Inorg. Chem. **1997,** *36,* 1786−1791

Synthesis and Coordination Chemistry of the First Water-Soluble Dithio−Bis(phosphine) Ligands $[(HOH_2C)_2P(CH_2)_2S-X-S(CH_2)_2P(CH_2OH)_2]$ ($X = (CH_2)_3$ or C_6H_4). X-ray Crystal Structure of $[Pd(HOH_2C)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(CH_2OH)_2](Cl)_2$[1]

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Received October 31, 1996[⊗]

The thioether-functionalized, water-soluble, bis(phosphines) $(HOH_2C)_2PCH_2CH_2S(CH_2)_3SCH_2CH_2P(CH_2OH)_2$ (**9**) and $C_6H_4\{1,2\text{-}SCH_2CH_2P(CH_2OH)_2\}_2$ (**10**) were synthesized in near quantitative yields by the formylation of the appropriate phosphine hydrides in the presence of formaldehyde in ethanol. The reactions of **9** and **10** with $Pt(COD)Cl_2$ and $Pd(C_6H_5CN)_2Cl_2$ in biphasic media (aqueous/organic) produced the water-soluble Pt(II) and Pd(II) complexes $[Pt(HOH_2C)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(CH_2OH)_2](Cl)_2$ (**11**), $[Pd(HOH_2C)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(CH_2OH)_2](Cl)_2$ (**12**), $[Pt\{(C_6H_4)\{1,2\text{-}S(CH_2)_2P(CH_2OH)_2\}_2\}](Cl)_2$ (**13**), and $[Pd\{(C_6H_4)\{1,2\text{-}S(CH_2)_2P(CH_2OH)_2\}_2\}](Cl)_2$ (**14**) in near quantitative yields. The X-ray crystal structure of **12** confirms a square-planar Pd(II) structure for this new generation of water-soluble transition metal complexes. All of the complexes were characterized by MS, ^1H, ^{13}C, and ^{31}P NMR spectroscopy. X-ray data for **12**: triclinic, $P\bar{1}$, $a = 9.9761(6)$ Å, $b = 10.2049(7)$ Å, $c = 11.6954(7)$ Å , $\alpha = 67.730(10)°$, $\beta = 69.943(10)°$, $\gamma = 79.828(10)°$, $Z = 2$, $R = 0.0307$ ($R_w = 0.0797$).

Introduction

Design and discovery of appropriate ligand systems has become central to the development of water-soluble transition metal organometallic compounds.[2−5] For example, numerous studies have demonstrated that the sulfonated phosphines, when used as ligands, give water-soluble characteristics to the resulting transition metal compounds.[3−6] In fact, the utility of rhodium complexes derived from sulfonated phosphines as water-soluble catalysts for hydroformylation reactions, at the industrial scale, exemplifies the commercial importance of water-soluble transition metal compounds.[2] The preferential solubility of transition metal catalysts in aqueous phases enable high recovery of catalysts, easy separation of the organic products/chemicals, and, therefore, present enormous scope for achieving cost efficiency in specific chemical transformations.[2] Water-soluble transition metal compounds also present significant potential for use as catalytic agents in photochemical water-splitting reactions for applications in solar energy conversion.[7−9] In fact, recent studies by Tyler et al. demonstrate the ability of a hydroxymethyl water-soluble phosphine as a building block to produce catalytically active molybdenum complexes for photochemical reactions in water.[10]

We have recently described the synthesis of water-soluble palladium(II) and platinum(II) complexes derived from aqueous-soluble bis(phosphines) (Figure 1).[11,12] Each of the bis(phosphines), described in Figure 1, produced metal complexes with 1:2 metal to ligand ratios exclusively. Therefore, we reasoned that the incorporation of heteroatomic donors, such as nitrogen or sulfur centers, across the diphosphine bridge might result in transition metal complexes of a 1:1 metal to ligand ratio *via* coordination through sulfur (or nitrogen) and the P^{III} centers. Recent studies by Noyori et al. on the coordination chemistry of ruthenium precursors with the P_2N_2 ligand frameworks exemplifies the importance of bridging-donor centers in achieving tetradentate coordination *via* the two N and P^{III} centers.[13] In addition, recent reports by Darensbourg et al. and Aurivillius and Bertinsson demonstrate the development and coordination chemistry of a dithio−bis(phosphine) chelate of type **A**.[14,15] However, the presence of bulky phenyl substituents on the P^{III} centers renders them insoluble in aqueous media. As part of our ongoing studies in the development of fundamental coordination chemistry using water-soluble phosphines,[11,12,16−19]

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[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1997.

(1) This paper is part 6 of our series on “Chemistry in Environmentally Benign Media”. Part 5. See ref 19.

(2) (a) Cornils, B.; Wiebus, E. *Chemtech* **1995**, *25*, 33, and references cited therein. (b) *Aqueous Organometallic Chemistry and Catalysis, Proceedings of the NATO Advanced Research Workshop*, Debrecen, Hungary, Aug 29-Sept 1, 1994; Preprints.

(3) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1994**, *34*, 219.

(4) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.

(5) Katti, K. V. *Curr. Sci.* **1996**, *70*, 219.

(6) (a) Kuntz, E. G. *Chemtech* **1987**, *17*, 570. (b) Kuntz, E. G. Rhône-Poulenc Ind., French Pat. 2 349 562, 1976. (c) Kuntz, E. G. Rhône-Poulenc Ind., French Pat. 2 366 237, 1976. (d) Kuntz, E. G. Rhône-Poulenc Ind., French Pat. 2 733 516, 1976.

(7) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607.

(8) Avey, A.; Tyler, D. R. *Organometallics* **1992**, *11*, 3856.

(9) Avey, A.; Schut, D. M.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1993**, *32*, 233.

(10) Nieckarz, G. F.; Weakley, T. J. R.; Miller, W. K.; Miller, B. E.; Lyon, D. K.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 1721.

(11) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *Inorg. Chim. Acta* **1995**, *240*, 367.

(12) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *J. Chem. Soc., Dalton Trans.* **1996**, 1301.

(13) Gao, J. X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087.

