

Palladium(II) Complexes of 2-Dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl (MAP) with Unique P,C_σ-Coordination and Their Catalytic Activity in Allylic Substitution, Hartwig–Buchwald Amination, and Suzuki Coupling

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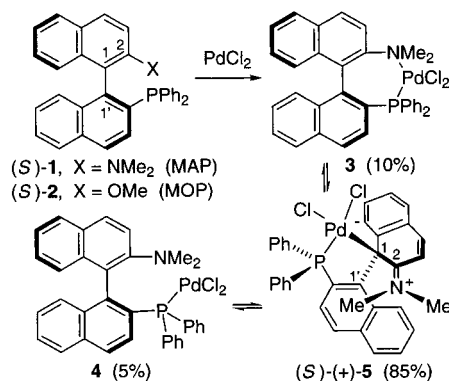
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In addition to C₂-symmetrical ligands¹ and their nonsymmetrical congeners,^{2–4} we have recently introduced a new class of aminophosphines, e.g., the title compound **1** (MAP),⁵ which can be regarded as a nitrogen analogue of Hayashi's² MOP (**2**). The MAP ligands exhibited asymmetric induction in Pd(0)-catalyzed allylic substitution⁵ and a dramatic acceleration of the Hartwig–Buchwald⁶ amination of aryl halides.^{3d,7} The latter effect was simultaneously reported by Buchwald for the (*t*-Bu)₂P counterpart of **1** and its biphenyl analogues.⁸ These ligands were assumed to coordinate Pd via P,N-chelation (**3**).^{5,8} Herein, we present evidence that **1** actually acts as a P,C_σ-ligand with an unusual C_σ–Pd bonding mode **5** (Scheme 1) and demonstrate a substantial acceleration of Suzuki coupling in its presence.

Scheme 1



Single-crystal X-ray crystallography of the Pd/**1** complex, prepared from (PhCN)₂PdCl₂ and (*S*)-(+)-**1**, excluded the P,N-chelate **3** structure and revealed its P,C_σ-ligating alternative (*S*)-(+)-**5** (Figure 1),⁹ whose formation apparently reflects the ligand's enamine-like character^{10–13} combined with the known tendency of Pd to form five-membered palladacycles in preference to other ring-sizes.¹⁴ In solution, an 85:10:5 mixture of three species has been detected by ¹H NMR spectroscopy. In the most abundant complex, the singlet of Me₂N was shifted to 3.11 ppm (from 2.23 ppm in **1**). The signal of C(1) in the ¹³C NMR spectrum appeared at 72.64 ppm, whereas C(2) was shifted to 173.35 ppm, which is compatible with the P,C_σ-chelated structure **5**.¹⁵ The less abundant complex exhibited two doublets for the Me₂N at 2.56 and 4.06 ppm (⁴J_{H,P} = 5.0 and 4.9 Hz, respectively), which is indicative of P,N-chelation **3**. The least populated species was characterized only by ³¹P NMR spectroscopy, which demonstrated a P–Pd coordination, suggesting the P-monocoordinated complex **4**. Exchange cross-peaks, observed in the NOESY spectrum between the signals of **5** and **3**, indicate a dynamic equilibration.

(9) Crystal data for (*S*)-(+)-**5**: orthorhombic, red crystals, space group P2₁2₁2₁, *a* = 10.163(2) Å, *b* = 14.443(3) Å, *c* = 19.680(3) Å, *V* = 2888.7(9) Å³, *Z* = 4, *d*_{calc} = 1.515 g cm⁻³, *μ* = 0.908 mm⁻¹, *R*_F = 0.0314. The valence angle Pd–C(1)–C(1') 112.46° and the distances C(1)–C(2) and C(1)–C(9) 1.475 and 1.502 Å, respectively, are close to sp³ geometry at C(1). Other parameters: P–Pd–C(1) = 85.02°, Pd–C(1)–C(2) = 103.63°, Pd–P = 2.195 Å, Pd–C(1) = 2.187 Å, C(2)–N = 1.319 Å. The estimated error in C–C bond lengths is 0.008 Å.

