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Article

Chiral Bisphosphinite Metalloligands Derived from a P-Chiral Secondary Phosphine Oxide

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Interaction of $PdCl_2(MeCN)_2$ with 2 equiv of (S_P)-$^tBuPhP(O)H$ (**1**H) followed by treatment with Et_3N gave [Pd{(**1**)$_2$H}]$_2$(μ-Cl)$_2$ (**2**). Reaction of **2** with Na[S_2CNEt_2] or K[N(PPh_2S)$_2$] afforded Pd[(**1**)$_2$H](S_2CNEt_2) (**3**) or Pd[(**1**)$_2$H)-[N(PPh_2S)$_2$] (**4**), respectively. Treatment of **3** with V(O)(acac)$_2$ (acac = acetylacetonate) and $CuSO_4$ in the presence of Et_3N afforded bimetallic complexes V(O)[Pd(**1**)$_2$(S_2CNEt_2)]$_2$ (**5**) or Cu[Pd(**1**)$_2$(S_2CNEt_2)]$_2$ (**6**), respectively. X-ray crystallography established the S_P configuration for the phosphinous acid ligands in **3** and **6**, indicating that **1**H binds to Pd(II) with retention of configuration at phosphorus. The geometry around Cu in **6** is approximately square planar with the average Cu–O distance of 1.915(3) Å. Treatment of **2** with HBF_4 gave the BF_2-capped compound [Pd{(**1**)$_2$$BF_2$}]$_2$($\mu$-Cl)$_2$ (**7**). The solid-state structure of **7** containing a PdP_2O_2B metallacycle has been determined. Chloride abstraction of **7** with $AgBF_4$ in acetone/water afforded the aqua compound [Pd{(**1**)$_2$$BF_2$}($H_2O$)$_2$][$BF_4$] (**8**) that reacted with [NH_4]$_2$[WS_4] to give [Pd{(**1**)$_2$$BF_2$}$_2$]$_2$[$\mu$-$WS_4$] (**9**). The average Pd–S and W–S distances in **9** are 2.385(3) and 2.189(3) Å, respectively. Treatment of [(η^6-*p*-cymene)$RuCl_2$]$_2$ with **1**H afforded the phosphinous acid adduct (η^6-*p*-cymene)$RuCl_2$(**1**H) (**10**). Reduction of [Cp*$RuCl_2$]$_x$ (Cp* = η^5-C_5Me_5) with Zn followed by treatment with **1**H resulted in the formation of the Zn(II) phosphinate complex [{Cp*Ru(η^6-C_6H_5)}$^tBuPO_2$}]$_2$($ZnCl_2$)$_2$ (**11**) that contains a $Zn_2O_4P_2$ eight-membered ring.

Introduction

The coordination chemistry of secondary phosphine oxides (sPOs) $R_2P(O)H$ (R = alkyl, aryl)[1−3] is of interest due to their applications to metal-catalyzed organic reactions and homogeneous catalysis.[4−10] In solution, $R_2P(O)H$ is in tautomeric equilibrium with the phosphinous acid $R_2P(OH)$ that can bind to transition metal ions via the phosphorus atom. Thus, reaction of sPOs with soft metal ions such as Pd(II) and Pt(II) results in the formation of the phosphinous acid complex M{$PR_2(OH)$}, which, in the presence of base, can be further reacted to give the metallacycle M{(R_2PO)$_2$H} (Scheme 1).[1−3,7] Hydrogen-bonded M{(R_2PO)$_2$H} metallacycles have also been prepared by treatment of R_2P-X (X = Cl,[11] R′O,[12,13] or C≡CCF_3[14]) with metal ions via hydrolysis and nucleophilic attack at phosphorus. Recently, Li reported that Pd(II) in conjunction with $^tBu_2P(O)H$ is an active catalyst

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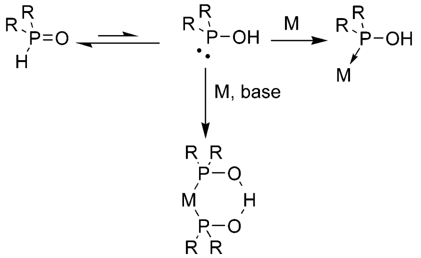
Scheme 1



for C−C coupling reactions.[7] This prompts us to explore chiral Pd phosphinite catalysts based on P-chirogenic sPOs.[15] In addition, P-chiral $[M\{(RR'P{=}O)_2\}]^-$ complexes are of special interest because they may serve as *O,O*-bidentate ligands[16,17] that are analogues of acetylacetonate and $[N(R_2P{=}O)_2]^-$.

Although Pd-catalyzed cross coupling of P-chiral phosphonate diesters[18] and oxidative addition of phenylphosphinates with Pt(0)[19] are known to proceed with retention of configuration at phosphorus, to our knowledge, the stereochemistry for binding of P-chiral sPOs to metal ions has not been established. Recently, Haynes and co-workers developed a multigram synthesis of a P-chiral sPO $^tBuPhP(O)H$. Significantly, both the S_P and R_P isomers of $^tBuPhP(O)H$ could be isolated in enantiomerically pure form.[20] (S_P)-$^tBuPhP(O)H$ (**1**H) has been used for metal-catalyzed asymmetric hydrogenation of imines[9] and allylic alkylation,[10] implying that **1**H binds to metal ions stereoselectively. In this connection, we set out to investigate the stereochemistry for the reaction between **1**H and Pd(II). Herein, we report on the synthesis and crystal structures of Pd(II) complexes with a P-chiral phosphinite ligand confirming that **1**H binds to Pd with retention of configuration at phosphorus. The synthesis and crystal structures of bimetallic complexes containing the P-chiral bidentate, anionic metalloligand $[Pd(\mathbf{1})_2]^-$ will be described.