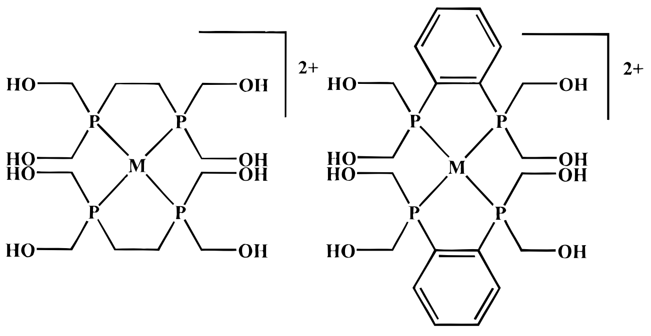
(14) Hsiao, Y.; Chojnacki, S. S.; Hinton, P.; Reibenspies, J. H.; Darensbourg, M. Y. *Organometallics* **1993**, *12*, 870.

(15) Aurivillius, K.; Bertinsson, G. *Acta Crystallogr.* **1981**, *B37*, 2073.

(16) Reddy, V. S.; Berning, D. E.; Katti, K. V.; Volkert, W. A.; Ketring, A. L.; Barnes, C. L. *Inorg. Chem.* **1996**, *35*, 1753.

(17) Berning, D. E.; Katti, K. V.; Singh, P. R.; Higginbothom, C.; Reddy, V. S.; Volkert, W. A. *J. Nucl. Med. Biol.* **1996**, *23*, 617.

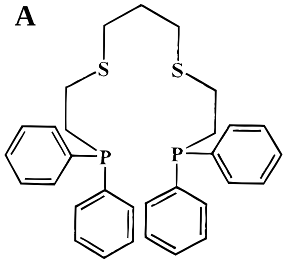
S0020-1669(96)01319-5 CCC: $14.00



(M = Pd, 1; M = Pt, 2) **(M = Pd, 3; M = Pt, 4)**

Figure 1. Representation of bis chelates derived from (hydroxymethyl)-bis(phosphines).

A



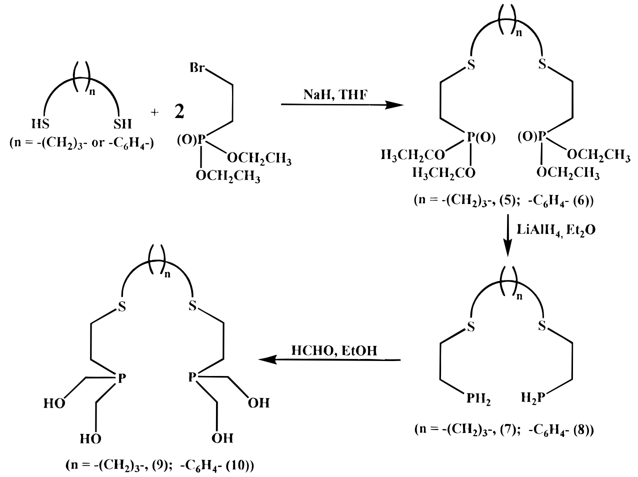
we, herein, describe the synthesis of a new class of thioether-functionalized, water-soluble bis(phosphines) (P_2S_2) (Scheme 1). The coordination chemistry of this class of multifunctional water-soluble phosphines with Pd(II) and Pt(II) has resulted in the development of water-soluble metal complexes. Details of X-ray structural investigations of a representative Pd(II) complex are discussed.

Results and Discussion

The syntheses of thioether-functionalized bis(phosphines) **9** and **10** were accomplished in a two step procedure as described in Scheme 1. First, the thiother-functionalized bis(phosphonates) **5** and **6** were prepared *via* the reactions of the appropriate thiols with diethyl 2-bromoethylphosphonate. The bis(phosphonates) **5** and **6** were reduced to the corresponding bis(phosphine) hydrides **7** and **8** in diethyl ether using lithium aluminum hydride. The formylation of P−H bonds to produce $P-CH_2OH$ linkages are usually catalyzed by Pt(II) precursors.[20] However, the use of Pt(II) catalysts to transform the thioether-functionalized phosphine hydrides **7** and **8** to the corresponding alkylhydroxyphosphines resulted in complicated side reactions with poor yields of **9** and **10**. In fact, formylation of **7** and **8** occurred best when these reactions were carried out in oxygen-free ethanol in the presence of formaldehyde.

The new compounds **5**−**10** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. FAB mass spectrometry was used to identify the molecular ions for all of the compounds excluding the bis(phosphine) hydrides **7** and **8**. Parent ions at $[M + H^+]$, $m/z = 437.13$ and $[M + H^+]$, $m/z = 439.12$ were observed for the bis(phosphonate) precursors **5** and **6**, respectively. Compounds **9** and **10** showed parent ions corresponding to $[M + H^+]$, $m/z = 349.08$ and $[M + H^+]$, $m/z = 383.06$. The ^{31}P NMR spectra of **5** and **6** consisted of singlets at 29.1 and 29.4 ppm respectively. The conversions of the bis(phosphonates) **5** (δ 29.1) and **6** (δ 29.4) to the corresponding phosphine hydrides **7** (δ −137.1) and **8** (δ −136.3) were monitored by ^{31}P NMR spectroscopy. The one bond P−H coupling constants of **7** and **8** were obtained by recording proton coupled phosphorus spectra. The P-H coupling constants for each **7** and **8** are 196 Hz. These values are consistent with those noted for PH_3 (187 Hz)[21] and $H_2PCH_2CH_2PH_2$ (193 Hz).[22] The spectrum of **7**, as depicted in Figure 2, is not a simple triplet of triplet pattern as might be expected. This is due in part to phosphorus coupling to the two hydride protons as well as the two adjacent ethylene protons. Additional coupling of phosphorus with the second set of two ethylene protons across three bonds may, presumably, be responsible for the five line pattern (Figure 2). The average of $^2J_{PH}$ and $^3J_{PH}$ as calculated from the line spacings is 5.46 Hz. The P_2S_2 phosphines **9** and **10** resonate as singlets at −25.0 and −23.3 ppm, respectively. These chemical shifts are comparable to those noted for the water-soluble bis(phosphines) of the type $(HOH_2C)_2PXP(CH_2OH)_2$ ($x = (CH_2)_2$ (δ −25.1); C_6H_4 (δ −31.2)).[12] Compounds **5**, **6**, **9**, and **10** were further characterized by C and H analysis.

Scheme 1



The P_2S_2−alkylhydroxyphosphines **9** and **10** are highly soluble in water and ethanol. It is to be noted that **9** and **10** are oxidatively stable in aqueous solutions. However, they showed oxidative instability in ethanolic solutions, presumably, as a result of alcoholysis of the P^{III} centers.