(10) Similar C_σ-bonding of Pd(II) has been observed for (biphen)Pd-(MeCN)₂, prepared from (MeCN)₂Pd(NO₃)₂ and a dianion of biphenanthrol; here, the product arose by replacement of 2 × NO₃⁻ with the biphenanthrolate oxygens,^{11a} in contrast to our exchange of neutral ligands. A related example has been reported for Me₂BINOL and Pt(II).^{11b} The enolate character of binaphtholate-type nucleophiles is further manifested by *ipso*-alkylation of BINOL dianion with ethylene glycol ditosylate.^{11c,d}

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(12) Based on the upfield ¹H NMR shifts of protons at C(7) and C(8), η²-coordination of Pd to the C(7)=C(8) bond has been proposed for the Pd-(0) complex obtained on reaction of (η³-cyclohexenyl)Pd(MOP) with NaCH-(CO₂Me)₂.^{13a} However, similar upfield shifts are also observed for 7-H, 8-H, and 8'-H in the ¹H NMR spectra of **5** and **6**, suggesting that Pd(0) may, instead, be coordinated to C(1)=C(2) of MOP. Recently, η²-bonding to the aryl unit has also been identified for [(MeO–Biphen)Ru(η⁵-C₅H₅)]⁺ and [(BINAP)RuCp]⁺.^{13b–e}

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(15) In the ¹³C NMR spectrum of **5**, the Me₂N signal was observed at 47.03 ppm (at 43.40 for free **1**); all ¹³C and most of the ¹H signals were assigned using 2D techniques. The other two complexes could not be fully characterized owing to their minute quantities and signal overlap.

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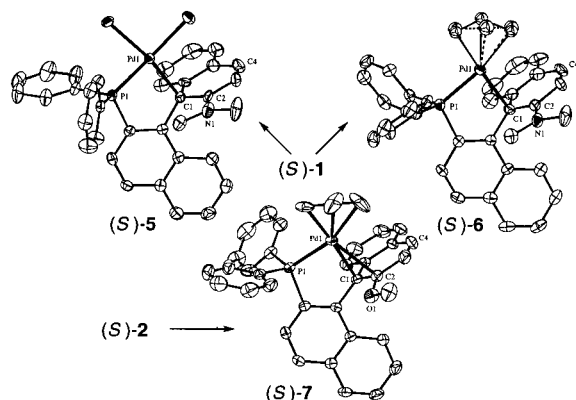


Figure 1. ORTEP diagrams for **5–7**; H and TfO⁻ are omitted.

Crystallographic analysis of the η^3 -allyl complex, prepared from (S)-(+)-**1** and [(MeCN)₂Pd(η^3 -C₃H₅)]⁺ TfO⁻ (Figure 1), again revealed the unusual P,C_o-chelated structure (+)-**6**¹⁶ that exists as a ~3:2 mixture of two diastereoisomers resulting from the positioning of the allyl unit. NMR spectroscopy confirmed the presence of the two latter species in solution in a ~1.1:1 ratio, whose interconversion is slower than the NMR time scale at ambient temperature; C(1) is characterized by signals at 92.9 and 94.3 ppm in the ¹³C NMR spectrum of the mixture, whereas C(2) appears at 155.4 ppm.^{17,18}

These results seem to be in sharp contrast to Hayashi's X-ray structure of (MOP)Pd(prenyl)Cl, where MOP is monocoordinated to Pd by P.¹⁹ However, inspection of this structure revealed that Pd is, in fact, positioned right above the C(1)–C(2) bond with Pd–C(1) and Pd–C(2) distances being 3.38 and 3.50 Å, respectively. Hence, on creation of a vacant coordination site (e.g., by loss of Cl⁻), minimal distortion would permit bonding in a manner analogous to **6**. Indeed, we have now found this to be the case for [(MOP)Pd(η^3 -C₃H₅)]⁺ TfO⁻ (**7**), in which Pd–C(1) and Pd–C(2) distances of 2.34 and 2.47 Å were observed by single crystal X-ray analysis, clearly demonstrating η^2 -coordination.²⁰

While **2** proved to have relatively weak effect on the Hartwig–Buchwald amination,^{7,21} we have observed a substantial acceleration, e.g., for the reaction of 4-(*t*-Bu)C₆H₄Br with *n*-Bu₂NH in the presence of Pd/**1** (3 mol %, 50 °C, 12 h)^{7,22} to produce 4-(*t*-Bu)C₆H₄N(*n*-Bu)₂. Even more dramatic acceleration was attained for Suzuki coupling:^{23,24} thus, phenylation of 4-Cl-C₆H₄CHO with

