# Palladium(II) complexes of bis(phosphine)monooxide and bis(phosphine)monosulphide ligands bearing *o*-*N*,*N*-dimethylanilinyl substituents[1]

**Nathan D. Jones and Brian R. James**

**Abstract:** Palladium(II) complexes of bis(phosphine)monooxide and bis(phosphine)monosulphide ligands with the general formula $Ar_2P(CH_2)_nP(E)Ar_2$ are described ($n$ = 1 (dmapmE), E = O, S; $n$ = 2 (dmapeE), E = O; Ar = *o*-*N*,*N*-dimethylanilinyl). The precursor, $PdCl_2$(dmapm), which exists in solution as an equilibrium mixture of the *P*,*P*- and *P*,*N*-ligated isomers, reacts with peroxides to form $PdCl_2$(*P*,*N*-dmapmO) and with sulphur to give [PdCl(*P*,*N*,*S*-dmapmS)]Cl, probably by direct oxidation of the "dangling" P atom of the *P*,*N*-isomer. $PdCl_2$(dmape), which exists in solution as a mixture of $PdCl_2$(*P*,*P*-dmape) and [PdCl(*P*,*P*,*N*-dmape)]Cl, reacts with hydroxide in $H_2O$–$CH_2Cl_2$ under argon to give the face-to-face $Pd(II)_2$ complex containing the cation $[Pd_2Cl_2(\mu\text{-}P,N:O\text{-dmapeO})_2]^{2+}$, which was isolated and crystallographically characterized as the $PF_6$ salt. The remarkable structure, consisting of two face-to-face Pd(II) square planes in a head-to-tail orientation, reveals a 12-membered ring containing the two non-bonded metal centres (Pd—Pd = 4.873(2) Å). The dmapmS complex shows marginal activity as a catalyst for the hydration of maleic to malic acid.

*Key words:* phosphine, phosphine oxide, phosphine sulphide, palladium.

**Résumé :** On décrit les complexes du palladium(II) de ligands bis(phosphine)monooxyde et bis(phosphine)monosulfure avec des composés de formule générale $Ar_2P(CH_2)_nP(E)Ar_2$ dans lesquels $n$ = 1 (dmapmE), E = O, S; $n$ = 2 (dmapeE), E = O; Ar = *o*-*N*,*N*-diméthylanilinyle. Le précurseur $PdCl_2$(dmapm), qui existe en solution sous la forme d'un mélange à l'équilibre des ligands isomères *P*,*P* et *P*,*N*, réagit avec les peroxydes pour former le $PdCl_2$(*P*,*N*-dmapmO) et avec le soufre pour donner le [PdCl(*P*,*N*,*S*-dmapmS)]Cl, probablement par une oxydation directe de l'atome de P qui se « balance » dans l'isomère *P*,*N*. Le $PdCl_2$(dmape), qui existe en solution sous la forme d'un mélange de $PdCl_2$(*P*,*P*-dmape) et de [PdCl(*P*,*P*,*N*-dmape)]Cl, réagit avec l'ion hydroxyde dans un mélange $H_2O$–$CH_2Cl_2$, sous argon, pour conduire à la formation du complexe face à face $Pd(II)_2$ contenant le cation $[Pd_2Cl_2(\mu\text{-}P,N:O\text{-dmapeO})_2]^{2+}$ qui a été isolé et caractérisé cristallographiquement sous la forme de sel de $PF_6$. La structure remarquable, formée de deux Pd(II) plans carrés, face à face et en position tête à queue, comporte un cycle à douze chaînons avec deux centres métalliques non liés (Pd—Pd = 4,873(2) Å). Le complexe dmapmS présente une activité marginale comme catalyseur pour l'hydratation de l'acide maléique en acide malique.

*Mots clés :* phosphine, oxyde de phosphine, sulfure de phosphine, palladium.

[Traduit par la Rédaction]

## Introduction

Our group recently reported (1–4) on platinum(II) and palladium(II) complexes containing bis(phosphine) ligands bearing two *o*-*N*,*N*-dimethylanilinyl substituents at each P atom, including 1,1-bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)-methane (dmapm) and 1,2-bis(di(*o*-*N*,*N*-dimethylanilinyl)-phosphino)ethane (dmape). The ligand structures, for example, are represented within complexes of formula $PdCl_2$(dmapm) and $PdCl_2$(dmape) in Schemes 1 and 2, respectively. We had designed such ligands primarily for the synthesis of water-soluble metal complexes, with one aim being to develop transition metal catalysts for olefin hydration, and indeed marginal activity for hydration of maleic to malic acid was noted for several of the complexes (4). The activity was better, for example, than that of the bridged-hydroxo complexes of the type $[(dppe)Pd(\mu\text{-}OH)]_2^{2+}$ (dppe = $Ph_2P(CH_2)_2PPh_2$) reported by Ganguly and Roundhill (5). This led us to attempts to synthesize bridged-hydroxo complexes of this type but using dmape as the bisphosphine. We thus reacted $PdCl_2$(dmape) with KOH in aqueous–$CH_2Cl_2$, but (to our surprise) a complex containing the bisphosphine

Received 30 November 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 2 June 2005.