Coordination Chemistry of the Thioether-Functionalized Bis(phosphines) 9 and 10. The hydrophilic nature of **9** and **10** necessitates the development of their coordination chemistry under biphasic (aqueous-organic) reaction conditions. For example, the P_2S_2 bis(phosphines) **9** and **10**, upon dissolution in water, interact with $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene), dissolved in CH_2Cl_2, to produce the new Pt(II) complexes **11** and **13**, respectively (Scheme 2). The reactions of **9** and **10** with $Pd(C_6H_5CN)_2Cl_2$ were also carried out under similar biphasic conditions to produce the corresponding Pd(II) complexes **12** and **14** in good yield (Scheme 2). In all of the reactions outlined in Scheme 2, it is important to recognize that more than 99% of the Pt(II) or Pd(II) precursors, from the organic phase, were transferred into the aqueous phase in the form of complexes **11**−**14**. All of the complexes were isolated from the aqueous phase upon removal of water *in vacuo*.

The fast atom bombardment mass spectrometric analysis of **11**−**14** showed parent ions corresponding to $[M + H^+]$. The ^1H, ^{13}C, and ^{31}P NMR spectra of **11**−**14** indicate them to be

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(18) Reddy, V. S.; Katti, K. V.; Volkert, W. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4459.

(19) Smith, C. J.; Reddy, V. S.; Katti, K. V. *J. Chem. Soc., Chem. Commun.* **1996**, 2557.

(20) Reuter, M.; Orthner, L. Ger. Pat. 1 035 135, 1958; *Chem. Abstr.* **1960**, *54*, 14124I.

(21) Birchall, T.; Jolly, W. L. *Inorg. Chem.* **1966**, *5*, 2177.

(22) Maier, von L.; *Helv. Chim. Acta* **1966**, *49* (2), 842.

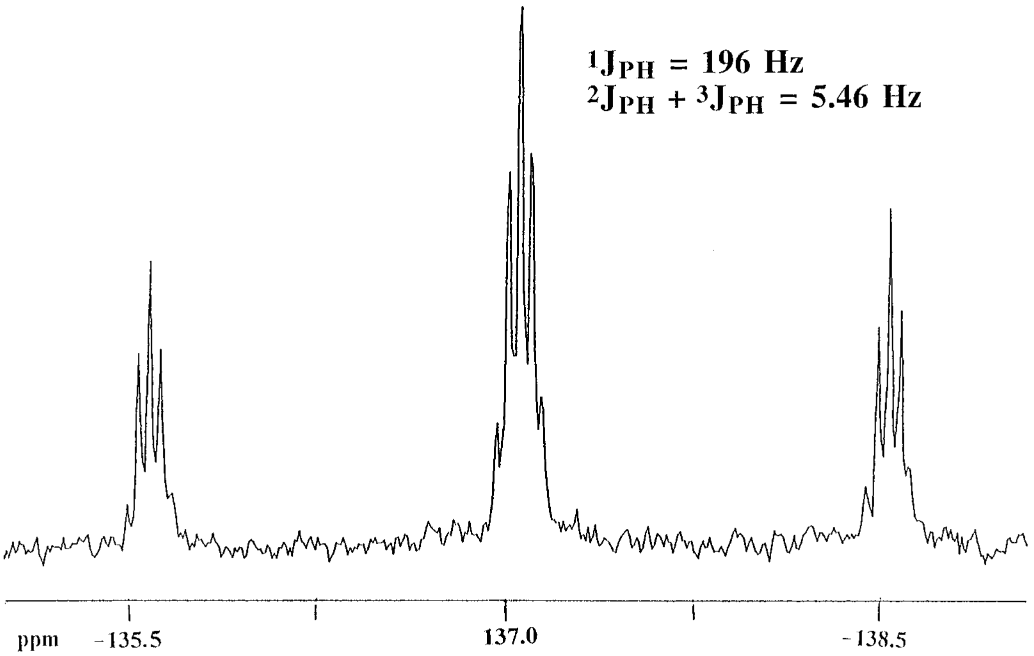
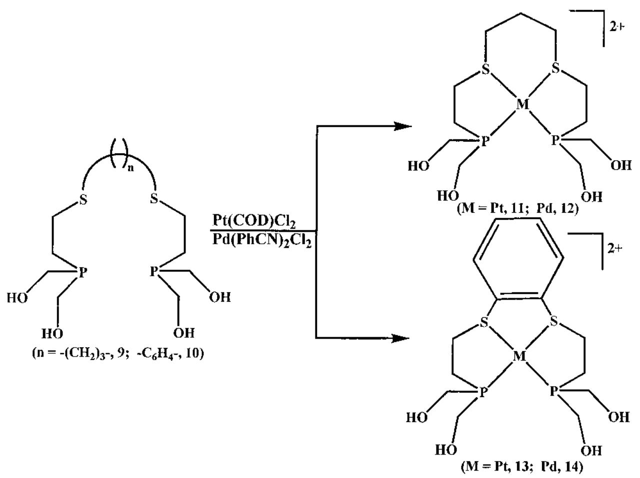


Figure 2. Proton coupled ^{31}P NMR (121.5 MHz) spectrum of **7**.

Scheme 2



~99% pure. It appears that the impurities remain in the organic phase, while complexes **11**−**14** selectively partition into the aqueous phase. Complexes **11**−**14** were further characterized by C and H analysis. Conductivity studies of **11** and **12** were performed to elucidate the cationic structures of the Pd(II) and Pt(II) complexes as shown in Scheme 2. Each of the complexes was referenced to a standard KCl solution (1413 μS) with a specific conductivity of 9.00 μS/cm at 25 °C. The specific conductivities of **11** (1.56×10^{-3} mol) and **12** (2.72×10^{-3} mol) were 1605 and 2896 μS/cm, respectively.

The ^{31}P NMR spectra of **11** and **13** consisted of triplet signals as a result of coupling with the Pt metal center ($^1J_{PtP} = 2780$ Hz for **11** and 2897 Hz for **13**). The ^{31}P NMR signals of **11** and **13** were centered at 54.8 and 52.0 ppm, respectively. Considerable deshielding in the ^{31}P chemical shifts was noted in the corresponding Pd(II) complexes **12** (δ 70.2) and **14** (δ 70.6).