Experimental Section

General Considerations. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 121.5, and 282.4 MHz for ^1H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H and ^{13}C), $CF_3C_6H_5$ (^{19}F), and H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, and mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

Materials. (S_P)-$^tBuPhP(O)H$ (**1**H),[20] $PdCl_2(MeCN)_2$,[21] and $K[N(Ph_2PS)_2]$[22] were prepared according to literature methods. $[NH_4]_2[WS_4]$ and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ were purchased from Aldrich Ltd.

Preparation of $[Pd\{(1)_2H\}]_2(\mu\text{-}Cl)_2$ (2). Compound **2** was prepared according to Li's procedure.[7] To a solution of $PdCl_2(MeCN)_2$ (71 mg, 0.274 mmol) in CH_2Cl_2 (15 mL) was added **1**H (100 mg, 0.549 mmol), and the mixture was stirred at room-temperature overnight, during which time the color changed from orange to yellow. The volatiles were removed and the residue was extracted into hexane (3 × 25 mL). Et_3N (0.211 g, 2.089 mmol) in CH_2Cl_2 (15 mL) was added and the resulting mixture was stirred at room temperature for an additional 3 h. The solvents were removed in vacuo and the residue was recrystallized from Et_2O/hexane to give yellow crystals. Yield: 99 mg (72%). ^1H NMR (acetone-d_6): δ 1.28 (d, $^3J(PH) = 16.5$ Hz, 36H), 7.67 (m, 12H), 8.05−8.10 (m, 8H); the O−H proton signal was not observed. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 95.6 (s). MS (FAB): *m/z* 1010 ($M^+ + 1$). Anal. Calcd for $C_{40}H_{58}Cl_2O_4P_4Pd_2$: C, 47.5; H, 5.74. Found: C, 47.1; H, 5.88.

Preparation of $Pd[(1)_2H](S_2CNEt_2)$ (3). To a solution of **2** (60 mg, 0.059 mmol) in acetone (15 mL) was added $Na[S_2CNEt_2]\cdot 3H_2O$ (27 mg, 0.119 mmol), and the reaction mixture was stirred at room-temperature overnight. The volatiles were removed and the residue was recrystallized from Et_2O/hexane to give pale yellow crystals suitable for X-ray diffraction analysis. Yield: 35 mg (48%). ^1H NMR (acetone-d_6): δ 1.17 (d, $^3J(PH) = 15.6$ Hz, 18H), 1.46 (t, $J = 7.2$ Hz, 6H), 4.03 (q, $J = 7.2$ Hz, 4H), 7.61 (m, 6H), 8.05−8.10 (m, 4H). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 96.9. MS (FAB): *m/z* 619 ($M^+ + 1$). Anal. Calcd for $C_{25}H_{39}NS_2O_2P_2Pd$: C, 48.6; H, 6.36; N, 2.27. Found: C, 48.6; H, 6.52; N, 2.21.

Preparation of $Pd[(1)_2H][N(Ph_2PS)_2]$ (4). This compound was prepared similarly as for **3** using $K[N(Ph_2PS)_2]$ (55 mg, 0.112 mmol) in place of $Na[S_2CNEt_2]\cdot 3H_2O$, and recrystallized from Et_2O/hexane. Yield: 58 mg (56%). ^1H NMR (acetone-d_6): δ 1.18 (d, $^3J(PH) = 15.3$ Hz, 18H), 7.37−8.19 (m, 30H). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 96.2 (s), 38.7 (s). MS (FAB): *m/z* 918 ($M^+ + 1$). Anal. Calcd for $C_{44}H_{49}NS_2O_2P_4Pd\cdot 1/2C_6H_{14}\cdot H_2O$: C, 57.7; H, 5.93; N, 1.43. Found: C, 57.1; H, 5.95; N, 1.42.

Preparation of $V(O)[Pd\{(1)_2\}(S_2CNEt_2)]_2$ (5). To a solution of $VO(acac)_2$ (6 mg, 0.021 mmol) in acetone (10 mL) was added **3** (26 mg, 0.042 mmol), and the mixture was stirred overnight. The volatiles were removed in vacuo and the residue was recrystallized from Et_2O/hexane to give a yellow powder. Yield: 12 mg (43%). IR (KBr, cm^{-1}): 1015 ($\upsilon_{V=O}$). MS (FAB): *m/z* 1302 ($M^+ + 1$). Anal. Calcd for $C_{50}H_{76}N_2O_5P_4S_4Pd_2V\cdot H_2O$: C, 45.4; H, 5.91; N, 2.12. Found: C, 45.4; H, 5.94; N, 2.08.

Preparation of $Cu[Pd\{(1)_2\}(S_2CNEt_2)]_2$ (6). To a solution of $CuSO_4\cdot 5H_2O$ (6 mg, 0.024 mmol) in MeOH (10 mL) was added **3** (30 mg, 0.048 mmol), and then an excess of Et_3N (0.1 mL) was added. The mixture was stirred at room temperature for 10 min. The blue precipitate was collected and recrystallized from CH_2Cl_2/Et_2O to give pale blue crystals suitable for X-ray analysis. Yield: 18 mg (58%). MS (FAB): *m/z* 1299 ($M^+ + 1$). Anal. Calcd for $C_{50}H_{76}N_2CuO_4P_4S_4Pd_2$: C, 45.6; H, 5.93; N, 2.13. Found: C, 45.9; H, 6.03; N, 2.05.