*This paper is dedicated to Howard Alper, close friend and research collaborator with one of us (BRJ) and distinguished scholar.*

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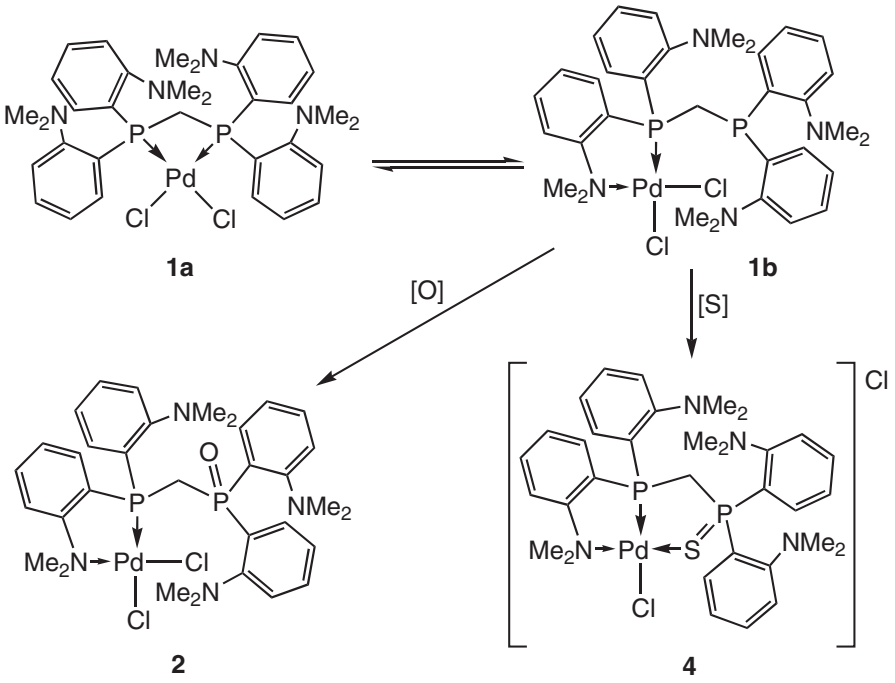
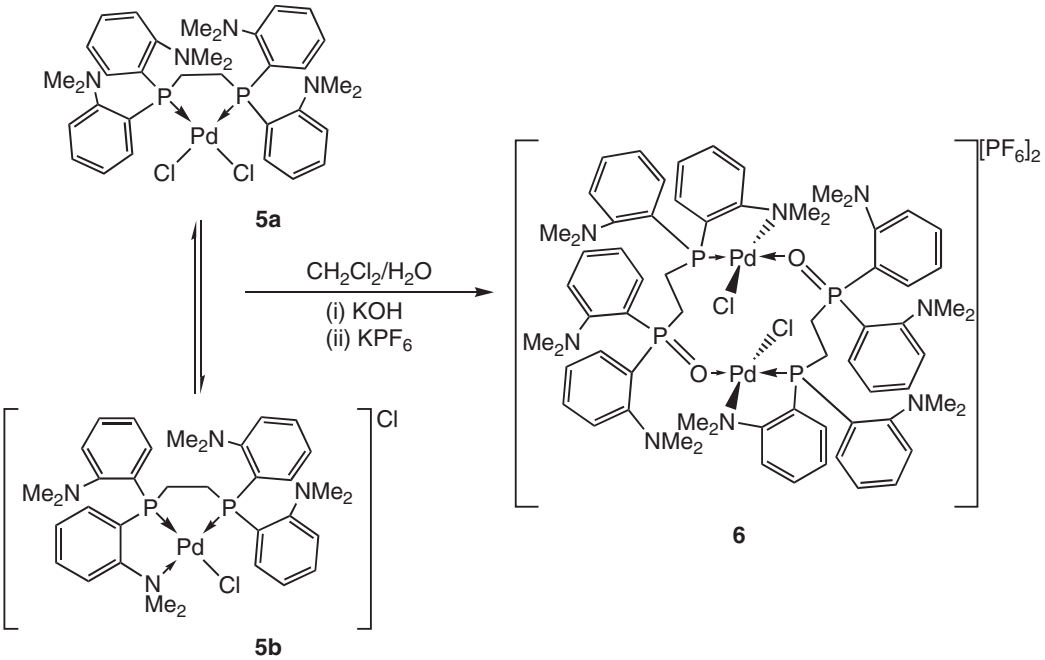
 doi: 10.1139/V05-067 

**Scheme 1.** Direct oxidation of one P atom of **1b** with peroxide and sulphur.




**Scheme 2.** Reaction of **5** with KOH in $CH_2Cl_2$–$H_2O$.




monoxide, dmapeO, was isolated, and because of the current interest in such ligands, we pursued this line of research, and the findings are reported here.

