Syntheses and Structures of Silver(I) and Palladium(II) Complexes with Ferrocenyl-phosphonodithiolate Ligands

Xi-Ying Wang, Hua-Tian Shi, Qing Ma, and Qian-Feng Zhang

Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology,
Ma'anshan, Anhui 243002, P. R. China

Reprint requests to Dr. Qian-Feng Zhang. Fax: +86-555-2312041. E-mail: zhangqf@ahut.edu.cn

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Coordinative interaction of $[Ag(PPh_3)_2NO_3]$ or $[Pd(MeCN)_2Cl_2]$ with *in situ*-prepared $Na[FcP(OR)S_2]$ afforded 1 : 1 products $[FcP(OR)S_2Ag(PPh_3)_2]$ (R = Me **1**, *n*-Pr **2**) or the 1 : 2 product $[\{FcP(OMe)S_2\}_2Pd]$ (**3**). Complexes **1** – **3** were characterized by elemental analysis, mass spectrometry, NMR (^{1}H, ^{31}P) and IR spectroscopy, as well as by X-ray crystallography. The distorted tetrahedral silver(I) coordination led to non-planar and distorted four-membered AgS_2P rings in **1** and **2**, whereas the square-planar palladium(II) coordination resulted in four-membered co-planar PdS_2P rings in **3**.

Key words: Synthesis, Crystal Structure, Ferrocenyl-dithiophosphonate, Heterobimetallic Complex

Introduction

Organophosphorus-containing dithiolato-type compounds are of interest due to their agricultural and industrial applications [1, 2]. From the point of view of coordination chemistry, dithiophosphonates are bidentate ligands which can form stable complexes with transition metal ions. Since Woollins reported the dithiodiphosphetane disulfide $[FcP(S)(\mu\text{-}S)]_2$ [Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$] as an analog of Lawesson's reagent (LR) $[AnP(S)(\mu\text{-}S)]_2$ (An = 4-anisyl), the study of phosphonodithiolate derivatives in the field of ferrocene chemistry has been actively extended [3 – 5]. For example, a series of new ferrocenyl-phosphonothiolate derivatives were successfully isolated from the reactions of $[FcP(S)(\mu\text{-}S)]_2$ with alcohols or sodium alkoxides, silanols, dienes, alkenes, cyanamides, aminoethanols, and catechols [3, 6 – 11]. The typical ferrocenyl-dithiophosphonate $[FcP(OR)S_2]^-$ anions (R = alkyl, aryl) may directly react with a range of metal ions (Au^+, Rh^+, Ni^{2+}, Pd^{2+}, Pt^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Sn^{4+}, and Pb^{2+}), resulting in the formation of new heterometallic complexes containing the electron-rich and aromatic ferrocene groups [3 – 5, 8]. So far, the use of these ferrocenyl-phosphonodithiolate ligands as synthons for polynuclear metal clusters has been largely overlooked. Here we report the reactions of $[Ag(PPh_3)_2]^+$ and $[Pd(MeCN)_2]^{2+}$ species with $[FcP(S)(\mu\text{-}S)]_2$ in the presence of sodium methoxide or sodium *n*-proproxide. The molecular structures of $[FcP(OMe)S_2Ag(PPh_3)_2]$ (**1**), $[FcP(On\text{-}Pr)S_2Ag(PPh_3)_2]$ (**2**), and $[FcP(OMe)S_2]_2Pd$ (**3**) are also presented in this paper.

Experimental Section

Generals

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. All reagents, unless otherwise stated, were purchased as analysis grade and were used without further purification. $[FcP(S)(\mu\text{-}S)]_2$ [3] and $Pd(MeCN)_2Cl_2$ [12] were prepared according to procedures described in the literature. $[Ag(PPh_3)_2(NO_3)]$ was obtained from the reaction of PPh_3 with $AgNO_3$ in $CH_3OH : CH_2Cl_2$ (2 : 1) solution. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) are reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P), respectively. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with the use of pressed KBr pellets, and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. Elemental analysis was performed using a Perkin-Elmer 2400 CHN analyzer.

Syntheses

$[FcP(OMe)S_2Ag(PPh_3)_2]$ (1)

To a slurry of $[FcP(S)(\mu\text{-}S)]_2$ (112 mg, 0.20 mmol) and CH_3ONa (22 mg, 0.40 mmol) in methanol (10 mL) was added a solution of $[Ag(PPh_3)_2NO_3]$ (278 mg, 0.40 mmol)

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Table 1. Crystal data, data collection parameters and details of the structure refinement of complexes **1** – **3**.

