

Ruthenium Complexes with Dithiophosphonates [Ar(RO)PS₂]⁻ and $[Fc(RO)PS_2]^-$ (År = p-CH_3OC_6H_4, Fc = Fe(η^{5} -C₅H₄)(η^{5} -C₅H₅))

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Treatment of dimeric $[(\eta^6-p-\text{cymene})\text{RuCl}(\mu-\text{Cl})]_2$ with Lawesson's reagent $[\text{ArP}(S)(\mu-S)]_2$ (Ar = $p-C_6H_4OMe$) in THF gave $[(\eta^6-p-cymene)Ru\{\mu-\eta^1(S),\eta^2(S,S')-ArP(S)S_2\}]_2$ (1) as the sole isolable product. The chlorides in the starting ruthenium compound were substituted by $[ArP(S)S_2]^2$ as a bridging dithiolato ligand. Interactions of [Ru(PPh₃)₃Cl₂] and [RuHCl(CO)(PPh₃)₃] with Lawesson's reagent in the presence of ammonium hydroxide gave the dinuclear neutral complexes [Ru(μ - η^{1} - $(O), \eta^{1}(S), \eta^{1}(S, S')$ -ArPOS₂)(PPh₃)₂]₂(**2**) and [Ru(CO)(μ - $\eta^{1}(O), \eta^{2}(S, S')$ -ArPOS₂)(PPh₃)]₂(**3**), respectively, in which the $[ArPOS_2]^{2-}$ ligands bind the two Ru atoms via both sulfur and oxygen atoms. Reaction of dimeric $[Cp*Ru(OMe)]_2$ ($Cp* = \eta^5 - C_5Me_5$) with Lawesson's reagent in the presence of ammonium hydroxide led to isolation of a novel ruthenium(IV) complex, $[Cp*Ru{(ArPS_2O)_2H}](4)$. Reaction of [Ru(PPh₃)₃Cl₂] or [RuHCl(CO)(PPh₃)₃] with Na[FcP(OMe)S₂], which was prepared from $[FcP(S)(u-S)]_2$ (Fc = Fe(η^3 -C₅H₄)(η^3 -C₅H₅)) and MeONa in methanol, gave the neutral mononulcear complexes cis-[Ru{Fc(OCH₃)PS₂}₂(L')(PPh₃)] (L' = PPh₃ 5, CO 6). Interaction of [Ru(PPh₃)₃Cl₂] or [RuHCl(CO)(PPh₃)₃] with [FcP(S)(µ-S)]₂ in the presence of ammonium hydroxide in THF gave $[Ru{Fc(OH)PS_2}_2(L')(PPh_3)]$ (L' = PPh₃ 7, CO 8). Treatment of $[(\eta^6-p-cymene) \operatorname{RuCl}(\mu$ -Cl)₂ with [FcP(OH)S(SH)] in the presence of excess NaHCO₃ led to isolation of [(η^6 p-cymene)Ru{ $\eta^1(S), \eta^2(S, S')$ -FcPS₂OP(S)SFc] (9). The crystal structures of 1, 2, 3 · CH₂Cl₂·THF, $4 \cdot CH_2Cl_2 \cdot 0.5H_2O$, 6, $7 \cdot CH_2Cl_2 \cdot 3/4C_6H_{14}$, and $9 \cdot CH_2Cl_2$ along with their spectroscopic properties are reported.

Introduction

Ruthenium-sulfur complexes with sulfur-donor ligands are well known for their industrial applications in hydrodesulfurization (HDS) and related processes,^{1,2} partly because of the high catalytic activity of RuS₂ in various hydrogenation processes.^{3,4} The chemistry of ruthenium complexes with dithioacid-based ligands such as dithiocarbamate and dithiocarbonate has been the subject of continuous study to

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date;⁵⁻⁹ however, the corresponding chemistry of dithiophosphate and dithiophosphonate has not been well developed.^{9,10} Indeed, thiophosphorus species are an important class of sulfur-donor ligands.¹¹ For example, the notable Lawesson's dimer $[(p-C_6H_4OMe)P(S)(\mu-S)]_2$ can undergo a ring-opening reaction by nucleophilic attack under suitable conditions, resulting in formation of the typical dithiophosphate and dithiophosphonate ligands.^{12–14} Even though the synthesis and characterization of thiophosphorus ligands $[(RO)_2PS_2]^$ and $[(RO)RPS_2]^-$ of a few transition metal derivatives have been investigated in depth, $^{11-18}$ very little is known about the chemistry of ruthenium-dithiophosphonate and -dithiophosphonate complexes.^{9,10} Similarly, although the coordinative

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behavior of ferrocenyl-dithiophosphonate $[FcP(OR)S_2]^-$ (R = Me, Et, *i*-Pr, and CH₂C₆H₄N₃, Fc = Fe(η^{2} -C₅H₄)(η^{2} -C₅H₅)) with transition metals was recently studied by Woollins and Süss-Fink et al.,^{19–22} no ruthenium complex with ferrocenylphosphonodithiolate as a dithio ligand has been reported to date.