Bisphosphine monooxides (BPMOs) with the mixed P atom and O atom donors are within a class of chelating agents that, because of their potential for hemilabile coordination (6), have garnered attention in homogeneous catalysis. Transition metal complexes of such ligands have been used in a variety of catalyzed organic transformations such as hydroformylation and other carbonylation processes (7, 8), hydrosilylation (9), hydrovinylation (10), polymerization (11), and allylic alkylation (12), including asymmetric processes (9, 10, 12) Bis(phosphine)monosulphide (BPMS) complexes have also begun to attract interest and have found application in asymmetric allylic alkylation (13).

More generally, BPMO ligands can be made via metal-free organic synthesis (for example, by benzylation of a bis(tertiary phosphine) followed by basic hydrolysis of the resulting phosphonium salt) (14) or by a Pd-catalyzed process involving reaction of 1,2-bromoethane and hydroxide in a two-phase aqueous system (8). Metal-bound BPMOs may be synthesized via oxidation of a "dangling" (i.e., nonbonded)

P atom in complexes bearing polydentate ligands, exemplified in Co (15, 16), Mo (17), Rh (18), and Pd (9, 19) systems, but only in a few cases does this result in coordination of the phosphine oxide (16, 17). Less common is oxidation of a coordinated bis(phosphine) to give a BPMO in which both the P(III) atom and the O atom are bound. Examples that typically involve aerobic oxidation are those of RhCl(CO)(*P*,*P*-BINAP), which generates RhCl(CO)(*P*,*O*-BINAPO) (20), a Pd(II)-dppm species (dppm = $Ph_2PCH_2PPh_2$) that forms a Pd(II)-*P*,*O*-dppmO complex (21), and $RuCl_2$(BINAP)(N–N) complexes that give [RuCl($\eta^4$-BINAPO)(N–N)]Cl (N–N = bipy, phen), where the BINAPO ligand is coordinated via the P(III) atom, the O atom, and two C atoms of the naphthyl ring proximate to the P(V) atom (22). An excellent introduction to the syntheses and uses of BPMOs can be found in Cyr's Ph.D. thesis (23).

This paper describes the oxidation of one P atom of $PdCl_2$(dmapm) (**1**) (3) to give $PdCl_2$(*P*,*N*-dmapmO) (**2**) and the salts [PdCl(*P*,*N*,*S*-dmapmS)]X (X = $PF_6$, **3**; Cl, **4**) and the similar oxidation of $PdCl_2$(dmape) (**5**) (4) to give, after anion exchange, the dipalladium complex [PdCl(μ-*P*,*N*:*O*-dmapeO)]$_2$[$PF_6$]$_2$ (**6**). This last reaction constitutes another example of the oxidation of a coordinated bis(phosphine) to give a complex in which both the P(III) and O atoms of the BPMO are coordinated, but it is unique in that the BPMO serves as a bridging ligand. The topic is particularly appropriate for a paper dedicated to Howard Alper because he must have experienced many times phosphine oxidation concomitant with reduction of Pd(II) to Pd(0) species, including the unwanted metal!

## Experimental

Unless otherwise noted, synthetic procedures were performed using standard Schlenk techniques under an atmosphere of dry Ar or $N_2$. The precursors, *trans*-$PdCl_2$(PhCN)$_2$ (24), $PdCl_2$(dmapm) (**1**) (3), and $PdCl_2$(dmape) (**5**) (4), and the dmapm and dmape ligands (25) were made according to literature procedures. All other reagents were purchased from commercial sources and used as supplied. Solvents were dried over the appropriate agents and distilled under $N_2$ prior to use. NMR spectra were recorded in $CDCl_3$ solution on a Varian AV300 (121 MHz for $^{31}$P) or AV400 (162 MHz for $^{31}$P) spectrometer at 300 K. Residual solvent proton ($^1$H, relative to external $SiMe_4$ δ 0.00) and external $P(OMe)_3$ ($^{31}$P{$^1$H}, δ 141.00 vs. external 85% aq. $H_3PO_4$) were used as references. Downfield shifts were taken as positive; s = singlet, d = doublet, m = multiplet, br = broad, spt = septet, and all *J*-values are given in Hz. Conductivity measurements were obtained using a Thomas Serfass conductance bridge model RCM151B1 (Arthur H. Thomas Co. Ltd.) connected to a 3404 cell (Yellow Springs Instrument Co.); measurements were made at 25 °C using ~$10^{-3}$ mol $L^{-1}$ solutions of the complexes and are reported as $\Lambda_M$ in $\Omega^{-1}$ $mol^{-1}$ $cm^2$. Elemental analyses were conducted in the UBC Chemistry Department by Mr. Peter Borda using a Carlo Erba 1108 analyzer.

### $PdCl_2$(*P*,*N*-dmapmO) (2)

This complex was prepared at room temperature either in a single phase using cumene hydroperoxide as oxidant or in a two-phase mixture using aqueous $H_2O_2$.