(16) Crystal data for (S)-(+)-**6**: monoclinic, dark-yellow crystals, space group P2₁, *a* = 8.7103(9) Å, *b* = 16.688(2) Å, *c* = 11.829(2) Å, β = 100.198(10)°, *V* = 1692.2(4) Å³, *Z* = 2, *d*_{calc} = 1.527 g cm⁻³, μ = 0.713 mm⁻¹, *R*_F = 0.0282. Characteristic parameters: P–Pd = 2.268 Å, Pd–C(1) = 2.265 Å, C(1)–C(2) = 1.437 Å, C(1)–C(9) = 1.480 Å, C(2)–N = 1.345 Å; Pd–C(1)–C(1') = 110.49°, Pd–C(1)–C(2) = 93.46°, P–Pd–C(1) = 84.21°. The estimated error in C–C bond lengths is 0.006 Å.

(17) The C(1) signals were broadened; the assignment was confirmed by long-range CH correlation with 3-H and 8-H.

(18) (a) When applied to the reaction of PhCH=CHCH(OAc)Ph,⁵ one of the rotamers of the P,C-model predicts the same sense of asymmetric induction as the P,N-chelate. (b) In the ¹³C NMR spectrum of **6**, the allylic carbons *trans*-disposed to C(1) appear at 59.3 and 56.4 ppm, whereas those *trans*-disposed to P are located at 89.9 and 93.6 ppm. Furthermore, in the solid-state structure of **6**, the C–Pd bond length at the allylic terminus *trans*-related to P is longer than that *trans*-related to C (by ~0.15 Å and 0.16 Å, respectively). Thus, both the NMR and X-ray data demonstrate substantial difference in double bond character and electrophilicity between the two allylic termini. (c) These findings are consistent with a powerful memory effect (vide infra) involving ionization and nucleophilic attack *trans* to P.

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PhB(OH)₂ occurred in <20 h at room temperature²⁶ in the presence of (AcO)₂Pd (3 mol %), **1** (4.5 mol %), and either CsF⁸ or Cs₂CO₃²⁴ (3 equiv).

The enhanced reactivity of the Pd/MAP complexes may originate from the presence of the low-abundant P-monocoordinated species (analogous to **4**), in line with Buchwald's suggestion (made without spectroscopic evidence),⁸ while the P,C-complex would serve as an inactive depot. On the other hand, the P,C-chelate (analogous to **5**) can also be conjectured to play a role, and the reactivity of Pd/**1** could be understood in terms of accelerated oxidative addition (the rate-limiting step^{6e}) owing to the electron richness of the "palladate" species. The lack of accelerating effect of **2**^{7,21} (which tends to avoid bidentate coordination in the presence of Cl ligand¹⁹) seems to further support the importance of P,C-coordination of **1**, at least in some parts of the catalytic cycle.²⁶ Furthermore, the reaction of (±)-[1-²H]-cyclopent-2-enyl pivalate with NaCH(CO₂Me)₂ and (S)-(+)-**6** (5 mol %) was found to proceed with 88% regiochemical retention and nearly identical results were observed with **2**.²⁷ This powerful memory effect proved to be attenuated by Cl⁻ (5 mol %), which can be understood in terms of accelerated collapse of an ion-paired²⁸ intermediate [η^3 -(*c*-C₅H₇)-PdL]⁺ [O₂C-*t*Bu]⁻ (L = **1** or **2** in P,C-mode) and chloride-catalyzed diastereoisomer equilibration.^{29,30} Kinetic resolution (*k*_R/*k*_S ≈ 4–7)³⁰ and high catalyst stability²⁹ further support bidentate coordination of MAP and MOP, since monodentate ligation would be expected to be less rigid and unlikely to effectively discriminate enantiomers.

In conclusion, we have structurally characterized the unusual Pd(II) complexes **5–7**, which proved to be P,C-chelates (both in the solid state and in solution). Our experiments have demonstrated that the P,C-ligation must be considered as a potential binding mode in reactions involving MAP and MOP, even though some parts of the active cycle may involve other modes of ligation. Pd/**1** complexes can be viewed as the first examples of chiral analogues of the recently reported P,C_o-chelates.²⁶

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Supporting Information Available: Experimental procedures and ¹H, ¹³C, and ³¹P NMR spectral data for the complexes, their MS spectral data, and crystallographic characterization with fully labeled ORTEP diagrams and atomic coordinates, and ¹H NMR spectra of the new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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