81 (d, 2H, *Ar*, $^3J_{HH}$ = 8.8 Hz), 8.45 (d, 2H, *Ar*, $^3J_{HH}$ = 8.4 Hz), 7.18−7.98 (m, 8H, *Ar*), 3.49 (br s, 4H, CH_2), 2.58 (br s, 4H, CH_2), 2.33 (br s, 3H, CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, DMSO-d_6, δ): 44.7 (s).

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 methanol. The correct amount of catalyst was added as a methanol solution made up of multiple volumetric dilutions of stock solutions. After stirring for 5 min, aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), and K_2CO_3 (0.138 g, 1 mmol) were introduced into the reaction flask. The mixture was heated at 60 °C for the required time under an atmosphere of nitrogen (the course of reaction was monitored by GC analysis). Then, the solvent was removed under reduced pressure. The

resulting residual mixture was diluted with H_2O (8 mL) and Et_2O (8 mL), followed by extraction twice (2 × 6 mL) with Et_2O. The combined organic fraction was dried ($MgSO_4$) and stripped of the solvent under vacuum, and the residue was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated versus aryl halides or dodecane as an internal standard.

X-ray Crystallography. Crystals of **1**, **2a**, **2b**, **4a**, and **6a** 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 APEX charge-coupled device (CCD) diffractometer. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at ϕ = 0, 120, and 240° using the SMART software package.[33] The raw data were reduced to F^2 values using the SAINT+ software,[34] and a global refinement of unit cell parameters using 3890−9590 reflections chosen from the full data set 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 the data collection (SADABS[35]). The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.[36] 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.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**, **2a**, **2b**, **4a**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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