#### *Cumene hydroperoxide*

Precursor **1** was prepared in situ by the reaction of dmapm (140 mg, 0.25 mmol) and *trans*-$PdCl_2$(PhCN)$_2$ (94 mg, 0.25 mmol) in $CH_2Cl_2$ (10 mL), and to the yellow solution was added cumene hydroperoxide (75 μL, 0.41 mmol). The solution was stirred overnight and then reduced in vacuo to ~2 mL, when $Et_2O$ (20 mL) was added to precipitate the yellow product, which was isolated by filtration, washed with $Et_2O$ (3 × 3 mL), and dried under vacuum. Yield: 155 mg (84%).

#### *$H_2O_2$*

To a $CH_2Cl_2$ solution (5 mL) containing **1** (28 mg, 0.038 mmol) was added a 3% $H_2O_2$ (2 mL) solution. The two-phase mixture was stirred for 1 h, and the aqueous phase was removed. The volume of $CH_2Cl_2$ was reduced in vacuo to ~1 mL, and $Et_2O$ (10 mL) was added to precipitate the product. Yield: 25 mg (88%). $^1$H NMR δ: 1.7–3.3 (br, 12H, NC$H_3$), 2.35 (s, 3H, NC$H_3$), 2.51 (s, 3H, NC$H_3$), 3.47 (s, 3H, NC$H_3$), 3.70 (s, 3H, NC$H_3$), 4.27 (m, 1H, C$H_2$), 4.81 (m, 1H, C$H_2$), 6.8–7.9 (br m, 16H, Ar). $^{31}$P{$^1$H} NMR δ: 26.2 (d, $^2J_{PP}$ = 7.0), 26.5 (d, $^2J_{PP}$ = 7.0). $\Lambda_M$ ($CH_2Cl_2$): <1. Anal. calcd. for $C_{33}H_{42}ON_4Cl_2P_2Pd$: C 52.9, H 5.6, N 7.5; found: C 53.0, H 6.0, N 7.0.

### [PdCl(*P*,*N*,*S*-dmapmS)]$PF_6$ (3)

To a mixture of **1** (44 mg, 0.060 mmol) and $S_8$ (13 mg, 0.42 mmol of S) was added 1,2-dichloroethane (5 mL), and the resulting yellow solution was refluxed for 3.5 h. The solvent was removed in vacuo, and the residue was dissolved in warm $H_2O$ (20 mL). After filtration of the mixture through Celite 545 to remove excess $S_8$ and unreacted **1**, aq. $KPF_6$ solution (5 mL, 90 mg, 0.49 mmol) was added; this immediately precipitated a yellow-orange solid that was isolated by filtration and washed with $H_2O$ (10 mL). Yield: 30 mg (56%). $^1$H NMR δ: 2.15 (s, 12 H, NC$H_3$), 2.86 (s, 12 H, NC$H_3$), 4.50 (br m, 2H, C$H_2$), 7.30 (m, 4H, Ar), 7.46 (m, 4H, Ar), 7.57 (m, 4H, Ar), 7.87 (m, 2H, Ar), 8.50 (dd, 2H, Ar, $^2J_{HH}$ = 7.39, $^4J_{HP}$ = 15.3). $^{31}$P{$^1$H} NMR δ: 37.0 (d, $^2J_{PP}$ = 33.6), 48.6 (d, $^2J_{PP}$ = 33.6), –145 (spt, $^1J_{PF}$ = 710, $PF_6^-$). Anal. calcd. for $C_{33}H_{42}N_4ClF_6P_3PdS$: C 45.3, H 4.8, N 6.4; found: C 45.2, H 5.0, N 6.2.

### [PdCl(*P*,*N*,*S*-dmapmS)]Cl (4)

This compound was made in the same manner as outlined for **3**, except that, after the reaction of **1** (130 mg, 0.18 mmol) and $S_8$ (45 mg, 1.4 mmol), the reaction mixture was cooled to room temperature and then filtered through Celite 545. The filtrate volume was reduced in vacuo to ~1 mL, and $Et_2O$ (20 mL) was added to precipitate the yellow product. Yield: 100 mg (71%). The NMR data for **4**, except for the absence of the $PF_6^-$ resonance, are the same as for **3**. $\Lambda_M$ ($H_2O$): 99.

### [PdCl(μ-*P*,*N*:*O*-dmapeO)]$_2$[$PF_6$]$_2$ (6)

To a $CH_2Cl_2$ (10 mL) solution of **5** (30 mg, 0.041 mmol) was added aq. KOH solution (5 mL, 1 mol $L^{-1}$). This caused an immediate colour change in the organic layer from yellow to orange-red. The two phase mixture was stirred for 1 h at room temperature, and then the aqueous layer was removed. $H_2O$ (5 mL) was then added to the organic layer, fol-

lowed by $KPF_6$ (83 mg, 0.45 mmol), and stirring was continued for 0.5 h. The aqueous layer was removed, and the $CH_2Cl_2$ phase was washed with $H_2O$ (3 × 10 mL) before being filtered through Celite 545. The filtrate was reduced to dryness in vacuo, and the residue taken up in $CDCl_3$ for analysis by $^{31}P\{^1H\}$ NMR spectroscopy. About 10% of the dioxide, dmapeO$_2$ ($\delta_P$ 31.5), was apparent in the residue. A satisfactory elemental analysis was not obtained for **6**, but X-ray diffraction quality, pale yellow, irregular-shaped crystals of **6**·4$CDCl_3$ (~60% yield) were formed by slow evaporation of the $CDCl_3$ solution. $^{31}P\{^1H\}$ NMR δ: 28.1 (d, $^2J_{PP}$ = 62), 29.3 (d, $^2J_{PP}$ = 62), –145 (spt, $PF_6^-$, $^1J_{PF}$ = 710).