The ^{195}Pt NMR spectrum of **11** is diagnostic of a 1:1 metal to ligand ratio as formulated in Scheme 2. Compound **11** resonates as a triplet signal at −5067 ppm in the ^{195}Pt NMR spectrum, consistant with the Pt metal center coupling to two equivalent P^{III} nuclei. The $^1J_{PtP}$ value of 2780 Hz, in **11**, is identical to the value derived from its ^{31}P NMR spectrum. The $^1J_{PtP}$ values in closely related water-soluble Pt(II) complexes **2** and **4** (Figure 1) were found to be 2165 and 2203 Hz, respectively.[11,12] The larger values of $^1J_{PtP}$ in **11** and **13** (where P is *trans* to S), as compared to **2** and **4** (where P is *trans* to P), may be attributed to the fact that sulfur has a weaker *trans* influence than that of phosphorus. Therefore, square-planar compounds wherein P is *trans* to S (e.g., **11** and **13**) have Pt−P bonds that are shorter and stronger in comparison to compounds where P is *trans* to P (e.g., **2** and **4**). The comparison of the $^1J_{PtP}$ values of **11** and **13** to those of **2** and **4** is reminiscent of the ^{31}P spectroscopic data of *cis*- and *trans*-(R$_3$P)$_2$PtCl$_2$. For example, the $^1J_{PtP}$ value is 2400 Hz when P is *trans* to P. However, $^1J_{PtP}$ increases to 3500 Hz when P is *trans* to Cl. Phosphorus has a larger *trans* influence than chlorine, and, therefore, shorter (and stronger) bonds are seen in *cis*-(R$_3$P)$_2$-PtCl$_2$ than in the *trans* isomer.[23,24] Additional evidence for the molecular structures of **11** and **12** has come from 2D NMR spectroscopy (spectra available in Supporting Information).

X-ray Structural Analysis of 12. The structure of dithio−bis(phosphine) metal complex **12** was further confirmed by X-ray crystallography. An ORTEP diagram of the cation is shown in Figure 3, and selected bond distances and angles are listed in Table 1. The asymmetric unit consists of the complex cation [PdL]$^{2+}$, two noncoordinating chloride anions, and a single water molecule. The geometry around the palladium center is square-planar. Two phosphine subunits along with the sulfur moieties from the thioether linkages are coordinated to the metal center in a chelating fashion. The two thioether units and the phosphine centers are each coordinated to the Pd(II) center in a *cis* disposition. The Pd−P(1) and Pd−P(2) bond distances are 2.266 and 2.285 Å respectively. The Pd−S(1) and Pd−S(2) bond distances are 2.34 and 2.351 Å and are within the normal range.[25] The average Pd−P distances in **12** (2.275

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(23) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(24) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

(25) (a) Katti, K. V.; Singh, P. R.; Barnes, C. L. *Inorg. Chem.* **1992**, *31*, 4588. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen. A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, S1. (c) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

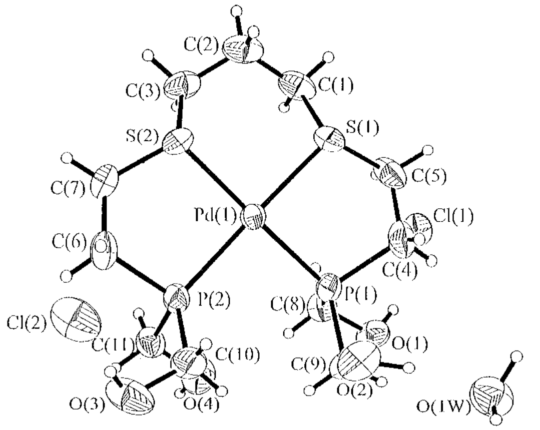


Figure 3. ORTEP diagram of **12** with 50% probability ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **12**

Pd−P(1)	2.266(7)	S(1)−C(1)	1.822(3)
Pd−P(2)	2.285(7)	S(1)−C(5)	1.823(3)
Pd−S(1)	2.340(7)	S(2)−C(3)	1.817(3)
Pd−S(2)	2.351(7)	S(2)−C(7)	1.823(3)
P(1)−Pd−P(2)	97.5(3)	P(1)−Pd−S(1)	86.6(3)
P(2)−Pd−S(1)	171.2(3)	P(1)−Pd−S(2)	175.4(3)
P(2)−Pd−S(2)	86.9(3)	S(1)−Pd−S(2)	88.8(3)
C(1)−S(1)−Pd	105.6(12)	C(5)−S(1)−Pd	103.8(11)
C(3)−S(2)−Pd	105.6(12)	C(7)−S(2)−Pd	100.5(11)
C(9)−P(1)−Pd	121.5(11)	C(4)−P(1)−Pd	105.5(11)
C(8)−P(1)−Pd	114.9(10)	C(11)−P(2)−Pd	118.8(11)
C(6)−P(2)−Pd	105.2(11)	C(10)−P(2)−Pd	117.8(12)

Å) are shorter in comparison to the Pd−P bond distances (2.317 Å) observed in $[Pd\{(CH_2OH)_2PC_6H_4P(CH_2OH)_2\}_2](Cl)_2$.[12] This is consistent because in the palladium complex, $[Pd\{(CH_2OH)_2PC_6H_4P(CH_2OH)_2\}_2](Cl)_2$, P is *trans* to P, whereas in **12** P is *trans* to S. The weaker *trans* influence of the sulfur, as compared to phosphorus, results in stronger and shorter Pd−P bonds. This, clearly, supports a strong Pt−P interaction and hence the high $^1J_{PtP}$ coupling constant values obtained for **11** and **13**. The P(1)−Pd−S(1) and P(2)−Pd−S(2) chelate angles are 86.6 and 86.9° respectively. The S(1)−Pd−S(2) chelate angle is 88.8°. The non-chelate angle of P(1)−Pd−P(2) is 97.5°.

The structure of **12** reveals the tetracoordination of Pd(II) to produce one six-membered and two five-membered metallocycles (Figure 3). The six-membered ring Pd(1)−S(1)−C(1)−C(2)−C(3)−S(4) adopts a distorted chair conformation. The five-membered ring Pd(1)−P(2)−C(6)−C(7)−S(2) forms a distorted envelope with C(7) as the flap, whereas the Pd(1)−P(1)−C(4)−C(5)−S(1) ring forms a twisted envelope. The overall structure is stabilized by an extended hydrogen bonded framework running parallel to [001]. There are no significant *inter*- or *intra*molecular hydrogen bonds involving the cation since all of the hydroxyl moieties act as hydrogen bond donors to either water molecules or chloride ions situated in the lattice. However, O(2) and O(4) of two separate cations hydrogen bond to the lone pairs of a single water molecule as depicted in Figure 4. In turn, the water molecule, which is situated close to a center or inversion, hydrogen bonds to two symmetry-related chloride ions, Cl(2). This chloride Cl(2) also accepts hydrogen bonds from a water molecule across the inversion center. Cl(2) also accepts a hydrogen bond from O(3) of yet another separate cation, thereby adding a second dimension to the hydrogen bonded array which lies on [110]. Only one hydrogen bond is made to Cl(1), i.e., by O(4) of the cation (Figure 4).