Preparation of $[Pd\{(1)_2BF_2\}]_2(\mu\text{-}Cl)_2$ (7). To a solution of **2** (52 mg, 0.051 mmol) in Et_2O (15 mL) was added HBF_4 (0.2 mL

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Table 1. Crystallographic Data and Experimental Details for Complexes **2**, **6**, **7**, **9**, and **11**

compound	**2**	**6**	**7**	**9**	**11**
formula	$C_{26}H_{39}O_2P_2S_2Pd$	$C_{50}H_{76}N_2O_4P_4S_4CuPd_2$	$C_{40}H_{56}B_2O_4F_4P_4Cl_2Pd_2$	$C_{40}H_{56}B_2O_4F_4P_4S_4Pd_2W$	$C_{40}H_{58}O_4P_6Cl_4Zn_2Ru_2$
fw	618.03	1297.59	1106.05	1347.24	1139.48
a, Å	9.5361(8)	10.298(2)	17.4581(8)	14.9250(17)	12.0114(10)
b, Å	15.3206(12)	11.961(2)	16.6780(8)	10.5019(12)	13.8565(12)
c, Å	20.0421(16)	46.690(9)	18.0894(9)	16.968(2)	15.0639(13)
α, deg	90	90	90	90	85.173(2)
b, deg	90	90	115.650(1)	112.281(2)	87.444(2)
γ, deg	90	90	90	90	72.980(2)
V, $Å^3$	2928.1(4)	5751(2)	4747.8(4)	2461.0(5)	2375.0(4)
Z	4	4	4	2	2
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_1$	$P\bar{1}$
ρ_{calcd} g·cm^{-3}	1.397	1.499	1.547	1.818	1.593
T, K	293(2)	100(2)	100(2)	100(2)	100(2)
m, mm^{-1}	0.906	1.284	1.058	3.408	1.950
F(000)	1276	2668	2240	1328	1152
no. of reflns	17972	35509	28686	12257	17038
no. of indep reflns	6923	12131	20362	6599	8250
R_{int}	0.0290	0.0521	0.0199	0.0580	0.0408
$R1^a$, $wR2^b$($I > 2s(I)$)	0.0397, 0.0868	0.0480, 0.0800	0.0303, 0.0669	0.0388, 0.0687	0.0484, 0.1015
*R*1, *wR*2 (all data)	0.0564, 0.0942	0.0562, 0.0827	0.0323, 0.0679	0.0595, 0.0739	0.0741, 0.1082
GOF^c	1.020	1.059	1.017	0.843	0.990
Flack parameter	−0.02(3)	−0.013(13)	−0.023(10)	0.005(7)	

[a] $R1 = \sum 1/2|F_o| - |F_c|1/2/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w|F_o{}^2|^2]^{1/2}$. [c] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

of a 54% solution in Et_2O, 1.45 mmol) at 0 °C, and the mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo and the residue was washed with hexane and recrystallized from Et_2O/hexane to give pale yellow crystals suitable for X-ray diffraction (yield: 25 mg, 43%). ^1H NMR ($CDCl_3$): δ 1.17 (d, ^3J(PH) = 17.4 Hz, 36H), 7.44−7.49 (m, 12H), 7.94−8.05 (m, 8H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 111.4 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −138.2. MS (FAB): *m/z* 1106 ($M^+ + 1$). Anal. Calcd for $C_{40}H_{56}B_2Cl_2F_4O_4P_4Pd_2{\cdot}H_2O$: C, 42.7; H, 5.16. Found: C, 42.9; H, 5.39.

Preparation of [Pd{(1)$_2$BF$_2$}(H$_2$O)$_2$][BF$_4$] (8). To a solution of **7** (65 mg, 0.059 mmol) in acetone/H_2O (15 mL, 10:1) was added $AgBF_4$ (24 mg, 0.122 mmol), and the mixture was stirred at room temperature for 2 h. The solution was filtered and evaporated to dryness. Recrystallization from acetone/CH_2Cl_2/hexane afforded pale yellow crystals. Yield: 30 mg (69%). ^1H NMR (acetone-d_6): δ 1.21 (d, ^3J(PH) = 17.1 Hz, 18H), 4.75 (s br., 4H), 7.74−7.96 (m, 6H), 8.05−8.17 (m, 4H). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 110.2 (s). ^{19}F NMR (acetone-d_6): δ −137.7 (BF_2), −149.3 (BF_4). MS (FAB): *m/z* 518 ($M^+ - 2H_2O - BF_4 + 1$). Anal. Calcd for $C_{20}H_{32}B_2F_6O_4P_2Pd{\cdot}2Me_2CO$: C, 41.3; H, 5.86. Found: C, 40.3; H, 5.65.