### Catalytic hydration of maleic acid

Complex **4** was tested as a catalyst (at $10^{-3}$ mol $L^{-1}$) for hydration of maleic acid (0.1 mol $L^{-1}$) in aqueous solution at 100 °C. The experimental procedure has recently been described (4), including the determination, by $^1H$ NMR spectroscopy, of the conversion of the maleic acid (*cis*-$CH(CO_2H)$=$CH(CO_2H)$) to the hydration (malic acid) and isomerization (fumaric acid) products.

### X-ray crystallographic analysis of complex 6

Data (see Table 1) were collected on a Siemens SMART system at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames, oriented such that orthogonal wedges of reciprocal space were surveyed. This produced orientation matrices determined from 20 reflections. Final cell constants were calculated from a set of 7876 strong reflections from the actual data collection. The so-called hemisphere data collection technique, where a randomly oriented region of reciprocal space is surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å, was used. Three major swaths of frames were collected with 0.30° steps in ω and, in case the lattice was found to be triclinic (as for **6**), additional sets of frames were collected to better model the absorption correction. The space group was determined based on systematic absences and intensity statistics (26), and a direct-methods solution provided the location of most of the non-H atoms, with several full-matrix least-squares – difference Fourier cycles locating the remaining non-H atoms. All non-H atoms were refined anistropically, and H atoms were included as riding atoms with relative isotropic displacement parameters. The structure is dimeric, with half being in the asymmetric unit that also contains one $PF_6^-$ anion and two $CDCl_3$ molecules. Several SAME and DELU restraints were added to assist in the refinement of the solvent molecules, one of which had considerable translational motion that affected the apparent bond lengths. Complete crystallographic information is available.[4]

**Table 1.** Selected crystallographic data for the "half molecule" of **6**·4$CDCl_3$.

| | **6**·4$CDCl_3$ |
|---|---|
| Empirical formula | $C_{36}H_{46}Cl_7F_6N_4OP_3Pd$ |
| Formula mass | 1 112.23 |
| Crystal size ($mm^3$) | 0.20 × 0.10 × 0.10 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ (No. 2) |
| *a* (Å) | 12.8710(3) |
| *b* (Å) | 14.0672(3) |
| *c* (Å) | 15.4779(4) |
| α (°) | 72.938(1) |
| β (°) | 68.222(1) |
| γ (°) | 73.376(1) |
| Volume ($Å^3$) | 2 437.8(1) |
| *Z* | 2 |
| $D_{calcd.}$ (Mg $m^{-3}$) | 1.515 |
| Absorption coefficient ($mm^{-1}$) | 0.919 |
| *F*(000) | 1 124 |
| θ range for data collection | 1.45–25.00 |
| Reflections collected | 16 763 |
| Independent reflections | 8 168 ($R_{int}$ = 0.0639) |
| Observed reflections | 5 134 ($I > 2\sigma(I)$) |
| No. variables | 531 |
| Final *R* indices ($I > 2\sigma(I)$)[a] | $R_1$ = 0.071, $wR_2$ = 0.1563 |
| R indices (all data)[b] | $R_1$ = 0.1179, $wR_2$ = 0.1768 |
| Goodness-of-fit on $F^2$ | 0.96 |
| Largest diff. peak and hole (e $Å^{-3}$) | 1.328 and –0.90 |

[a] $R_1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ (observed data).
[b] $wR_2 = (\Sigma(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2)^{1/2}$ (all data).