Recently, Woollins and co-workers successfully developed a series of metal complexes with the bidentate chelating ligands $[N(R_2PQ)_2]^-$ (Q = O, S, Se; R = alkyl or phenyl), which exhibit interesting stereochemistry.²³ We studied the coordinatively unsaturated ruthenium-sulfur complexes Ru[N(R2PS)2]2-(PPh₃) (R = Ph, *i*-Pr), which are capable of activating H₂, SO₂, and hydrazine.^{24,25} Five-coordinate ruthenium-sulfur carbene complexes Ru[N(R₂PS)₂]₂(=CHPh) were found to be active catalysts for the ring-opening polymerization of norbornene.²⁶ As part of our ongoing studies of ruthenium-sulfur complexes, we are interested in the coordination properties of phosphorus-1,1-dithiolates as a general class of ligands toward ruthenium. The versatile bonding and structural features as well as fascinating chemical and electrochemical reactivities of ruthenium 1,1dithiolates complexes have prompted us to make a systematic study of ruthenium dithiophosphonate complexes.⁸ The synthesis and crystal structures of ruthenium-dithiophosphonate complexes, obtained from the a series of reactions of ruthenium compounds such as [Ru(PPh₃)₃Cl₂], [RuHCl(CO)(PPh₃)₃], [$(\eta^{6}$ *p*-cymene)RuCl(μ -Cl)]₂, and [Cp*Ru(OMe)]₂ (Cp* = η^5 -C₅Me₅) with dithiophosphonates [Ar(RO)PS2] and [Fc(RO)PS2] $(Ar = p-CH_3OC_6H_4, Fc = Fe(\eta^5-C_5H_4)(\eta^5-C_5H_5)), respec$ tively, will be reported in this paper.

Experimental Section

General Considerations. All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. Lawesson's reagent, $[ArP(S)(\mu-S)]_2$ (Ar = p-CH₃OC₆H₄), was purchased from Aldrich and used without further purfication. $[FcP(S)(\mu-S)]_2$,¹⁹ [Ru(PPh₃)₃Cl₂],²⁷ [RuHCl(CO)(PPh₃)₃],²⁸ [(η^6 - *p*-cymene)RuCl(μ -Cl)]₂,²⁹ and [Cp*Ru(OMe)]₂³⁰ were prepared according to literature methods. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ¹H and ³¹P, respectively. Chemical shifts (δ , ppm) were reported with reference to SiMe₄ (¹H) and H_3PO_4 (³¹P). 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.

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Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

Preparation of $[(\eta^6 - p\text{-cymene}) \operatorname{Ru} \{\mu - \eta^1(S), \eta^2(S, S') - \operatorname{ArP}(S) S_2\}]_2$ (1). To a solution of Lawesson's reagent (82 mg, 0.20 mmol) in THF (10 mL) was added a solution of $[(\eta^6-p-\text{cymene})\text{RuCl}-(\mu-\text{Cl})]_2$ (122 mg, 0.20 mmol) in THF (10 mL). The mixture was heated at reflux for 1 h. The solvent was removed in vacuo, and the residue was recrystallized from CH₂Cl₂/hexane to give orange crystalline solids in two days at room temperature. Yield: 113 mg, 0.12 mmol, 56% (based on Ru). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.34 (d, 6H, CH(CH₃)₂), 2.15 (s, 3H, PhCH₃), 3.04 (septet, 1H, CH(CH₃)₂), 3.74 (s, 6H, OCH₃), 5.40 and 5.68 (dd, 4H, J = 8.2 Hz, aryl H in cymene), 6.79 (d, 4H, J = 7.6 Hz, aryl H),7.72–7.90 (dd, 4H, J = 7.7 Hz, aryl H). ³¹P{¹H} NMR (121.5 MHz, $CDCl_3$): δ (ppm) 84.2 (s) ppm. Selected IR (KBr, cm⁻): 1582 (s), 1432 (s), 1246 (s), 685 (s), 558 (s), 534 (m), 501 (s). MS (FAB): m/z 939 [M⁺], 468 [$^{1}/_{2}$ M⁺ – 1]. Anal. Calcd for C₃₄H₄₂-O₂P₂S₆Ru₂: C, 43.5; H, 4.51. Found: C, 43.3; H, 4.47.