Preparation of [Pd{(1)$_2$BF$_2$}]$_2$(μ-WS$_4$) (9). To a solution of $[NH_4]_2[WS_4]$ (5 mg, 0.015 mmol) in acetone (10 mL) was added **8** (20 mg, 0.031 mmol), and the mixture was stirred for 3 h. The solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/hexane to give pale yellow needles. Yield: 12 mg (59%). ^1H NMR (acetone-d_6): δ 1.38 (d, ^3J(PH) = 17.7 Hz, 36H), 7.72 (m, 12H), 8.14 (m, 8H). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 110.8 (s). $^{19}F\{^1H\}$ NMR (acetone-d_6): δ −136.6. MS (FAB): *m/z* 1327 ($M^+ - F$). Although **9** has been fully characterized by spectroscopic methods and X-ray diffraction, we have not been able to obtain satisfactory elemental analyses for the compound.

Preparation of (η^6-*p*-cymene)Ru(1H)Cl$_2$ (10). To a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (75 mg, 0.125 mmol) in CH_2Cl_2 (15 mL) was added **1**H (50 mg, 0.275 mmol), and the mixture was stirred at room-temperature overnight. The residue was washed with Et_2O and hexane, and then extracted into CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane gave an orange powder. Yield: 35 mg (32%). ^1H NMR (acetone-d_6): δ 1.25 (dd, J_1= 6.0 Hz, J_2 = 48 Hz, 6H), 1.42 (d, ^3J(PH) = 16.4 Hz, 9H), 2.12 (s, 3H), 2.80 (q, *J* = 6.0 Hz, 1H), 5.89 (d, *J* = 6.0 Hz, 2H), 6.61 (d, *J* = 6.0 Hz, 2H), 7.71−7.80 (m, 3H), 8.03−8.12 (m, 2H). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 118.0 (s). MS (FAB): *m/z* 490 ($M^+ + 1$). Anal. Calcd for $C_{20}H_{29}Cl_2OPRu{\cdot}1/2CH_2Cl_2$: C, 46.3; H, 5.64. Found: C, 46.2; H, 5.74.

Preparation of [{Cp*Ru(η^6-C$_6$H$_5$)}^{t}BuPO$_2$]$_2$(ZnCl)$_2$ (11). $[Cp{*}RuCl_2]_x$ was reduced by Zn in the presence of NH_4PF_6 in MeCN according to a literature method.[23] After filtration, the crude product was treated with **1**H (110 mg, 0.60 mmol) and Et_3N (65 mg, 0.60 mmol) in THF (10 mL). The mixture was stirred for 30 min during which the solution turned brown. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/Et_2O to give yellow single crystals. Yield: 54 mg (35%). ^1H NMR (DMSO-d_6): δ 0.96 (d, ^3J(PH) = 7.2 Hz, 18H), 1.89 (s, 30H), 5.93 (m, 10H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 149.8 (s). MS (FAB): *m/z* 569 ($1/2M^+ + 1$). Anal. Calcd for $C_{40}H_{58}Cl_4O_4P_2Ru_2Zn_2{\cdot}1/2CH_2Cl_2$: C, 41.2; H, 5.00. Found: C, 41.8; H, 4.69.

X-ray Diffraction Measurements. A summary of crystallographic data and experimental details for complexes **3**, **6**, **7**, **9**, and **11** are compiled in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100(2) K. The collected frames were processed with the software SAINT. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL[24] software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions (C−H bond fixed at 0.96 Å).

Results and Discussion

Pd[(1)$_2$H] Complexes. The preparations of complexes containing the Pd[(**1**)$_2$H] metallacycle are summarized in Scheme 2. The starting material [Pd{(**1**)$_2$H}]$_2$(μ-Cl)$_2$ (**2**) was synthesized from $PdCl_2(MeCN)_2$ and **1**H in the presence of

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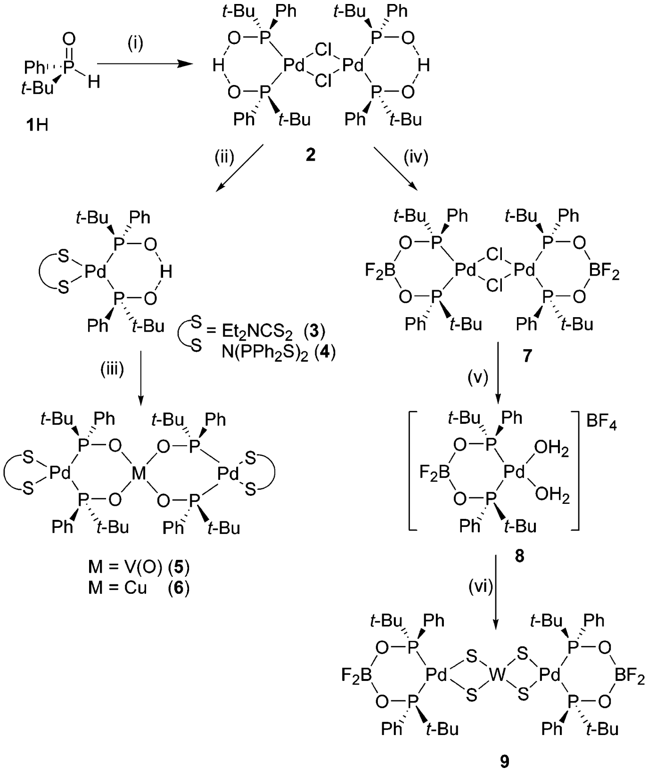
Scheme 2[a]



[a] Reagents and conditions: (i) $PdCl_2(MeCN)_2$, Et_3N, CH_2Cl_2; (ii) $Na(S_2CNEt_2)\cdot 3H_2O$ or $K[N(PPh_2S)_2]$, acetone; (iii) $CuSO_4\cdot 5H_2O/Et_3N$ or $VO(acac)_2$; (iv) HBF_4, Et_2O; (v) $AgBF_4$, acetone/H_2O; (vi) $[NH_4]_2[WS_4]$, acetone.