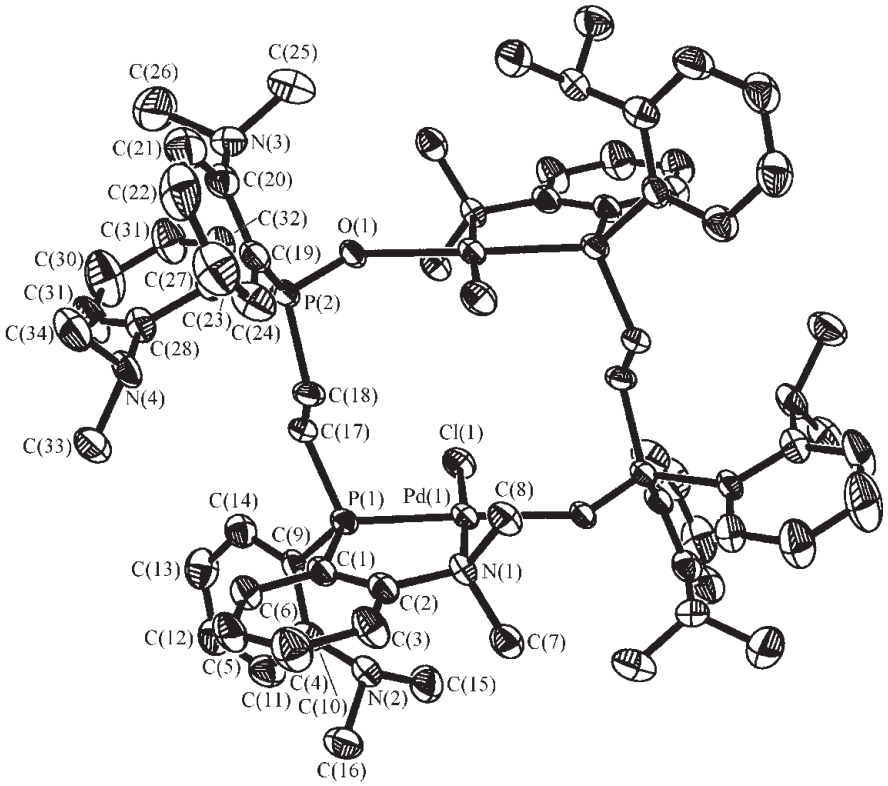
## Results and discussion

The P(III)-containing precursor $PdCl_2$(dmapm) (**1**) exists in solution as an equilibrium mixture of the neutral *P*,*P*- (**1a**) and *P*,*N*-ligated (**1b**) isomers (3), as shown in Scheme 1. Net O atom or S atom addition to **1** results in formation of BPMO and BPMS complexes: room temperature reactions with cumene hydroperoxide in $CH_2Cl_2$ or with $H_2O_2$ in $CH_2Cl_2$–$H_2O$ and with $S_8$ in refluxing 1,2-dichloroethane cleanly give $PdCl_2$(*P*,*N*-dmapmO) (**2**) and [PdCl(*P*,*N*,*S*-dmapmS)]Cl (**4**), respectively (Scheme 1). Presumably, the oxidations occur at the free P atom of isomer **1b**. Complex **2** is a non-electrolyte in $CH_2Cl_2$ solution ($\Lambda_M$ < 1) and does not dissolve in $H_2O$, while **4** dissolves in $H_2O$ as a 1:1 electrolyte ($\Lambda_M$ = 99), and the $Cl^-$ counterion is easily exchanged for $PF_6^-$ by reaction with $KPF_6$ to give [PdCl(*P*,*N*,*S*-dmapmS)]$PF_6$ (**3**). That the NMR data for **4** in $CH_2Cl_2$ are the same as those for the cation of **3** (see below) argues strongly that it is not the dissolution of **4** in water that promotes dissociation of a chloride and that **4** is ionic, unlike the neutral **2**. The softer S atom of the P=S fragment (vs. the harder O atom of P=O fragment) is apparently a sufficiently good ligand to displace a coordinated chloride in these Pd(II) systems.

We recently observed a Pt analogue of **2**, $PtI_2$(*P*,*N*-

[4] Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3660. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 262359 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

**Fig. 1.** ORTEP representation (50% ellipsoids) of the molecular structure of the cation of **6**. H atoms are omitted for clarity.




dmapmO), that formed as an aerobic decomposition product of the heterobimetallic catalyst precursor $PtPdCl_4$(μ-*N*,*P*:*P*′,*N*′-dmapm) during the Heck coupling of PhI and styrene in DMF–$H_2O$ with $K_2CO_3$ as base (1).

Unlike **1**, $PdCl_2$(dmape) (**5**) exists in $CH_2Cl_2$ as an equilibrium mixture of the neutral $PdCl_2$(*P*,*P*-dmape) (**5a**) and ionic [PdCl(*P*,*P*,*N*-dmape)]Cl (**5b**) isomers (4), as shown in Scheme 2. Reaction of this mixture with KOH in a biphasic $H_2O$–$CH_2Cl_2$ medium at room temperature, followed by $Cl^-$–$PF_6^-$ anion exchange, gives the remarkable dipalladium complex [PdCl(μ-*P*,*N*:*O*-dmapeO)]$_2$[$PF_6$]$_2$ (**6**, Scheme 2). An ORTEP of the structure of the cation is shown in Fig. 1, and selected bond distances and angles appear in Table 2.

The structure of **6** consists of two face-to-face, square planar Pd(II) moieties in a head-to-tail orientation (i.e., they are related by an inversion centre that lies at the mid-point of the Pd–Pd axis). The metal centres are separated by a distance of 4.873 Å, and each is *P*,*N*-chelated by the dmape(O) and *P*,*O*-bridged to the other, thus forming a 12-membered ring containing the metal centres. The ring is flanked on either side by two $CDCl_3$ molecules (not shown in Fig. 1). The P-C-C angles in the dmape(O) ligand "backbone" (113.8° and 111.2°) are very similar to that of 110.7° found for dmape (25), indicating that the dmape(O) ligand is unstressed, with the Pd centres being too far removed from one another to interact. The Pd—P and Pd—N bond lengths (2.182 and 2.114 Å), as well as the P-Pd-N angle (87.17°), are similar to those found for **1b** (2.180 Å, 2.132 Å, and 86.10°, respectively) (4).