Preparation of $[\operatorname{Ru}(\mu - \eta^{1}(O), \eta^{1}(S), \eta^{1}(S, S') - \operatorname{ArPOS}_{2})(\operatorname{PPh}_{3})_{2}]_{2}$ (2). To a slurry of Lawesson's reagent (41 mg, 0.10 mmol) and 17% NH₃·H₂O (0.2 mL) in THF (10 mL) was added a solution of [Ru(PPh₃)₃Cl₂] (192 mg, 0.20 mmol) in THF (10 mL). The mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo, and the residue was recrystallized from CH₂Cl₂/hexane to give orange crystalline solids in three days at room temperature. Yield: 95 mg, 0.06 mmol, 56% (based on Ru). ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.74 (s, 6H, OCH_3), 6.71 (d, 4H, J = 7.6 Hz, aryl H), 7.24-7.47 (m, 60H, PPh₃), 7.82–8.04 (dd, 4H, J = 7.6 Hz, aryl H). ³¹P{¹H} NMR (121.5 MHz, $CDCl_3$): δ (ppm) 36.9 (s, 4P, PPh₃), 59.3 (s, 2P, ArPS₂O). Selected IR (KBr, cm⁻¹): 1587 (s), 1431 (s), 1245 (s), 1022 (s), 676 (s), 558 (s), 533 (m), 499 (s). MS (FAB): m/z 1688 [M⁺], 843 $1/_2M^+$ – 1]. Anal. Calcd for $C_{86}H_{74}O_4P_6S_4Ru_2$: C, 61.2; H, 4.42. Found: C, 61.1; H, 4.40.

Preparation of $[\operatorname{Ru}(\operatorname{CO})(\mu - \eta^1(O), \eta^2(S, S') - \operatorname{ArPOS}_2)(\operatorname{PPh}_3)_2]_2$. CH₂Cl₂·THF (3·CH₂Cl₂·THF). To a slurry of Lawesson's reagent (41 mg, 0.10 mmol) and 17% NH₃·H₂O (0.2 mL) in THF (10 mL) was added a solution of [RuHCl(CO)(PPh₃)₃] (190 mg, 0.20 mmol) in THF (10 mL). The mixture was heated at reflux for 4 h. The solvent was removed in vacuo, and the residue was recrystallized from CH₂Cl₂/THF/hexane to give orange crystalline solids in a week at room temperature. Yield: 89 mg, 0.05 mmol, 47% (based on Ru). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 2.52 (s, 4H, THF), 3.62 (s, 4H, THF), 3.76 (s, 6H, OCH₃), 5.32 (s, 2H, CH₂Cl₂), 6.75 (d, 4H, J = 7.8 Hz, aryl H), 7.23-7.45 (m, 60H, PPh₃), 7.81-8.02 (dd, 4H, J = 7.6 Hz, aryl H). ${}^{31}P{}^{1}H$ NMR (121.5 MHz, CDCl₃): δ (ppm) 34.9 (s, 4P, *PPh*₃), 56.2 (s, 2P, Ar*P*S₂O). Selected IR (KBr, cm⁻¹): 1985 (vs), 1586 (s), 1437 (s), 1242 (s), 1021 (s), 679 (s), 556 (s), 531 (m), 502 (s). MS (FAB): m/z 1744 [M⁺], 871 [$^{1}/_{2}$ M⁺ - 1], 843 [$^{1}/_{2}$ M⁺ -CO - 1]. Anal. Calcd for $C_{88}H_{74}O_6P_6S_4Ru_2 \cdot (CH_2Cl_2) \cdot (C_4H_8O)$: C, 58.8; H, 4.55. Found: C, 58.2; H, 4.51.