	1	**2**	**3**
Empirical formula	$C_{47}H_{42}OP_3S_2FeAg$	$C_{49}H_{46}OP_3S_2FeAg$	$C_{22}H_{24}O_2P_2S_4Fe_2Pd$
Formula weight	943.56	971.61	728.69
Color, habit	orange, block	orange, block	orange, block
Crystal size, mm^3	$0.29 \times 0.22 \times 0.14$	$0.55 \times 0.45 \times 0.38$	$0.26 \times 0.19 \times 0.12$
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	17.6541(3)	10.4014(2)	10.0083(1)
b, Å	21.0026(4)	11.4684(2)	11.6216(1)
c, Å	11.6711(2)	19.7555(4)	12.2022(1)
α, deg	90	83.727(1)	90
β, deg	70.723(1)	80.158(1)	109.04(1)
γ, deg	90	76.857(1)	90
Volume, Å^3	4327.09(13)	2254.99(7)	1341.65(2)
Z	4	2	2
Density (calcd.), g cm^{-3}	1.45	1.43	1.80
Absorption coefficient, mm^{-1}	1.0	1.0	2.2
Temperature, K	296(2)	296(2)	296(2)
$F(000)$, e	1928	996	728
Radiation; λ, Å	MoK_α; 0.71073	MoK_α; 0.71073	MoK_α; 0.71073
Reflections collected	43066	41830	12723
Independent reflections / R_{int}	9933 / 0.0119	10334 / 0.0184	3063 / 0.0192
Reflections with $I \geq 2\sigma(I)$	8547	9153	2775
Parameters refined	497	514	153
Final $R1/wR2$ indices (all data)[a]	0.034 / 0.068	0.031 / 0.070	0.025 / 0.055
Goodness of fit (GoF)[b]	1.01	1.01	1.04
Final max / min difference peaks, e Å^{-3}	+0.49 / −0.39	+0.38 / −0.39	+0.37 / −0.29

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + aP^2 + bP]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$, a = 0.0317 and b = 2.0123 for **1**, a = 0.0375 and b = 0.8186 for **2**, and a = 0.0265 and b = 0.4332 for **3**; [b] GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

in THF (15 mL). The mixture was stirred at r. t. for 4 h. The solvents were pumped off, and the residue was recrystallized from CH_2Cl_2/hexane to give an orange crystalline solid within five days. Yield: 284 mg (76 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (d, *J*(P,H) = 8.46 Hz, 3H, OCH_3), 4.41 (s, 5H, C_5H_5 in Fc), 4.53 (m, 4H, C_5H_4 in Fc), 7.21 – 7.49 (m, 30H, *Ph*). – ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 43.2 (s, 1P, *P*Ph_3), 111.3 (s, 1P, Fc*P*S_2). – Selected IR bands (KBr, cm^{-1}): ν(P–O–C) 1189 (m) and 1027 (s), ν(P–S) 633 (s) and 579 (s), ν(P–C) 523 (s) 512 (s) and 483 (m). – MS (FAB): *m/z* = 943 [M]$^+$, 681 [M–PPh_3]$^+$, 419 [M–2PPh_3]$^+$. – Anal. for $C_{47}H_{42}OP_3S_2FeAg$: calcd. C 59.81, H 4.49; found C 59.27, H 4.45.

*[FcP(O^{n}Pr)S_2Ag(PPh_3)$_2$] (**2**)*

To a slurry of [FcP(S)(μ-S)]$_2$ (112 mg, 0.20 mmol) and *n*-PrONa (33 mg, 0.40 mmol) in *n*-PrOH (5 mL) was added a solution of [Ag(PPh_3)$_2$$NO_3$] (278 mg, 0.40 mmol) in THF (15 mL). The mixture was stirred at r. t. for 6 h. The solvents were pumped off, and the residue was recrystallized from CH_2Cl_2/hexane to give an orange crystalline solid within a week. Yield: 273 mg (71 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, 3H, CH_3), 1.56 (m, 2H, CH_2), 4.39 (m, 2H, CH_2O), 4.44 (s, 5H, C_5H_5 in Fc), 4.51 (m, 4H, C_5H_4 in Fc), 7.23 – 7.46 (m, 30H, *Ph*). – ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 41.7 (s, 1P, *P*Ph_3), 109.2 (s, 1P, Fc*P*S_2). – Selected IR bands (KBr, cm^{-1}): ν(P–O–C) 1186 (m) and 1025 (s), ν(P–S) 636 (s) and 574 (s), ν(P–C) 527 (s), 511 and (s) 488 (m). – MS (FAB): *m/z* = 971 [M]$^+$, 709 [M–PPh_3]$^+$, 447 [M–2PPh_3]$^+$. – Anal. for $C_{49}H_{46}OP_3S_2FeAg$: calcd. C 60.62, H 4.77; found C 60.44, H 4.72.