The bond lengths of Pd—O (2.124 Å), Pd—P (2.182 Å), and P=O (1.515 Å), and the Pd-O=P angle (137.1(3)°) in **6**, are comparable to literature data that we have found for nine

**Table 2.** Selected bond lengths (Å) and angles (°) for **6**·4$CDCl_3$ (esds in parentheses).

| | | | |
|---|---|---|---|
| **Bond distances (Å)** | | | |
| Pd(1)—Cl(1) | 2.296(2) | Pd(1)—N(1) | 2.114(5) |
| Pd(1)—P(1) | 2.182(2) | Pd(1)—O(1*) | 2.124(4) |
| P(2)—O(1) | 1.515(4) | Pd(1)—Pd(1*) | 4.873(2) |
| **Bond angles** (°) | | | |
| P(1)-Pd(1)-N(1) | 87.17(14) | Cl(1)-Pd(1)-O(1*) | 95.71(13) |
| P(1)-Pd(1)-O(1*) | 174.99(13) | Cl(1)-Pd(1)-N(1) | 176.45(14) |
| Pd(1)-P(1)-Cl(1) | 89.29(7) | N(1)-Pd(1)-O(1*) | 87.8(2) |
| Pd(1)-P(1)-C(17) | 111.2(2) | P(1)-C(17)-C(18) | 113.8(5) |
| C(17)-C(18)-P(2) | 111.2(5) | C(18)-P(2)-O(1) | 108.7(3) |
| P(2)-O(1)-Pd(1*) | 137.1(3) | | |

other examples of crystallographically characterized Pd(II) complexes bearing *P*,*O*-bound BPMO ligands (12, 21, 27–31), where the average Pd—O, Pd—P, and P=O distances are 2.134, 2.241, and 1.507 Å, respectively, and the average P=O-Pd angle is 125°. There is no obvious correlation between these parameters, but it is interesting to note that in all cases, including **6**, the Pd—O distance is shorter than the Pd—P distance. The Pd-O=P angle in these complexes shows a wide variation between 108° and 144°. There are also very similar crystallographic data for Pd(II) complexes *P*,*O*-bonded to heterofunctional BPMOs of the type $R_2PN(H)P(O)R_2$ (32).

Complex **6** shows some similarities to a $Pd(II)_2$ compound made recently by Leung and co-workers via a fundamentally different route (30). Their complex was synthesized by an initial [4+2] cycloaddition reaction between a Pd-coordinated

phosphole and vinyl diphenylphosphine oxide, which generated a *P*,*O*-coordinated BPMO at a Pd(II) centre. Subsequent treatment with HCl to remove an ancillary cyclometallated benzylamine ligand afforded the $Pd(II)_2$ complex containing (like **6**) two bridging BPMO ligands, the cation of which can be formulated as $[Pd_2Cl_2(\mu\text{-}P{:}O\text{-BMPO})_2(\mu\text{-Cl})]^+$. This species contains a bridging chloride that serves to complete the square planar coordination at each Pd, and thus, instead of the 12-membered ring seen in **6**, the complex contains two fused eight-membered rings (30). We are not aware of any crystallographically characterized complexes other than **6** that contain two BPMO and no other bridging ligands. The observed P=O, Pd—P, and Pd—O bond lengths and the Pd-O=P angle in **6** are very similar to those found for Leung's compound.

The $^{31}P\{^1H\}$ data (δ and *J* values) for complexes **2** and **6** and for the cation within **3** and **4** reveal the expected doublet of doublet pattern for species containing two inequivalent P atoms, but there are insufficient data to assign the respective resonances of the P(III) and P(V) centres, even with knowledge of the $^{31}P\{^1H\}$ data for the precursor complexes **1** and **5** in both their isomeric forms (see Schemes 1 and 2) (3, 4). The two doublet resonances for **2** and **6** differ by only 0.3 and 1.2 ppm, respectively, and even though there is a larger difference of 11.6 ppm for the cation, assignments still cannot be made. The lower field resonances seen for **3/4** (δ 37.0, 48.6) vs. those seen for **2** (δ 26.2, 26.5) are, however, consistent with the usual trend of deshielding with formation of five-membered ring systems of metal bisphosphine chelate complexes (33).