Preparation of [Cp*Ru{(ArPS₂O)₂H}]·CH₂Cl₂·0.5H₂O (4· CH₂Cl₂·0.5H₂O). To a slurry of Lawesson's reagent (82 mg, 0.20 mmol) and 17% $NH_3 \cdot H_2O$ (0.2 mL) in THF (10 mL) was added a solution of [Cp*RuOMe]2 (107 mg, 0.20 mmol) in THF (10 mL). The mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo, and the residue was recrystallized from CH2Cl2/Et2O/hexane to give red crystalline solids in five days at room temperature. Yield: 89 mg, 0.13 mmol, 29% (based on Ru). ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.21 (s, 15H, Me), 3.72 (s, 6H, OCH₃), 5.31 (s, 2H, CH₂Cl₂), 6.74 (d, 4H, J = 7.6 Hz, aryl H), 7.79-8.01 (dd, 4H, J = 7.6 Hz, aryl H), 8.14 (br, 1H, POHOP). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ (ppm) 96.4 (s). Selected IR (KBr, cm⁻¹): 3274 (mbr), 1603 (s), 1430 (s), 1259 (s), 1029 (s), 678 (s), 556 (s), 531 (m), 504 (s). MS (FAB): m/z 672 [M⁺ – H – 1]. Anal. Calcd for C₂₄H₃₀O₄P₂S₄Ru· (CH₂Cl₂)·0.5(H₂O): C, 39.1; H, 4.33. Found: C, 38.5; H, 4.30.

Preparation of cis-[Ru{Fc(OMe)PS₂}₂(PPh₃)₂] (5). To a slurry of [FcP(S)(µ-S)]2 (56 mg, 0.10 mmol) and CH3ONa (11 mg, 0.20 mmol)

Table 1. Crystallographic Data and Experimental Details for $[(\eta^6-p\text{-cymene})\operatorname{Ru}\{\mu-\eta^1(S),\eta^1(S,S')-\operatorname{ArP}(S)S_2\}]_2$ (1), $[\operatorname{Ru}(\mu-\eta^1(O),\eta^1(S),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\operatorname{CO})(\mu-\eta^1(O),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\operatorname{CO})(\mu-\eta^1(S),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\operatorname{CO})(\mu-\eta^1(S),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S),\eta^2(S,S')-\operatorname{ArP}(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S),\eta^2(S,S')]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S)]_2$ (2), $[\operatorname{Ru}(\mu-\eta^1(S),\eta^2(S)]_2$ (2), $[\operatorname{Ru}($

	1	2	$3{\cdot}\mathrm{CH}_2\mathrm{Cl}_2{\cdot}\mathrm{THF}$	$\textbf{4}{\cdot}\text{CH}_2\text{Cl}_2{\cdot}0.5\text{H}_2\text{O}$	6	$\textbf{7}\boldsymbol{\cdot} CH_2Cl_2\boldsymbol{\cdot}^3/_4C_6H_{14}$	$9 \cdot CH_2Cl_2$
formula	$C_{34}H_{42}O_{2}$ - $P_{2}S_{6}Ru_{2}$	$C_{86}H_{74}O_{4}-P_{6}S_{4}Ru_{2}$	$C_{93}H_{84}O_{7}-C_{12}P_{6}S_{4}Ru_{2}$	C ₂₅ H ₃₃ O _{4.5} - P ₂ Cl ₂ S ₄ Ru	$C_{41}H_{39}O_3P_3-S_4Fe_2Ru$	$C_{61.5}H_{62.5}O_2$ - $Cl_2P_4S_4Fe_2Ru$	$C_{31}H_{34}OCl_2$ - $P_2S_4Fe_2Ru$
fw	939.12	1687.65	1900.70	767.66	1013.64	1407.32	896.43
a, Å	16.4138(6)	10.5303(1)	14.1406(6)	12.8560(2)	12.7476(2)	45.4230(12)	8.3220(1)
b, Å	21.4586(9)	14.3653(1)	15.1934(6)	22.4052(4)	21.9329(4)	11.9748(2)	22.9333(3)
c, Å	21.3596(9)	14.4226(1)	24.0947(10)	23.8151(5)	14.8253(3)	22.3738(4)	35.9063(4)
α, deg	90	65.843(1)	89.176(2)	90	90	90	90
β , deg	94.724(2)	85.502(1)	87.894(3)	90	95.300(1)	104.942(2)	90
γ , deg	90	71.413(1)	63.428(2)	90	90	90	90
$V, Å^3$	7497.7(5)	1883.41(3)	4626.7(3)	6859.7(2)	4127.31(13)	11758.3(4)	6852.75(14)
Z	8	1	2	8	4	8	8
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P\overline{1}$	$P\overline{1}$	Pbca	$P2_{1}/c$	C2/c	Pbca
$\rho_{\text{calcd}}, \text{g} \cdot \text{cm}^{-3}$	1.664	1.488	1.364	1.487	1.631	1.590	1.738
Т, К	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
μ , mm ⁻¹	1.256	0.692	0.630	0.979	1.412	1.181	1.790
F(000)	3808	864	1948	3128	2056	5756	3616
no. of reflns	69 864	35128	86057	56250	41 800	55 1 1 2	54 745
no. of indep reflns	17 066	8623	21 222	7795	9521	13410	7856
R _{int}	0.0792	0.0321	0.0746	0.0282	0.0732	0.0779	0.0440
R_1^{a} , wR_2^{b} $(I > 2\sigma(I))$	0.0757, 0.1383	0.0290, 0.0649	0.0516, 0.1051	0.0397, 0.0700	0.0445, 0.0868	0.0593, 0.1053	0.0311, 0.0667
R_1, wR_2 (all data)	0.0903, 0.1777	0.0374, 0.0691	0.0856, 0.1447	0.0543, 0.1127	0.0680, 0.1025	0.0764, 0.1342	0.0421, 0.0711
GoF ^c	1.107	1.043	1.020	1.045	1.004	1.009	1.023