Et_3N in 72% yield according to Li's procedure.[7] **2** is soluble in most common organic solvents except hexanes, and is air stable in both the solid state and solution. The IR spectrum shows P−O stretches at 1032 and 1096 cm^{-1} and the O−H stretch at 1261 cm^{-1}, characteristic for symmetrical O···H···O hydrogen bonding.[1,2] The $^{31}P\ \{^1H\}$ NMR spectrum of crude **2** shows a singlet δ 95.6, which is more downfield than that for **1**H (δ 44.8),[20] indicating that the sample mostly contained a single diastereomer.

As expected, treatment of dimeric **2** with bidentate sulfur ligands resulted in cleavage of the chloro bridges and the formation of mononuclear complexes. For example, treatment of **2** with $Na[S_2CNEt_2]$ and $K[N(SPPh_2)_2]$ led to the formation of $Pd[(\mathbf{1})_2H](S_2CNEt_2)$ (**3**) and $Pd[(\mathbf{1})_2H][N(Ph_2PS)_2]$ (**4**), respectively. It may be noted that the achiral analogue $Pd[(Ph_2PO)_2H](S_2CNEt_2)$ has been prepared from $Pd(S_2CNEt_2)_2$ and $PPh_2(OMe)$ previously.[12a] X-ray crystallography confirmed that **3** is chiral and the phosphinous acid ligands possess the S_P configuration (Figure 1). The Pd−P, Pd−S, and P−O distances in **3** [2.303(1), 2.387(1), and 1.550(3) Å, respectively] are similar to those in $Pd[(Ph_2PO)_2H](S_2CNEt_2)$.[12a] Like **2**, the IR spectra for **3** and **4** show the symmetrical O···H···O vibrational modes and the absence of ν_{OH} in the normal 3000−3500 cm^{-1} region. The $^{31}P\ \{^1H\}$ NMR spectrum of **3** in $CDCl_3$ exhibited a single resonance at δ 98.7 ppm, indicating that a single diastereomer was present in the sample. By contrast, reaction of racemic (S_P and R_P) $^tBuPhP(O)H$ with $PdCl_2(MeCN)_2$ and $Na(S_2CNEt_2)$ gave a product that exhibited two ^{31}P resonances at δ 98.7 and 100.4 ppm assignable to the racemic (S_P,S_P and R_P,R_P) and meso (S_P,R_P) isomers of **3**, respectively. Thus, the ^{31}P NMR and X-ray diffraction results confirmed that the sPO **1**H tautomerizes to the phosphinous acid S_P-$^tBuPhP(OH)$ that binds to Pd(II) with retention of configuration at the phosphorus.

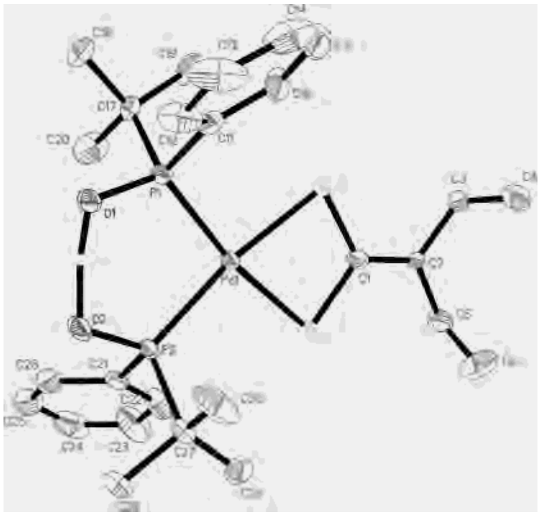


Figure 1. Perspective view of $Pd\{(\mathbf{1}_2)H\}(S_2CNEt_2)$ (**3**) (30% probability ellipsoids shown). Selected bond lengths (Å) and angles (deg): Pd(1)−P(1) 2.302(1), Pd(1)−P(2) 2.304(1), Pd(1)−S(1) 2.377(1), Pd(1)−S(2) 2.396(1), P(1)−O(1) 1.555(3), P(2)−O(2) 1.545(3); P(1)−Pd(1)−S(1) 97.2(4), P(2)−Pd(1)−S(1) 170.3(4), P(1)−Pd(1)−S(2) 170.5(4), P(2)−Pd(1)−S(2) 97.0(4), S(1)−Pd(1)−S(2) 73.4(4).