The coordination chemistry of the phenyl substituted analogue **A** with Pd(II), as reported by Aurivillius and Bertinsson et al.,[15] has revealed a structure comprising two metal centers per ligand in a bis-chelation pathway as shown below:

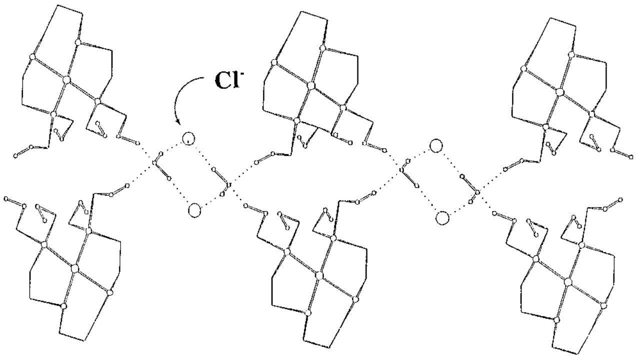
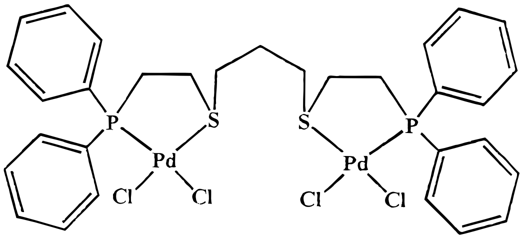


Figure 4. Molecular structure of **12** illustrating intramolecular hydrogen-bonding interactions.



Complex B

The tetradentate coordination of the mononuclear Pd(II) complexes **12** and **14** is in sharp contrast to the bidentate chelation of the dinuclear Pd(II) complex (**B**). This may be attributed to the effects exerted by substituents on the phosphorus center. Furthermore, the hydrogen bonding networks present in complexes **11**−**14**, presumably, stabilize the mononuclear structures present in the solution and solid states.

Conclusions

The new class of water-soluble complexes reported in this paper has demonstrated unusual kinetic stability in aqueous media. For example, aqueous solutions of **11**−**14**, when monitored by ^{31}P NMR spectroscopy, did not show any detectable decomposition for several weeks. These compounds did not decompose even upon boiling their aqueous solutions for 15−30 min. The interactions of a 4−6-fold excess of **9** and **10** with the metal complexes **11**−**14** did not produce bis chelates of 2:1 ligand to metal stoichiometry. This observation, conclusively, demonstrates the propensity of the P_2S_2 ligand frameworks to involve in monoligated coordination *via* tetradentate interactions with the late transition metals platinum(II) and palladium(II).

Experimental Section

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified by standard methods and distilled under nitrogen prior to use. Reagents such as $HS(CH_2)_3SH$, $HS(C_6H_4)SH$, $BrCH_2CH_2P(O)(OC_2H_5)_2$, NaH, $LiAlH_4$, 37% aqueous formaldehyde, $Pd(C_6H_5CN)_2Cl_2$, and $Pt(COD)Cl_2$ were purchased from Aldrich Chemical Co. and were used without further purification. Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer using D_2O, $CDCl_3$, and CD_3OD as solvents. The ^1H and ^{13}C chemical shifts are reported in parts per million, downfield from external standard $SiMe_4$. The ^{31}P NMR (121.5 MHz) spectra were recorded with 85% H_3PO_4 as an external standard, and positive chemical shifts lie downfield of the standard. ^{195}Pt NMR spectra were recorded in water with chemical shifts being referenced to external K_2PtCl_4. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Mass spectral analyses were performed by the Washington University Resource for Biomedical and Bio-Organic Mass Spectrometry, St. Louis, MO. Potentiometric analyses were performed by Fayette Environmental Services, Inc., Fayette, MO.

Synthesis of $(EtO)_2(O)PCH_2CH_2S(CH_2)_3SCH_2CH_2P(O)(OEt)_2$ (5). A sample of 60% NaH in mineral oil (95 mmol) was placed in a two-neck round bottom flask and charged with dry hexane (20 mL). This solution was allowed to stir for 10 min, after which the hexane−mineral oil layer was removed by syringe. The flask was then charged with dry tetrahydrofuran (100 mL), followed by dropwise addition of $HS(CH_2)_3SH$ (46 mmol) with constant stirring. The resulting solution was cooled at 0 °C, and $BrCH_2CH_2P(O)(OC_2H_5)_2$ (95 mmol) was added dropwise with constant stirring over a period of 30 min. Excess NaH was quenched by addition of 50 mL of deionized water. The solution was extracted from ethyl acetate (3 × 50 mL) and washed with a saturated sodium chloride solution. The organic layer was dried over anhydrous sodium sulfate. Upon filtering, the solvent was removed *in vacuo* to afford **5** in 90% yield along with a trace amount of diethyl vinylphosphonate. The compounds were separated on a silica gel column (20 cm; 60 mesh) using 90:10 ethyl acetate to hexane solvent mixture. Removal of the solvent *in vacuo* afforded compound **5** as a viscous, yellow-green oil with an overall yield of 88% (17.8 g). High-resolution FAB/MS Anal. Calcd for $C_{15}H_{34}O_6P_2S_2$: 436.1272. Found: $[M + H^+]$, $m/z = 437.1350$. Anal. Calcd for $C_{15}H_{34}O_6P_2S_2$: C, 41.27; H, 7.86. Found: C, 41.40; H, 7.78. ^{1}H NMR ($CDCl_3$): δ 1.34 (t, $^3J_{HH} = 9.0$ Hz, 12H, OCH_2CH_3), 1.87 (qn, 2H, $CH_2CH_2CH_2$), 2.03 (m, 4H, PCH_2CH_2), 2.65 (t, $^3J_{HH} = 9.0$ Hz, 4H, $CH_2CH_2CH_2$), 2.74 (m, 4H, PCH_2CH_2), 4.11 (m, 8H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 16.3 (d, $^3J_{PC} = 4.5$ Hz, OCH_2CH_3), 24.8 (d, $^2J_{PC} = 3.0$ Hz, PCH_2CH_2), 26.6 (d, $^1J_{PC} = 136.6$ Hz, PCH_2CH_2), 28.5 (s, $CH_2CH_2CH_2$), 30.5 (s, $CH_2CH_2CH_2$), 61.6(d, $^2J_{PC} = 6.0$ Hz, OCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 29.1 (s).