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}wR_{2} = \left[\sum w(|F_{o}^{2}| - |F_{c}^{2}|)^{2} / \sum w|F_{o}^{2}|^{2} \right]^{1/2} . {}^{c}GoF = \left[\sum w(|F_{o}| - |F_{c}|)^{2} / (N_{obs} - N_{param}) \right]^{1/2} .$

in methanol (8 mL) was added a solution of [Ru(PPh₃)₃Cl₂] (192 mg, 0.20 mmol) in THF (10 mL). The mixture was heated at reflux for 2 h. The solvent was removed *in vacuo*, and the residue was recrystallized from CH₂Cl₂/hexane to give orange solids in three days at room temperature. Yield: 128 mg, 0.10 mmol, 51% (based on Ru). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 3.91 (d, 6H, J = 6.2 Hz, CH_3), 4.38 (s, 10H, C₅H₅ in Fc), 4.49 (m, 8H, C₅H₄ in Fc), 7.26–7.43 (m, 30H, Ph). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ (ppm) 41.2 (s, 2P, PPh₃), 105.4 (s, 2P, FcPS₂). Selected IR (KBr, cm⁻¹): 1602 (vs), 1381 (s), 1179 (s), 1023 (vs), 825 (m), 787 (s), 751 (m), 682 (s), 630 (m), 592 (s), 533 (m), 501 (s). MS (FAB): m/z 1248 [M⁺¹, 986 [M⁺ – PPh₃], 724 [M⁺ – 2PPh₃]. Anal. Calcd for C₅₈H₅₄O₂P₄S₄Fe₂Ru: C, 55.8; H, 4.36. Found: C, 55.6; H, 4.32.

Preparation of cis-[Ru(CO){Fc(OMe)PS₂}₂(PPh₃)] (6). To a slurry of [FcP(S)(µ-S)]2 (56 mg, 0.10 mmol) and CH3ONa (11 mg, 0.20 mmol) in methanol (10 mL) was added a solution of [RuHCl(CO)(PPh₃)₃] (188 mg, 0.20 mmol) in THF (10 mL). The mixture was heated at reflux for 2 h. The solvent was removed in vacuo, and the residue was recrystallized from CH2Cl2/hexane to afford orange crystals suitable for X-ray diffraction at room temperature. Yield: 118 mg, 0.12 mmol, 59% (based on Ru). ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.91 (d, 6H, J = 6.4 Hz, CH₃), 4.38 (s, 10H, C₅H₅ in Fc), 4.49 (m, 8H, C₅H₄ in Fc), 7.26–7.43 (m, 15H, Ph). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ (ppm) 43.6 (s, 1P, PPh₃), 106.2 (s, 2P, FcPS₂). Selected IR (KBr, cm⁻¹): 1946 (vs), 1607 (vs), 1385 (vs), 1183 (s), 1029 (vs), 827 (m), 785 (vs), 754 (m), 699 (s), 637 (m), 593 (s), 537 (m), 503 (s). MS (FAB): $m/z 1013 [M^+]$, 985 $[M^+ - CO]$, 723 $[M^+ - PPh_3 - CO]$. Anal. Calcd for C₄₁H₃₉O₃P₃S₄Fe₂Ru: C, 48.6; H, 3.88. Found: C, 48.4; H, 3.83.