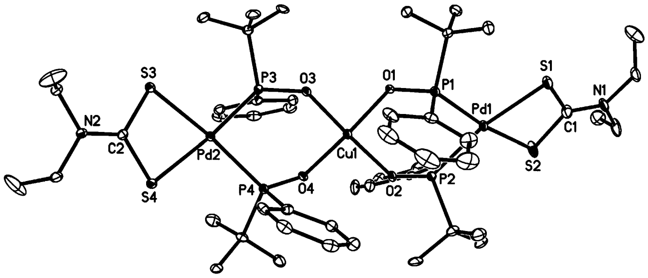


Figure 2. Perspective view of $Cu[Pd(\mathbf{1})_2(Et_2NCS_2)]_2$ (**6**) (30% probability ellipsoids shown). Selected bond lengths (Å) and angles (deg): Cu(1)−O(1) 1.927(3), Cu(1)−O(2) 1.914(3), Cu(1)−O(3) 1.897(3), Cu(1)−O(4) 1.922(3), Pd(1)−P(1) 2.284(1), Pd(1)−P(2) 2.302(1), Pd(2)−P(3) 2.277(1), Pd(2)−P(4) 2.305(1), Pd(1)−S(1) 2.412(1), Pd(1)−S(2) 2.393(1), Pd(2)−S(3) 2.398(1), Pd(2)−S(4) 2.395(1); O(2)−Cu(1)−O(1) 90.1(1), O(3)−Cu(1)−O(2) 168.9(1), O(3)−Cu(1)−O(4) 91.6(1), O(2)−Cu(1)−O(4) 92.4(1), O(3)−Cu(1)−O(1) 87.8(1), O(4)−Cu(1)−O(1) 169.4(1).

Bimetallic Complexes. As previously reported, **2** and **3** can serve as anionic *O*,*O*-bidentate metalloligands for transition metal ions.[16] For example, treatment of **3** with $VO(acac)_2$ (acac = acetylacetone) and $CuSO_4\cdot 5H_2O$ in the presence of Et_3N led to formation of trinuclear $V(O)[Pd\{(\mathbf{1})_2\}(S_2CNEt_2)]_2$ (**5**) and $Cu[Pd\{(\mathbf{1})_2\}(S_2CNEt_2)]_2$ (**6**), respectively. The structure of **6** has been established by X-ray diffraction. Figure 2 shows a perspective view of the molecule confirming the S_P configuration for the phosphinous acid ligands in **6**. The geometry around Cu is approximately square planar with the Cu atom ca. 0.14 Å above the O_4 plane. The two six-membered CuO_2P_2Pd metallacycles are found to adopt a puckered chair conformation. The average Cu−O distance in **6** (1.915(3) Å) is comparable to that in

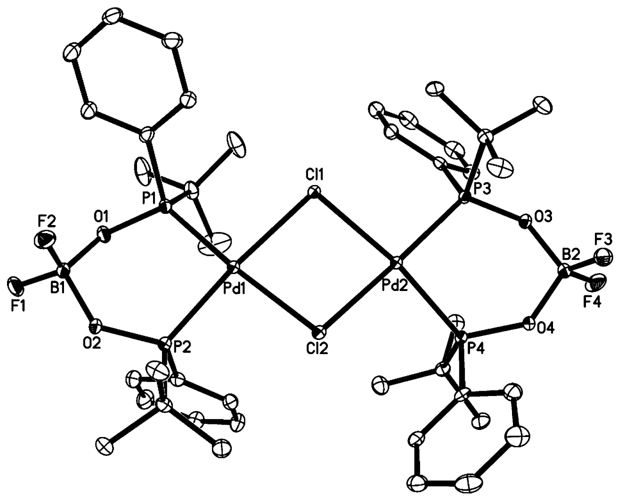


Figure 3. Perspective view of one of the two independent molecules in the asymmetric unit of $[Pd\{(\mathbf{1})_2BF_2\}]_2(\mu\text{-}Cl)_2$ (**7**) (30% probability ellipsoids shown). Selected bond lengths (Å) and angles (deg): Pd(1)−P(1) 2.268(1), Pd(1)−P(2) 2.273(1), Pd(2)−P(3) 2.261(1), Pd(2)−P(4) 2.250(1), Pd(3)−P(5) 2.261(1), Pd(3)−P(6) 2.248(1), Pd(4)−P(7) 2.262(1), Pd(4)−P(8) 2.269(1), P(1)−O(1) 1.574(2), P(2)−O(2) 1.568(2), P(3)−O(3) 1.563(2), P(4)−O(4) 1.558(2), P(1)−Pd(1)−P(2) 89.7(3), P(3)−Pd(2)−P(4) 90.0(3), P(5)−Pd(3)−P(6) 90.9(3), P(7)−Pd(4)−P(8) 90.7(3).

$Cu[N(PPh_2O)_2]_2$ (1.918(2) Å).[25] The Pd−P and P−O distances (av 2.292(2) and 1.542(3) Å, respectively) are similar to those in **3**.

BF$_2$-Capped Complexes. Treatment of **2** with HBF_4 in Et_2O led to the formation of the BF$_2$-capped complex $[Pd\{(\mathbf{1})_2BF_2\}]_2(\mu\text{-}Cl)_2$ (**7**). Compounds containing $MP_2O_2BF_2$ metallacycles have been prepared previously.[26] The presence of the BF$_2$ group in **7** is evidenced by ^{19}F NMR (δ −138) and IR spectroscopy (884 cm^{-1} (ν_{BF})). The ^{31}P resonance for **7** at δ 111.4 is more downfield than that for **2**. The crystal structure of **7** has been determined. The asymmetric unit of **7** consists of two independent molecules. A perspective view of one such molecule is shown in Figure 3. The crystal structure confirms the S_P configuration for the phosphinous acid ligands in **7**. The Pd−P distances in the range of 2.248(1) to 2.273(1) Å are shorter than those in **3**. The P−O and B−O distances (av 1.558(2) and 1.476(3) Å, respectively) are typical for $MP_2O_2BF_2$ metallacycles.[26c]