Synthesis of $H_2PCH_2CH_2S(CH_2)_3SCH_2CH_2PH_2$ (7). Compound **5** (18 mmol) was placed in 75 mL of dry diethyl ether and cooled to 0 °C. An ether solution of 1.0 M lithium aluminum hydride (45 mmol, 45 mL) was slowly added dropwise to this solution with constant stirring. An aqueous solution of 6 N hydrochloric acid (50 mL) was added dropwise to the solution to quench any remaining $LiAlH_4$. The ether layer was separated by cannula, and the solvent was removed *in vacuo* to afford **7** in 96% (3.89 g) yield as a colorless viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.83 (m, 6H, PCH_2CH_2, $CH_2CH_2CH_2$), 2.70 (m, 12H, PH_2, $CH_2CH_2CH_2$, PCH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 14.8 (d, $^1J_{PC} = 11.3$ Hz, PCH_2CH_2), 29.1 (s, $CH_2CH_2CH_2$), 30.6 (s, $CH_2CH_2CH_2$), 35.1 (s, PCH_2CH_2). ^{31}P NMR ($CDCl_3$): δ −137.1 (s).

Synthesis of $(HOH_2C)_2PCH_2CH_2S(CH_2)_3SCH_2CH_2P(CH_2OH)_2$ (9). Aqueous formaldehyde (78 mmol) was placed in 50 mL of oxygen free ethanol and purged with nitrogen gas for 2 h at 25 °C. Compound **7** (18 mmol) was then added dropwise to the solution *via* syringe with constant stirring at 25 °C. The reaction was complete in 12 h, as monitored by ^{31}P NMR spectroscopy. Removal of the solvent *in vacuo* afforded compound **9** in 96% (6.05 g) yield as a colorless viscous oil. High-resolution FAB/MS Anal. Calcd for $C_{11}H_{26}O_4P_2S_2$: 348.0748. Found: $[M + H^+]$, $m/z = 349.0826$. Anal. Calcd for $C_{11}H_{26}O_4P_2S_2$: C, 37.92; H, 7.53. Found: C, 37.12; H, 6.76. ^{1}H NMR (D_2O): δ 1.80 (m, 6H, PCH_2CH_2, $CH_2CH_2CH_2$), 2.57 (m, 8H, $CH_2CH_2CH_2$, PCH_2CH_2), 3.93 (m, 8H, PCH_2OH). ^{13}C NMR (D_2O): δ 19.6 (d, $^2J_{PC} = 9.1$ Hz, PCH_2CH_2), 27.7 (d, $^1J_{PC} = 18.2$ Hz, PCH_2CH_2), 28.1 (s, $CH_2CH_2CH_2$), 29.7 (s, $CH_2CH_2CH_2$), 57.8 (d, $^1J_{PC} = 9.8$ Hz, PCH_2OH). ^{31}P NMR (D_2O): δ −25.0 (s).

Synthesis of $C_6H_4\{1,2\text{-}SCH_2CH_2P(O)(OEt)_2\}_2$ (6). A sample of 60% NaH in mineral oil (32 mmol) was placed in a two-neck round bottom flask and charged with dry hexane (20 mL). This solution was allowed to stir for 10 min, after which the hexane−mineral oil layer was removed by syringe. The flask was then charged with dry tetrahydrofuran (100 mL), followed by dropwise addition of 1,2-$HS(C_6H_4)SH$ (14 mmol) with constant stirring. The resulting solution was cooled at 0 °C and $BrCH_2CH_2P(O)(OC_2H_5)_2$ (30 mmol) was added dropwise with constant stirring over a period of 30 min. Excess NaH was quenched by addition of 50 mL of deionized water. The solution was extracted from ethyl acetate (3 × 50 mL) and washed with a saturated sodium chloride solution. The organic layer was dried over anhydrous sodium sulfate. Upon filtering, the solvent was removed *in vacuo* to afford **6** in 94% yield along with a trace amount of diethyl vinylphosphonate. The compounds were separated on a silica gel column (20 cm; 60 mesh) using 90:10 ethyl acetate to hexane solvent mixture. Removal of the solvent *in vacuo,* afforded compound **6** as a viscous, yellow-green oil with an overall yield of 91% (6.02 g). High-resolution FAB/MS Anal. Calcd for $C_{18}H_{32}O_6P_2S_2$: 470.1115. Found: $[M + H^+]$, $m/z = 471.1119$. Anal. Calcd for $C_{18}H_{32}O_6P_2S_2$: C, 45.95; H, 6.86. Found: C, 45.72; H, 7.01. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, $^3J_{HH} = 9.0$ Hz, 12H, OCH_2CH_3), 2.02 (m, 4H, PCH_2CH_2), 3.06 (m, 4H, PCH_2CH_2), 4.05 (m, 8H, OCH_2CH_3), 7.2 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 16.3 (d, $^3J_{PC} = 6.0$ Hz, OCH_2CH_3), 25.8 (d, $^1J_{PC} = 136$ Hz, PCH_2CH_2), 26.2 (s, PCH_2CH_2), 61.7 (d, $^2J_{PC} = 6.0$ Hz, OCH_2CH_3), 126.9 (s, *m*-C), 129.5 (s, *o*-C), 136.0 (s, C−S). ^{31}P NMR ($CDCl_3$): δ 29.4 (s).

Synthesis of $C_6H_4\{1,2\text{-}SCH_2CH_2PH_2\}_2$ (8). Compound **6** (12 mmol) was placed in 75 mL of dry diethyl ether and cooled to 0 °C. An ether solution of 1.0 M lithium aluminum hydride (31 mmol, 31 mL) was slowly added dropwise to this solution with constant stirring. An aqueous solution of 6 N hydrochloric acid (50 mL) was added dropwise to the solution to quench any remaining $LiAlH_4$. The ether layer was separated by cannula, and the solvent was removed *in vacuo* to afford **8** in 96% (3.01 g) yield as a colorless viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.81 (s, 4H, PCH_2CH_2), 2.77 (d, 4H, $^1J_{PH} = 196$ Hz, PH_2), 3.07 (m, 4H, PCH_2CH_2), 7.21 (m, 4H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 14.2 (d, $^1J_{PC} = 15.1$ Hz, PCH_2CH_2), 36.4 (s, PCH_2CH_2), 126.6 (s, *m*-C), 129.5 (s, *o*-C), 136.7 (s, C−S). ^{31}P NMR ($CDCl_3$): δ −136.3 (s).