Preparation of *cis*-[**Ru**{**Fc**(**OH**)**PS**₂}₂(**PPh**₃)₂]·**CH**₂**Cl**₂·³/₄-**C**₆**H**₁₄ (7·**CH**₂**Cl**₂·³/₄**C**₆**H**₁₄). To a slurry of [FcP(S)(μ -S)]₂ (56 mg, 0.10 mmol) and 17% NH₃·H₂O (0.2 mL) in THF (10 mL) was added the solid [Ru(PPh₃)₃Cl₂] (192 mg, 0.20 mmol). The mixture was stirred at room temperature overnight, and a brown solution was obtained. The solvent was removed *in vacuo*, and the residue was recrystallized from CH₂Cl₂/hexane to give orange-red crystalline solids in a week at room temperature. Yield: 98 mg, 0.08 mmol, 47% (based on Ru). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.98 (s, CH₃ in hexane), 1.31 (d, *J* = 6.4 Hz, CH₂ in hexane), 4.26 (s, 10H, C₅H₅ in Fc), 4.38 (m, 8H, C₅H₄ in Fc), 5.30 (s, 2H, CH₂Cl₂), 7.26–7.85 (m, 30H, Ph), 8.14 (br, 2H, POH). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ (ppm) 29.0 (s, 2P, FcPS₂), 43.2 (s, 2P, PPh₃). Selected IR (KBr, cm⁻¹): 3139 (brs), 1636 (vs), 1384 (vs), 1184 (s), 1107 (vs), 1025 (m), 742 (m), 696 (s), 532 (m), 518 (m). MS (FAB): m/z 1268 [M⁺], 1006 [M⁺ – PPh₃], 744 [M⁺ – 2PPh₃]. Anal. Calcd for C₅₆H₅₀O₂P₄-S₄Fe₂Ru · (CH₂Cl₂) · (C_{4.5}H_{10.5}): C, 50.8; H, 4.48. Found: C, 50.5; H, 4.44.

Preparation of cis-[Ru(CO){Fc(OH)PS₂}₂(PPh₃)]·CH₂Cl₂ $(8 \cdot CH_2Cl_2)$. Complex 8 was synthesized in a similar procedure to 7 except that [RuHCl(CO)(PPh₃)₃] (188 mg, 0.20 mmol) was used instead of [Ru(PPh₃)₃Cl₂]. Orange crystalline solids of 8. CH₂Cl₂ were obtained by the recrystallization from CH₂Cl₂/ hexane in a week at room temperature. Yield: 91 mg, 0.09 mmol, 47% (based on Ru). ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.94 $(d, 6H, J = 6.2 \text{ Hz}, CH_3), 4.36 (s, 10H, C_5H_5 \text{ in Fc}), 4.51 (m, 8H,$ C_5H_4 in Fc), 5.31 (s, 2H, CH_2Cl_2), 7.23–7.41 (m, 15H, Ph), 8.21 (br, 2H, POH). ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, CDCl₃): δ (ppm) 31.3 (s, 2P, FcPS₂), 44.3 (s, 1P, PPh₃). Selected IR (KBr, cm⁻¹): 3216 (brs), 1948 (vs), 1631 (vs), 1382 (vs), 1189 (s), 1102 (s), 1021 (m), 748 (m), 684 (s), 535 (m), 516 (s). MS (FAB): m/z 985 [M⁺], 957 [M⁺ - CO], 695 [M⁺ - PPh₃ - CO]. Anal. Calcd for C₃₉H₃₅O₃P₃S₄Fe₂Ru·(CH₂Cl₂): C, 44.9; H, 3.40. Found: C, 45.2; H, 3.36.

Preparation of $[(\eta^6-p-\text{cymene})\text{Ru}\{\eta^1(S),\eta^2(S,S')-\text{FcPS}_2\text{OP}-$ (S)SFc}]·CH₂Cl₂ (9·CH₂Cl₂). To a fresh slurry of [FcP(S)(µ-S)]2 (112 mg, 0.20 mmol) and 17% NH3 · H2O (0.1 mL) in THF (10 mL) was added an excess of NaHCO₃ (101 mg, 1.20 mmol), and then the mixture was heated at 60 °C for 1 h. The solid $[(\eta^{\circ}$ p-cymene)RuCl(µ-Cl)]2 (108 mg, 0.20 mmol) was added after the solution had been cooled. The mixture was stirred at room temperature for an additional 4 h, and the reddish-brown solution was obtained. The solvent was removed in vacuo, and the residue was washed with hexane and further recrystallized from CH₂Cl₂/hexane at room temperature. Block orange crystals of 9. CH₂Cl₂ suitable for X-ray diffraction were obtained in five days. Yield: 147 mg, 0.18 mmol, 41% (based on Ru). ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.34 (d, 6H, J = 6.8 Hz, $CH(CH_3)_2$, 2.15 (s, 3H, Ph CH_3), 3.04 (septet, 1H, J = 7.2 Hz, $CH(CH_3)_2$, 4.45 (s, 10H, C_5H_5 in Fc), 4.52 (m, 8H, C_5H_4 in Fc), 5.32 (s, 2H, CH_2Cl_2), 5.40 and 5.68 (dd, 4H, J = 7.6 Hz, C_6H_4).