*[FcP(OMe)S_2]$_2$Pd (**3**)*

To a slurry of [FcP(S)(μ-S)]$_2$ (112 mg, 0.20 mmol) and CH_3ONa (22 mg, 0.40 mmol) in methanol (10 mL) was added a solution of [Pd(MeCN)$_2$$Cl_2$] (52 mg, 0.20 mmol) in MeCN (10 mL). The mixture was stirred at r. t. for 1 h. The solvents were pumped off, and the residue was recrystallized from CH_2Cl_2/hexane to give an orange crystalline solid within three days. Yield: 86 mg (56 %). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (d, *J*(P,H) = 8.02 Hz, 3H, OCH_3), 4.41 (s, 5H, C_5H_5 in Fc), 4.48 (m, 4H, C_5H_4 in Fc). – ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 119.5. – Selected IR bands (KBr, cm^{-1}): ν(P–O–C) 1189 (m) and 1027 (s), ν(P–S) 634 (s) and 574 (s), ν(P–C) 528 (s), 515 (s) and 485 (m). – MS (FAB): *m/z* = 728 [M]$^+$. – Anal. for $C_{22}H_{24}O_2P_2S_4Fe_2Pd$: calcd. C 36.22, H 3.32; found C 36.14, H 3.29.

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **1**, **2** and **3**[a].

Complexes	**1** (M = Ag)	**2** (M = Ag)	**3** (M = Pd)
M(1)–S(1)	2.8298(5)	2.7574(6)	2.3439(5)
M(1)–S(2)	2.6056(5)	2.6061(5)	2.3486(6)
Ag(1)–P(2)	2.4747(5)	2.4644(4)	
Ag(1)–P(3)	2.4743(5)	2.4593(4)	
P(1)–S(1)	1.9843(7)	1.9742(7)	2.0100(7)
P(1)–S(2)	1.9940(7)	1.9986(6)	2.0135(7)
P(1)–O(1)	1.6051(14)	1.6016(16)	1.5785(14)
S(1)–Ag(1)–S(2)	75.176(15)	76.503(15)	
P(2)–Ag(1)–S(1)	102.174(17)	100.45(2)	
P(2)–Ag(1)–S(2)	115.776(17)	119.137(16)	
P(3)–Ag(1)–S(1)	109.903(18)	112.20(2)	
P(3)–Ag(1)–S(2)	114.700(18)	119.137(16)	
P(2)–Ag(1)–P(3)	125.231(17)	124.399(15)	
P(1)–S(1)–M(1)	82.49(2)	82.99(2)	84.96(2)
P(1)–S(2)–M(1)	88.41(2)	86.62(2)	84.76(2)
S(1)–Pd(1)–S(2)			84.437(18)
S(1)–Pd(1)–S(1)$^{\#1}$			180.0
S(1)–Pd(1)–S(2)$^{\#1}$			95.563(18)
S(1)–P(1)–S(2)	113.14(3)	113.52(3)	103.20(3)
O(1)–P(1)–S(1)	112.75(7)	113.62(7)	114.56(7)
O(1)–P(1)–S(2)	110.10(7)	109.18(7)	112.68(6)

[a] Symmetry operation: $^{\#1}$ $-x, -y+2, -z$.

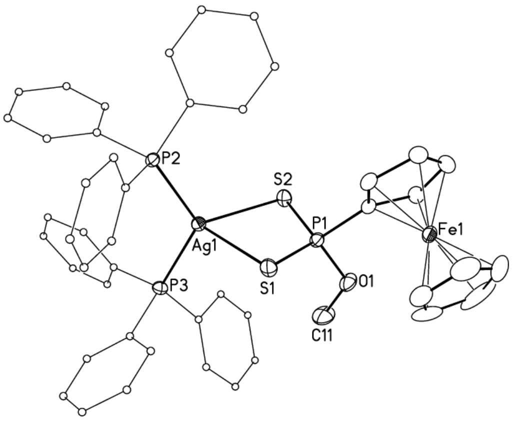

Fig. 1. Molecular structure of [FcP(OMe)S_2Ag(PPh_3)$_2$], **1**, with hydrogen atoms omitted for clarity.