Synthesis of $C_6H_4\{1,2\text{-}SCH_2CH_2P(CH_2OH)_2\}_2$ (10). Aqueous formaldehyde (53 mmol) was placed in 50 mL of oxygen free ethanol and purged with nitrogen gas for 2 h at 25 °C. Compound **8** (12 mmol) was then added dropwise to the solution *via* syringe with constant stirring at 25 °C. The reaction was complete in 30 h, as monitored by ^{31}P NMR spectroscopy. Removal of the solvent *in vacuo* afforded compound **10** in 91% yield as a colorless, viscous oil (4.21 g). High-resolution FAB/MS Anal. Calcd for $C_{14}H_{24}O_4P_2S_2$: 382.0591. Found: $[M + H^+]$, $m/z = 383.0651$. Anal. Calcd for $C_{14}H_{24}O_4P_2S_2$: C, 43.97; H, 6.33. Found: C, 44.23; H, 5.80. ^{1}H NMR (CD_3OD): δ 1.93 (m, 4H, PCH_2CH_2), 3.09 (m, 4H, PCH_2CH_2), 4.02 (d, $^2J_{PH} = 9.0$ Hz, 8H, PCH_2OH), 7.23 (m, 4H, C_6H_4). ^{13}C NMR (CD_3OD): δ 19.4 (d, $^2J_{PC} = 13.0$ Hz, PCH_2CH_2), 29.6 (d, $^1J_{PC} = 21.5$ Hz, PCH_2CH_2), 58.6 (d, $^1J_{PC} = 13.6$ Hz, PCH_2OH), 126.1 (s, *m*-C), 129.0 (s, *o*-C), 136.7 (s, C−S). ^{31}P NMR (CD_3OD): δ −23.3 (s).

Synthesis of $[Pt(HOH_2C)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(CH_2OH)_2](Cl)_2$ (11). An aqueous solution (10 mL) of compound **9** (0.587 mmol) was added dropwise to $Pt(COD)Cl_2$ (0.534 mmol) in dichloromethane (20 mL) at 25 °C with constant stirring. The stirring was continued for 30 min upon which the aqueous phase was separated from the organic phase. After filtration, the aqueous layer was concentrated to ∼5 mL *in vacuo* and allowed to evaporate slowly at room temperature to afford **11** as a clear, microcrystalline solid in 91% yield (0.30 g). FAB/MS Anal. Calcd for $C_{11}H_{26}O_4P_2S_2Pt$: 543.04. Found: $[M + H^+]$, $m/z = 544.04$. Anal. Calcd for $C_{11}H_{26}O_4P_2S_2PtCl_2$: C, 21.53; H, 4.27. Found: C, 21.91; H, 4.43. ^{1}H NMR (D_2O): δ 2.22 (m, 1H, CH_2CHHCH_2) 2.3 (m, 2H, $PCHHCH_2$), 2.67 (m, 2H, $PCHHCH_2$), 2.79 (m, 1H, CH_2CHHCH_2), 2.86 (m, 2H, PCH_2CHH), 3.22 (m, 2H, $CHHCH_2CHH$), 3.63 (m, 2H, PCH_2CHH), 3.71 (m, 2H, $CHHCH_2CHH$), 4.5 (m, 8H, PCH_2OH). ^{13}C NMR (D_2O): δ 23.9 (m, PCH_2CH_2), 25.8 (s, $CH_2CH_2CH_2$), 35.3 (s, PCH_2CH_2), 37.4 (s, $CH_2CH_2CH_2$), 55.9 (m, PCH_2OH). ^{31}P NMR (D_2O): δ 54.8 (s, $^1J_{PtP} = 2780$ Hz).

Synthesis of $[Pd(HOH_2C)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(CH_2OH)_2](Cl)_2$ (12). An aqueous solution (10 mL) of compound **9** (0.424 mmol) was added dropwise to $Pd(C_6H_5CN)_2Cl_2$ (0.386 mmol) in dichloromethane (20 mL) at 25 °C with constant stirring. The stirring was continued for 30 min upon which the aqueous phase was separated from the organic phase. After filtration, the aqueous layer was concentrated to ∼5 mL *in vacuo* and allowed to evaporate slowly at room temperature to afford **12** as a clear, microcrystalline solid in 90% yield (0.18 g). The solid was reconstituted in methanol/diethyl ether, 4:1, and allowed to slowly evaporate to afford X-ray quality crystals. FAB/MS Anal. Calcd for $C_{11}H_{26}O_4P_2S_2Pd$: 453.98. Found: $[M + H^+]$, $m/z = 454.99$. Anal. Calcd for $C_{11}H_{26}O_4P_2S_2PdCl_2$: C, 25.13; H, 4.98. Found: C, 24.87; H, 5.27. ^{1}H NMR (D_2O): δ 2.09 (m, 1H, CH_2CHHCH_2) 2.44 (m, 2H, $PCHHCH_2$), 2.80 (m, 1H, CH_2CHHCH_2), 2.85 (m, 2H, PCH*H*CH$_2$), 2.91 (m, 2H, PCH$_2$C*H*H), 3.28 (m, 2H, C*H*HCH$_2$C*H*H), 3.47 (m, 2H, CH*H*CH$_2$CH*H*), 3.62 (m, 2H, PCH$_2$CH*H*), 4.36 (m, 8H, PC*H*$_2$OH). ^{13}C NMR (D$_2$O): δ 25.3 (m, P*C*H$_2$CH$_2$), 25.8 (s, CH$_2$*C*H$_2$CH$_2$), 35.4 (s, PCH$_2$*C*H$_2$), 36.6 (s, *C*H$_2$CH$_2$*C*H$_2$), 56.4 (m, P*C*H$_2$OH). ^{31}P NMR (D$_2$O): δ 70.2 (s).