³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ (ppm) 107.1 (s, 1P, FcP(S)S), 110.8 (s, 1P, FcPS₂). Selected IR (KBr, cm⁻¹): 1617 (vs), 1400 (vs), 1186 (s), 1024 (s), 875 (m), 781 (s), 757 (m), 706 (s), 673 (s), 561 (s), 502 (m), 463 (m). MS (FAB): *m/z* 811 [M⁺]. Anal. Calcd for C₃₀H₃₂OP₂S₄Fe₂Ru · (CH₂Cl₂): C, 41.5; H, 3.82. Found: C, 41.2; H, 3.80.

X-ray Diffraction Measurements. Crystallographic data and experimental details for $1, 2, 3 \cdot CH_2Cl_2 \cdot THF, 4 \cdot CH_2Cl_2 \cdot 0.5H_2O$, 6, $7 \cdot CH_2Cl_2 \cdot 3/4C_6H_{14}$, and $9 \cdot CH_2Cl_2$ are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. The collected frames were processed with the software SAINT.³² The data were corrected for absorption using the program SADABS.³¹ Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.³³ All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically $(C_{sp3}-H = 0.96, C_{sp2}-H = 0.93, and O-H = 0.82 \text{ Å})$, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or oxygen atoms before the final cycle of least-squares refinement. The solvent molecules such as hexane in $7 \cdot CH_2Cl_2 \cdot 3/4C_6H_{14}$, dichloromethane in $3 \cdot CH_2Cl_2 \cdot 3/4C_6H_{14}$ THF, and water in $4 \cdot CH_2Cl_2 \cdot 0.5H_2O$ were isotropically refined without hydrogen atoms due to disorder.

Results and Discussion

Cleavage of Lawesson's reagent, $[ArP(S)(\mu-S)]_2$ (Ar = p-CH₃OC₆H₄), with sodium alkoxide normally generates [ArP(OR)S₂]⁻, which can act as the bidentate-S,S' ligands,^{19,20} in which the alkoxide group is usually involved in the coordaintion of alkali metal alkoxides.¹⁴ Treatment of $[ArP(S)(\mu-S)]_2$ with ammonium hydroxide $(NH_3 \cdot H_2O)$ in a THF solution resulted in a homogeneous slurry that contained the $[ArP(OH)S_2]^-$ species. The reactions between the $[ArP(OH)S_2]^-$ species and ruthenium compounds afforded a series of new ruthenium-dithiophosphonate complexes, as shown in Scheme 1. Interactions of [Ru(PPh₃)₃Cl₂] and [RuHCl(CO)(PPh₃)₃] with Lawesson's reagent in the presence of $NH_3 \cdot H_2O$ gave the dinuclear complexes $[Ru(\mu \eta^{1}(O), \eta^{1}(S), \eta^{2}(S, S')$ -ArPOS₂)(PPh₃)]₂ (2) and [Ru(CO)(μ - $\eta^1(O), \eta^2(S,S')$ -ArPOS₂)(PPh₃)]₂ (3), respectively, in which the $[ArPOS_2]^{2-}$ ligands bridge two $[Ru(PPh_3)_2]^{2+}$ in 2 and two $[Ru(CO)(PPh_3)_2]^{2+}$ in 3 via both the sulfur and oxygen atoms. The IR spectra of complexes 2 and 3 show broad absorption bands in the $1020-1045 \text{ cm}^{-1}$ region, which are assigned to the $\nu(P-O)$ vibration. The absorption bands in the 675–680 cm⁻¹ regions may be assigned to the ν (P–S) vibration. The $\nu(C=0)$ stretching vibration was found at 1985 cm⁻¹ in the IR spectrum of 3. The ${}^{31}P{}^{1}H{}$ NMR spectra of the two complexes in CDCl₃ show an intense singlet ($\delta = 36.9$ ppm for **2** and 34.9 ppm for **3**) and a weak singlet (δ = 59.3 ppm for **2** and 56.2 ppm for **3**), assignable to PPh_3 and $[ArPOS_2]^{2-}$, respectively. The positive ion FAB mass spectra of the two complexes display the expected peaks at m/z 1688 and 843 for 2 and m/z 1744 and 871 for 3, corresponding to the molecular ions $[M^+]$ and $[1/2M^+ - 1]$, respectively, with the characteristic isotopic distribution patterns.