Crystal structure determination

Single crystals of **1** (0.29 × 0.22 × 0.20 mm^3), **2** (0.55 × 0.45 × 0.38 mm^3) and **3** (0.26 × 0.19 × 0.12 mm^3) were mounted in random orientation on glass fibers. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 296 K using an ω scan mode. The collected frames were processed with the software SAINT [13]. The data were corrected for absorption using the program SADABS [14]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [15]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically ($C_{sp^3}-H$ = 0.96 and $C_{sp^2}-H$ = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters, but were not refined. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

CCDC 749601, 749602, and 749603 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The cleavage reaction of dimeric [FcP(S)(μ-S)]$_2$ with sodium alkoxide is known to give stable phosphonodithiolate salts Na[FcP(OR)S_2] for ligation to various metals [3, 5, 8]. Reaction of [Ag(PPh_3)$_2NO_3$] with *in situ*-prepared Na[FcP(OR)S_2] in THF afforded a clear orange solution from which an orange crystalline solid of [FcP(O*R*)S_2Ag(PPh_3)$_2$] (*R* = Me **1**, *n*-Pr **2**) was isolated. Complexes **1** and **2** were stable both as solid and in solution. Two ^{31}P signals at δ(P) = 43.2 and 111.3 ppm for **1** can be assigned to the [Ag(PPh_3)$_2$]$^+$ and [FcP(OMe)S_2]$^-$ units, respectively. Similarly, two single peaks at δ(P) = 41.7 and 109.2 ppm in the ^{31}P NMR spectrum of **2** may be ascribed to the two types of phosphorus atoms with different coordination environments. The ^{1}H NMR spectra of **1** and **2** confirmed the presence of the ferrocenyl moieties and the corresponding alkoxides. The IR spectra of the two complexes clearly showed two sets of strong bands at *ca.* 1187 and 1025, and 635 and 576 cm^{-1} which may be attributed to ν(P–O–C) and ν(P–S) absorptions, respectively. The three strong peaks in the range of 480–530 cm^{-1} for the ν(P–C) stretching vibrations indicated the presence of PPh_3 in the two complexes. Mass spectrometry showed the expected three ions [M]$^+$, [M–PPh_3]$^+$ and [M–2PPh_3]$^+$ with the characteristic isotopic distribution patterns.

The structures of the complexes **1** and **2** were determined by room-temperature single-crystal X-ray diffraction. The results are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are compiled in Table 2 for comparison. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with four neutral molecules in the cell, while complex **2** crystallizes in the triclinic space group $P\bar{1}$ with two neutral molecules in the cell. The silver

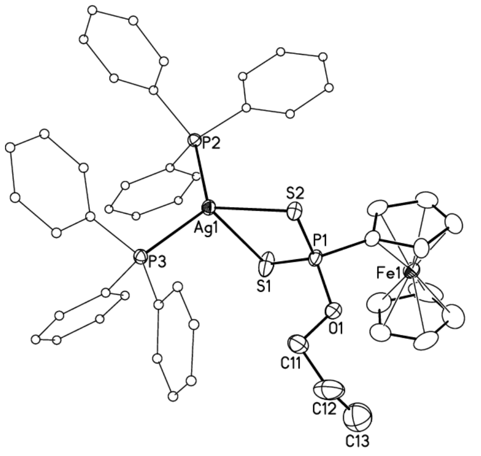

Fig. 2. Molecular structure of [FcP(O^{n}Pr)S$_2$Ag(PPh$_3$)$_2$], **2**, with hydrogen atoms omitted for clarity.

atoms in both complexes are in a tetrahedral geometry with some angle distortions, namely the narrow S(1) – Ag(1) – S(2) angles of 75.176(15)° for **1** and 76.503(15)° for **2** and wide P(2) – Ag(1) – P(3) angles of 125.231(17)° for **1** and 124.399(15)° for **2**, and are coordinated by the two sulfur atoms of one *S*,*S*-bidentate ligand. The four-membered AgS$_2$P rings are non-planar and distorted. Each ring contains a pair of long and short Ag – S bonds [Ag(1) – S(1) = 2.8298(5) Å (“long”) and Ag(1) – S(2) = 2.6056(5) Å (“short”) for **1**, and Ag(1) – S(1) = 2.7574(6) Å (“long”) and Ag(1) – S(2) = 2.6061(5) Å (“short”) for **2**]. The average Ag – S bond lengths in **1** (av. 2.7177(5) Å) and **2** (av. 2.6818(5) Å) are comparable to those found in other tetrahedral complexes such as [Ag(PPh$_3$)$_2${S$_2$P(O*i*-Pr)$_2$}] (2.654(2) – 2.683(2) Å) [16], [Ag(PPh$_3$)$_2$(S$_2$COEt)] (2.549(4) – 2.806(4) Å) [17], and [Ag(PPh$_3$)$_2${Fc(S$_2$CNEt$_2$)$_2$}]OTf (OTf = triflate, CF$_3$SO$_3$) (2.6047(6) – 2.7025(6) Å) [18]. The average Ag – P bond lengths of 2.4745(5) Å in **1** and 2.4619(4) Å in **2** are similar to that of 2.4690(6) Å in [Ag(PPh$_3$)$_2${Fc(S$_2$CNEt$_2$)$_2$}]OTf [18], but slightly longer than those in some mononuclear silver(I)-PPh$_3$ complexes with tetra-coordinate silver centers such as [Ag(PPh$_3$)$_2${S$_2$P(O^{i}Pr)$_2$}] (av. 2.449(1) Å) [16] and [Ag(PPh$_3$)$_2$(S$_2$COEt)] (av. 2.441(1) Å) [17]. The two P – S bonds are nearly equal in length [P(1)–S(1) = 1.9843(7) and P(1)–S(2) = 1.9940(7) Å for **1**, and P(1)–S(1) = 1.9742(7) and P(1)–S(2) = 1.9986(6) Å for **2**] and have a partial π character.