Synthesis of [Pt(C_6H_4){1,2-S(CH_2)$_2$P(CH_2OH)$_2$}$_2$](Cl)$_2$ (13). An aqueous solution (10 mL) of compound **10** (0.468 mmol) was added dropwise to Pt(COD)Cl$_2$ (0.425 mmol) in dichloromethane (20 mL) at 25 °C with constant stirring. The stirring was continued for 30 min upon which the aqueous phase was separated from the organic phase. After filtration, the aqueous layer was concentrated to ∼5 mL *in vacuo* and allowed to evaporate slowly at room temperature to afford **13** as a clear, microcrystalline solid in 93% yield (0.25 g). FAB/MS Anal. Calcd for $C_{14}H_{24}O_4P_2S_2Pt$: 577.02. Found: [M + H$^+$], *m/z* = 578.03. Anal. Calcd for $C_{14}H_{24}O_4P_2S_2PtCl_2$: C, 25.97; H, 3.74. Found: C, 24.85; H, 4.01. ^{1}H NMR (D$_2$O): δ 2.82 (m, 8H, PC*H*$_2$CH$_2$, PCH$_2$C*H*$_2$), 4.51 (m, 8H, PC*H*$_2$OH), 7.68 (m, 4H, C$_6$H$_4$). ^{13}C NMR (D$_2$O): δ 23.0 (m, P*C*H$_2$CH$_2$), 41.5 (m, PCH$_2$*C*H$_2$), 55.6 (m, P*C*H$_2$OH), 130.5 (s, *m*-C), 131.1 (s, *o*-C), 133.9 (s, C−S). ^{31}P NMR (D$_2$O): δ 52.0 (s, $^1J_{PtP}$ = 2897 Hz).

Synthesis of [Pd(C_6H_4){1,2-S(CH_2)$_2$P(CH_2OH)$_2$}$_2$](Cl)$_2$ (14). An aqueous solution (10 mL) of compound **10** (0.650 mmol) was added dropwise to Pd(C$_6$H$_5$CN)$_2$Cl$_2$ (0.591 mmol) in dichloromethane (20 mL) at 25 °C with constant stirring. The stirring was continued for 30 min upon which the aqueous phase was separated from the organic phase. After filtration, the aqueous layer was concentrated to ∼5 mL *in vacuo* and allowed to evaporate slowly at room temperature to afford **14** as a clear, microcrystalline solid in 91% yield (0.30 g). FAB/MS Anal. Calcd for $C_{14}H_{24}O_4P_2S_2Pd$: 487.96. Found: [M + H$^+$], *m/z* = 488.96. Anal. Calcd for $C_{14}H_{24}O_4P_2S_2PdCl_2$: C, 30.11; H, 4.34. Found: C, 29.82; H, 4.96. ^{1}H NMR (D$_2$O): δ 2.92 (m, 8H, PC*H*$_2$CH$_2$, PCH$_2$C*H*$_2$), 4.42 (m, 8H, PC*H*$_2$OH), 7.5 (m, 4H, C$_6$H$_4$). ^{13}C NMR (D$_2$O): δ 15.9 (s, P*C*H$_2$CH$_2$), 52.9 (s, PCH$_2$*C*H$_2$), 56.6 (s, P*C*H$_2$OH), 130.2−130.8 (aromatic). ^{31}P NMR (D$_2$O): δ 70.6 (s).

Potentiometric Analysis of 11 and 12. Each of the compounds **11** (0.019 04 g) and **12** (0.023 58 g) were dissolved in ∼20 mL of deionized water to afford solution concentrations of 0.9587 and 1.429 g/L, respectively. The conductivity of each solution was measured using a Checkmate Conductivity/TDS Sensor from Corning Inc., using a 1413 μS KCl standard as an external reference.

X-ray Data Collection and Processing. The crystal data and the details of data collection for complex **12** are listed in Table 2. Clear, yellow crystals of **12** suitable for X-ray diffraction were obtained by slow evaporation from methanol/diethyl ether, 4:1. Intensity data were collected on a Siemens SMART CDD system using the ω scan mode. Data were corrected for absorption using the program SADABS which is based on the method of Blessing.[26] Crystal decay was less than 1% and a correction deemed unnecessary. The structure was solved by direct methods using SHELXS-86[27] and refined by the full-matrix least-squares method on F2 using SHELXL-93.[28]

All non-hydrogen atoms were refined anisotropically, and C−H hydrogen atoms were placed in calculated positions. Water and hydroxyl hydrogen atoms were located in difference electron density maps and refined with their O−H distances restrained to 1.0 ± 0.1 Å. All hydrogen atom thermal parameters were fixed at values of 1.2 those of their parent atoms.

Table 2. Crystal Data for Complex **12**

formula	$C_{11}H_{28}Cl_2O_5P_2PdS_2$
space group	$P\bar{1}$ (No. 2)
fw	543.69
a, Å	9.9761(6)
b, Å	10.2049(7)
c, Å	11.6954(7)
α, deg	67.730(1)
β, deg	69.943(1)
γ, deg	79.828(1)
T, K	293(2)
λ,Å	0.710 70
Z	2
F(000)	552
V, Å^3	1033.52(11)
ρ_{calc}, g/cm^3	1.747
ρ_{obsd}, g/cm^3	not measured
μ, mm^{-1}	1.530
R_1, R_{w2}[a]	0.031, 0.080

[a] R_1 factor definition: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. SHELXL−93 R_{w2} factor definition: $R_{w2} = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$. Weighting scheme: $w = 1/[\sigma 2(F_o)^2 + (np)^2 + 0.00p]$, $p = (\max(F_o{}^2) + 2F_c{}^2)/3$.

Other pertinent details relating to data collection, structure solution, and refinement are give in Table 2.

Acknowledgment. This work was supported by funds provided by the Department of Energy Grant No. DEFG0289E R60875 and the Departments of Chemistry, Radiology, and Research Reactor, University of Missouri. Partial funding of the X-ray diffractometer by the National Science Foundation, Grant No. CHE[90-11804], is gratefully acknowledged. We would like to thank Dr. H. Jimenez for his assistance in 2D NMR investigations and Dr. Rhys Thomas at Fayette Environmental Services, Inc., for performing the conductivity measurements. Special thanks is also given to D. E. Berning for his assistance in the study. The encouragements of Professor W. A. Volkert and Dr. A. R. Ketring are gratefully acknowledged. We would like to thank the reviewers for their helpful suggestions.

Supporting Information Available: Text describing data collection details and 2D NMR analysis, tables giving complete crystallographic experimental details, distances and angles, positional parameters for all atoms, anisotropic thermal parameters, and hydrogen atom coordinates of **11** and figures showing a thermal ellipsoid plot, hydrogen bonding within the unit cell, and cross-correlation spectra (13 pages). Ordering information is given on any current masthead page.

IC961319G

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(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(27) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(28) Sheldrick, G. M. *Program for Crystal Structure Refinement*. University of Göttingen: Göttingen, Germany, 1993.