Chloride abstraction of **7** with $AgBF_4$ in acetone/water resulted in the formation of the aquo complex $[Pd\{(\mathbf{1})_2BF_2\}(H_2O)_2][BF_4]$ (**8**) that exhibited ν_{OH} at 3436 cm^{-1} in the IR spectrum. Complex **8** can serve as a building block for trinuclear complexes upon replacing the labile aquo ligands with tetrathiometalates. For example, treatment of **8** with $[NH_4]_2[WS_4]$ in acetone led to isolation of $[Pd\{(\mathbf{1})_2BF_2\}]_2(\mu\text{-}WS_4)$ (**9**). The FAB mass spectrum displayed the molecular ion signal at *m*/*z* 1327 corresponding to the molecular ion M$^+$ − F. The IR spectrum shows ν_{WS} at 478 cm^{-1} that is lower than for uncomplexed $[WS_4]^{2-}$ (509 cm^{-1}).[27] The

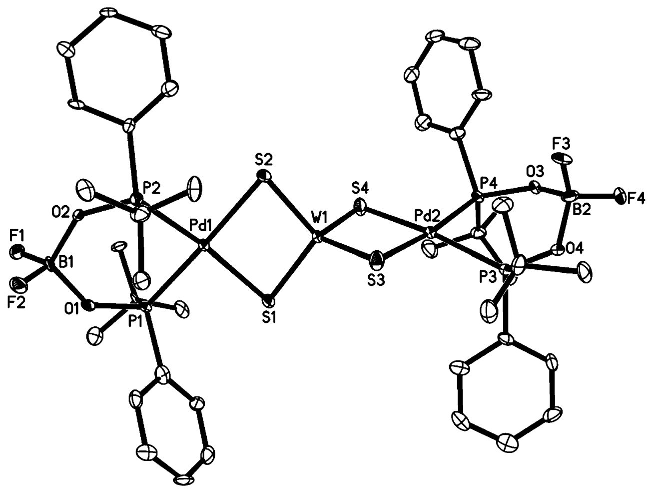


Figure 4. Perspective view of $[Pd\{(\mathbf{1})_2BF_2\}]_2(\mu\text{-}WS_4)$ (**9**) (30% probability ellipsoids shown). Selected bond lengths (Å) and angles (deg): W(1)−S(1) 2.188(3), W(1)−S(2) 2.187(3), W(1)−S(3) 2.191(3), W(1)−S(4) 2.188(3), Pd(1)−S(1) 2.386(3), Pd(1)−S(2) 2.369(3), Pd(2)−S(3) 2.387(3), Pd(2)−S(4) 2.398(3), Pd(1)−P(1) 2.303(3), Pd(1)−P(2) 2.320(3), Pd(2)−P(3) 2.304(3), Pd(2)−P(4) 2.291(3), W(1)···Pd(1) 2.931(1), W(1)···Pd(2) 2.940(1); S(2)−W(1)−S(4) 109.7(1), S(2)−W(1)−S(1) 105.8(1); S(4)−W(1)−S(1) 112.6(1), S(2)−W(1)−S(3) 111.0(1), S(4)−W(1)−S(3) 106.3(1), S(1)−W(1)−S(3) 111.6(1), W(1)−S(1)−Pd(1) 79.6(1), W(1)−S(2)−Pd(1) 80.0(1), W(1)−S(3)−Pd(2) 79.8(1), W(1)−S(4)−Pd(2) 79.6(1), Pd(1)···W(1)···Pd(2) 176.2(3).

solid-state structure of **9** featuring the S_P configuration has been characterized by X-ray diffraction (Figure 4). Whereas heterometallic clusters based on $[WS_4]^{2-}$ are well documented,[28] **9** is a rare example of such clusters containing stereogenic P-donor ligands. The geometry around Pd is square-planar and that around W is approximately tetrahedral (S−W−S′ angles ranging from 105.8(1) to 112.6(1)°). The average Pd−S bond distance of 2.385 Å in **9** is slightly longer than that in Pd(dppe)(WS$_4$) (dppe = $Ph_2PCH_2CH_2PPh_2$) (2.232(3) Å),[29] whereas the Pd−P distances (av 2.305(3) Å) are shorter than those in the latter (2.270(3) Å). Because of the longer Pd−S distances, the average Pd···W separation of 2.935(1) Å in **9** is longer than that in Pd(dppe)(WS$_4$) (2.887(2) Å).[29] Like other trinuclear heterothiometallic complexes,[28] the Pd(1)···W(1)···Pd(2) unit is approximately linear (176.2(3)°). The W−S distances in the range from 2.188(3) to 2.191(3) Å are slightly longer than those in $[NH_4]_2[WS_4]$ (av 2.17 Å).[30]

Ruthenium Complexes. Tripodal P═O ligands based on (η^6-arene)Ru(II)[31] and Cp*Ru(II)[32] phosphinite complexes were found to exhibit interesting coordination chemistry. To this end, efforts were made to synthesize Ru complexes with P-chiral phosphinous acid ligands. Treatment of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with **1**H afforded $(\eta^6\text{-}p\text{-cymene})Ru(\mathbf{1}H)Cl_2$ (**10**) characterized by MS and NMR spectroscopy. Attempts to prepare a bis-phosphinite compound by reacting $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with excess **1**H were not successful. Chlo-

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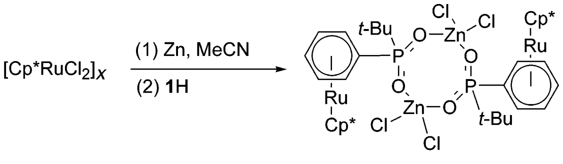
Scheme 3



11

ride abstraction of **10** with $AgBF_4$ followed by treatment with **1**H resulted in an intractable oil. Although X-ray diffraction data are not available, it seems likely that the phosphinous acid ligand in **10** also has the S_P configuration.