Treatment of [Pd(MeCN)$_2$Cl$_2$] with *in situ*-prepared Na[FcP(OMe)S$_2$] in MeCN/MeOH gave the substituted complex [{FcP(OMe)S$_2$}$_2$Pd] (**3**) as an orange solid in a yield of 56 %. A similar square-planar palladium(II) complex [{FcP(OEt)S$_2$}$_2$Pd] has been previously reported by Woollins and coworkers [5]. The ^{31}P NMR spectrum displayed a sharp singlet at δ(P) = 119.5 ppm whilst the ^{1}H NMR spectrum was as expected confirming the presence of both the ferrocenyl and ethoxy moieties. The IR spectrum of **3** shows distinct bands at 1189 and 1027, 634 and 574 cm^{-1} corresponding to ν(P – O – C) and ν(P – S) absorptions, respectively. The mass spectrum of **3** shows the molecular ion as [M$^+$] at *m/z* = 728. The structure of **3** is shown in Fig. 3, and selected bond lengths and angles are given in Table 2. The central palladium atom resides on a crystallographic inversion center and is coordinated by four sulfur atoms of the [FcP(OMe)S$_2$]$^-$ ligand, forming symmetric PdS$_2$P rings in a square-planar geometry. The ferrocenyl groups of the two bound ligands are in a *trans* arrangement. In **3**, the average Pd – S bond length is 2.3462(6) Å, and the bite angle S – Pd – S is 84.437(18)°, which agrees well with those in the similar complex [{FcP(OEt)S$_2$}$_2$Pd] [av. 2.355(3) Å, 84.211(10)°] [5]. The P – S bond lengths are almost equal and indicative of multiple bonding [2.0100(7) and 2.0135(7) Å], as expected for a delocalized system. A relatively short transannular Pd $\cdots$ P distance is observed in **3** (2.9507(2) Å), similar to that found in [{FcP(OEt)S$_2$}$_2$Pd] (2.9501(3) Å) [5].

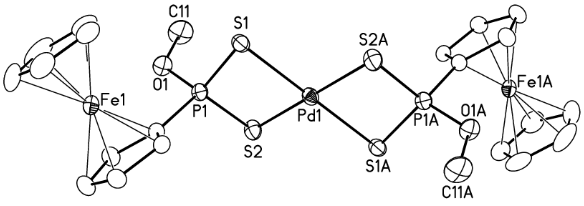

Fig. 3. Molecular structure of [FcP(OMe)S$_2$]$_2$Pd, **3**, with hydrogen atoms omitted for clarity.

In summary, three silver(I) and palladium(II) complexes with ferrocenylphosphonodithiolate ligands have been prepared and characterized. The crystal structures of the three complexes indicate that the *S*,*S*-bidentate [FcP(OMe)S$_2$]$^-$ anion acts as a chelating ligand for the metal atoms rather than as a bridging ligand. The reactions of [Ag(PPh$_3$)$_2$]NO$_3$ with [FcP(OR)S$_2$]$^-$ gave 1 : 1 products [FcP(OR)S$_2$Ag(PPh$_3$)$_2$] (R = Me **1**, *n*-Pr **2**), whereas the reaction of [Pd(MeCN)$_2$Cl$_2$] with [FcP(OR)S$_2$]$^-$ resulted in a 1 : 2 product [{FcP(OMe)S$_2$}$_2$Pd] (**3**). Thus, this work clearly demonstrates the coordination behavior of ferrocenylphosphonodithiolates as *S,S*-bidentate ligands towards transition metal ions. More coordination reactions involving functional $[FcP(OR)S_2]^-$ ligands are in active study in this laboratory.

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