The $^1H$ NMR data for **2** and **3/4** show the resonances of the $CH_2$ protons as two separate multiplets for the former complex (δ 4.27, 4.81) and one broad multiplet for the latter (δ 4.50); the signal is seen at δ 2.23 as a triplet ($^2J_{HP}$ = 4.2) for free dmapm (3). Peaks for all 24 NMe protons (δ 2.68 s for free dmapm) are also seen; for **2**, there is a very broad "background" signal (δ 1.7–3.3) and four other singlets of 3H each at δ 2.35, 2.51, 3.47, and 3.70. Complex **2** is clearly fluxional, but without low temperature $^1H$ NMR studies, like those done for the **1a** ↔ **1b** system (Scheme 1) (3), it is difficult to assign the NMe resonances. However, based on the δ values of 3.46 and 3.79 for the methyl protons of the coordinated $NMe_2$ group of **1b** (3), the singlets at δ 3.47 and 3.70 likely refer to the coordinated $NMe_2$ group of complex **2**. Fluxionality originating from exchange of free and coordinated anilinyl groups could arise via reversible formation of a five-coordinate $PdCl_2$(*P*,*N*,*O*-dmapeO) intermediate, analogous to the associative process envisioned for such exchange within $[PtCl(P,P,N\text{-dmapcp})]^+$ via a $[PtCl(P,P,N,N\text{-dmapcp})]^+$ intermediate (4); dmapcp is similar to dmape, but in place of the $-(CH_2)_2-$ backbone the ligand has the cyclopentane $-CH(CH_2)_3CH-$ moiety. The $^1H$ NMR data for **6**, consisting of broad, overlapping signals, were uninformative.

The mechanism of formation of complex **6** under an anaerobic atmosphere deserves comment, as we are unaware of other systems in which a metal–BMPO complex is isolated from a metal–bisphosphine precursor in the absence of an oxidant such as oxygen or some other O atom donor. It is well known that tertiary phosphines in the presence of base act as two-electron reductants, being themselves converted to the phosphine oxide, with the two electrons commonly reducing a metal centre (see eq. [1]). Such chemistry is of key importance in the reduction of Pd(II) to Pd(0) species, particularly in a range of Pd-catalyzed coupling reactions (e.g., Heck (34), Stille (35), and Suzuki (36) reactions), aminations (37), and formation of diaryl ethers (38), where the supposed Pd(0) active catalyst is generated in situ from Pd(II) precursors. In the Heck reaction, for example, the active catalyst is often derived from a mixture of $Pd(OAc)_2$ and a phosphine, and formation of Pd(0) from this combination has been studied by Amatore et al. (39). During a study of the Pd-catalyzed carbonylation of aryl halides, Grushin and Alper (40) showed by use of a chiral phosphine that Pd(II)–$PR_3$ complexes are reduced by $OH^-$ to Pd(0) species (eq. [1]) via a *cis*-hydroxo(phosphine)–Pd(II) intermediate, and not via attack at the phosphine by external hydroxide:

$$[1] \qquad [L_nPd(II)\text{-}PR_3]^{2+} + OH^- \rightarrow L_nPd(0) + O{=}PR_3 + H^+$$

where L = a general ligand. The intermediate then decomposes to Pd(0) by deprotonation and reductive elimination of phosphine oxide. Formation of **6** almost certainly occurs via such an initial reduction, following substitution of hydroxide for coordinated chloride or amine of **5a** or **5b** to give, after generation of HCl, a species such as "Pd(0)(dmapeO)". Subsequent oxidation to **6** is thought to occur via reaction with the $CH_2Cl_2$ solvent. Some indirect evidence for this is that **6** was not detected spectroscopically in the organic phase when the reaction of **5** with hydroxide was conducted in the absence of chlorinated solvent (for example, in $H_2O$–$CH_3NO_2$). Oxidative addition reactions of M(0)(phosphine) complexes (M = Pd, Pt) with chlorinated solvents to generate M(II)-chloro species are not uncommon (41), but further work is needed to substantiate the suggestion here.

Complex **4** was tested as a catalyst precursor for hydration of maleic to malic acid in aqueous solution at 100 °C, for comparison with corresponding, recently reported data using $PdCl_2$(dmape) (**5**) and the related [PdX(*P*,*P*,*N*-dmapcp]X complexes as catalyst precursors (4); X = Cl or I, and dmapcp is defined above. The activity of **4** is very similar to that found for [PdCl(*P*,*P*,*N*-dmapcp]Cl (4), as follows: after 24 h, 15% of the maleic acid has been converted to 7% malic acid and 8% fumaric acid, these percentages corresponding to the turn-over numbers, which are three times greater than those reported for hydration of diethylmaleate in THF–$H_2O$ at 120 °C using $[\{Ph_2P(CH_2)_2PPh_2\}Pd(\mu\text{-}OH)]_2^{2+}$ as the catalyst precursor (5). The activity remains marginal, and indeed is comparable to that of dilute HCl for the hydration. However, HCl gives about twice as much isomerization product than do our Pd-*P*,*P*,*N* and Pd-*P*,*P*,*S* complexes (4).

## Conclusions

We have demonstrated the formation of bisphosphine monoxide (BPMO) complexes of Pd(II), both by direct oxidation of a "dangling" P(III) atom and by reaction with aqueous hydroxide in a mixed solvent system, where deprotonation and reductive elimination of phosphine oxide from a *cis*-hydroxophosphine-Pd(II) intermediate is favoured. In

addition, we have shown that analogous monosulfide (BPMS) complexes can be made by the direct oxidation route.

## Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work, the University of British Columbia for a University Graduate Fellowship (NDJ), and Dr. Victor Young (X-Ray Crystallographic Laboratory, Chemistry Department, University of Minnesota, Minneapolis, MN 55455) for determining the crystal structure of **6**·4$CDCl_3$.

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