In an attempt to synthesize a Cp*Ru complex containing **1**H, $[Cp^*RuCl_2]_x$ was reduced by Zn and subsequently reacted with **1**H. However, instead of a Cp*Ru phosphinite complex, a dinuclear Zn(II) phosphinate complex $[\{Cp^*Ru(\eta^6\text{-}C_6H_5)\}^tBuPO_2]_2(ZnCl_2)_2$ (**11**) was isolated (Scheme 3). Apparently, the Zn in **11** was derived from $ZnCl_2$ produced by Zn reduction of $[Cp^*RuCl_2]_x$. Although the mechanism for formation of **11** is not clear, it seems likely that binding of Cp*Ru(II) to the phenyl ring in **1**H and air oxidation of the phosphine oxide to phosphinate are involved. No reaction was found between $ZnCl_2$ and **1**H. Complex **11** exhibited a simple ^1H NMR spectrum indicative of high symmetry of the molecule. The solid-state structure of **11** has been established by X-ray diffraction. The asymmetric unit of **11** consists of two independent molecules. A perspective view of one such molecule is shown in Figure 5. The structure can be viewed as consisting of two $ZnCl_2$ moieties bridged by two zwitterionic $\{Cp^*Ru(\eta^6\text{-}C_6H_5)\}^+(^tBu)PO_2^-$ ligands. The molecule is related by an inversion center located at the center of the eight-membered $P_2O_4Zn_2$ ring that has a pseudo chair conformation. The coordination geometry of Zn is tetrahedral with bond angles ranging from 106.4(1) to 111.4(2)°. The average Zn−O (1.976(3) Å) and P−O distances (1.504(3) Å) are comparable to those in $[Me_2HNCH_2CH_2NHMe_2][Zn_2(H_2PO_4)_6]$.[33]

Conclusion

In summary, we have confirmed that the P-chiral secondary phosphine oxide **1**H tautomerizes to the phosphinous acid $^tBuPhP(OH)$ that binds to Pd(II) with retention of configuration at phosphorus according to X-ray diffraction and NMR studies. This result provides a new methodology to design and synthesize metal complexes containing stereogenic phosphinous acid ligands that may find applications in asymmetric metal-catalyzed organic reactions. Recently, asymmetric hydrogenation of imines[9] and allylic alkylation[10] based on **1**H have been reported, demonstrating the potential of this air-stable, unidentate phosphinite ligand for asymmetric catalysis. In addition, the Pd(II) bisphosphinite complexes can serve as a chiral bidentate ligand that binds to metal ions to give heterobimetallic complexes. The study of catalytic activity of bimetallic complexes containing this P-chiral metal-bisphosphinite ligand is under way.

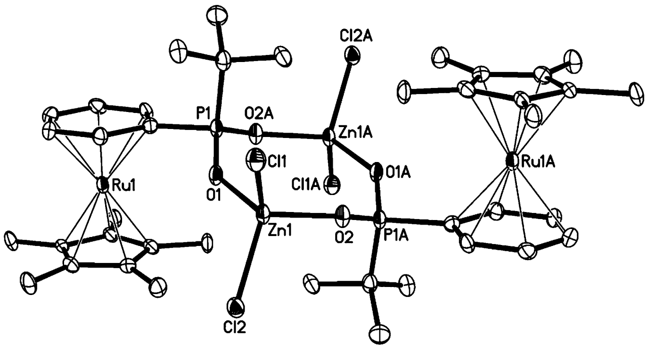


Figure 5. Perspective view of one of the two independent molecules in the asymmetric unit of $[Cp^*Ru\{(\eta^6\text{-}C_6H_5)(^tBu)PO_2\}]_2(ZnCl_2)_2$ (**11**) (30% probability ellipsoids shown). Selected bond lengths (Å) and angles (deg): Zn(1)−O(1) 1.985(3), Zn(1)−O(2) 1.976(4), Zn(2)−O(3) 1.975(3), Zn(2)−O(4) 1.967(3), Zn(1)−Cl(1) 2.233(2), Zn(1)−Cl(2) 2.246(2), Zn(2)−Cl(3) 2.235(2), Zn(2)−Cl(4) 2.235(2); O(1)−Zn(1)−O(2) 108.6(1), O(3)−Zn(2)−O(4) 106.6(1), Cl(1)−Zn(1)−Cl(2) 111.4(1), Cl(3)−Zn(2)−Cl(4) 110.4(1), O(1)−Zn(1)−Cl(1) 106.6(1), O(2)−Zn(1)−Cl(1) 111.2(1), O(1)−Zn(1)−Cl(2) 112.7(1), O(2)−Zn(1)−Cl(2) 106.4(1), O(3)−Zn(2)−Cl(3) 113.4(1), O(4)−Zn(2)−Cl(3) 107.7(1), O(3)−Zn(2)−Cl(4) 105.9(1), O(4)−Zn(2)−Cl(4) 112.9(1), O(2)#1−P(1)−O(1) 116.3(2), O(3)−P(2)−O(4)#2 117.7(2).

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Supporting Information Available: Listings of final atomic coordinates, anisotropic displacement parameters, bond lengths and angles for complexes **3**, **6**, **7**, **9**, and **11** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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