Scheme 1^a



^{*a*} Reagents and conditions: (i) $[(\eta^6-p\text{-cymene})\text{RuCl}(\mu\text{-Cl})]_2$, THF, reflux; (ii) NH₃·H₂O, THF, rt; (iii) [Ru(PPh₃)₃Cl₂], THF, rt; (iv) [RuHCl-(CO)(PPh₃)₃], THF, rt; (v) $[(\eta^5\text{-Cp}^*)\text{RuOMe}]_2$, THF, rt.

Treatment of dimeric $[(\eta^6-p-cymene)RuCl(\mu-Cl)]_2$ with Lawesson's reagent in the absence of NH₃·H₂O gave $[(\eta^6$ *p*-cymene)Ru{ μ - η ¹(S), η ²(S,S')-ArP(S)S₂}]₂ (1) as the sole isolable product. The chlorides in the starting ruthenium compound were substituted by the μ_3 -[ArP(S)S₂]²⁻ ligand. Reaction of [(η^6 *p*-cymene)RuCl(μ -Cl)]₂ with Lawesson's reagent in the presence of NH₃·H₂O at room temperature or reflux gave an orange powder that was difficult to characterize due to impurity. Reaction of dimeric $[Cp*RuCl(\mu-Cl)]_2$ with Lawesson's reagent under similar conditions afforded a paramagnetic dark red solid, presumably a ruthenium(III) species. Attempts to recrystallize the dark red solid in different solvents were unsuccessful. Interestingly, reaction of dimeric [Cp*Ru(OMe)]2 with Lawesson's reagent in the presence of NH₃·H₂O led to isolation of a novel ruthenium(IV) complex, [Cp*Ru{(ArPS₂O)₂H}] (4), in 29% yield. In the present reaction, the methoxy groups in the starting ruthenium compound were substituted by dithiophosphonate ligands. The oxidation of Ru(II) to Ru(IV) was probably caused by a disproportionation reaction because the synthesis and workup were carried out under dinitrogen. The IR spectrum of 1 shows the ν (P=S) and ν (P-S) stretching vibrations at 685, 558, and 677 cm⁻¹, respectively. The IR spectrum of 4 shows the unsymmetrical $O-H \cdots O$ vibrational mode at 1259 cm⁻¹ and the ν (O–H) at 3274 cm⁻¹ as a medium broad peak. The ³¹P{¹H} NMR spectra in CDCl₃ exhibited a single resonance at δ 84.1 ppm for 1 and 96.4 ppm for 4, indicating that a single diastereomer was present for each of the complexes.

⁽³¹⁾ SMART and SAINT+ for Windows NT Version 6.02a; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

⁽³²⁾ Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996.

⁽³³⁾ Sheldrick, G. M. SHELXTL Software Reference Manual, Version 5.1; Bruker AXS Inc.: Madison, WI, 1997.



^{*a*} Reagents and conditions: (i) MeONa, MeOH, rt; (ii) [Ru(PPh₃)₃Cl₂] or [RuHCl(CO)(PPh₃)₃], THF, rt; (iii) NH₃·H₂O, THF, rt; (iv) [Ru-(PPh₃)₃Cl₂] or [RuHCl(CO)(PPh₃)₃], THF, rt; (v) NaHCO₃, THF, 60 °C; (vi) [$(\eta^6$ -*p*-cymene)RuCl(μ -Cl)]₂, THF, rt.

The positive ion FAB mass spectrum of 1 shows the molecular ions $[M^+]$ and $[1/2M^+ - 1]$ with the characteristic isotopic distribution patterns. The molecular ion corresponding to the loss of a hydride was observed in the FAB⁺ mass spectrum of 4.

Encouraged by the previous reports on the ring-opening reaction involving the well-known thionation of Lawesson's reagent, $^{13-18}$ together with the successful isolation of the above ruthenium-dithiophosphonato complexes, we set out to study the reactions of ruthenium compounds such as [Ru- $(PPh_3)_3Cl_2$], [RuHCl(CO)(PPh_3)_3], and [$(\eta^6$ -p-cymene)RuCl- $(\mu$ -Cl)]₂ with the Lawesson's reagent analogue [FcP(S)(μ -S)]₂ $(Fc = Fe(\eta^{3}-C_{5}H_{4})(\eta^{3}-C_{5}H_{5}))$ under the alcoholysis and hydrolysis conditions in the presence of the alkoxide or base, as shown in Scheme 2. Similar to Lawesson's reagent $[ArP(S)(\mu-S)]_2$, dimeric $[FcP(S)(\mu-S)]_2$ reacts with two molar equivalents of NaOR (R = Me, Et, *n*-Pr, and *i*-Pr) to give stable ferrocenylphosphonodithiolate salts Na[FcP(OR)S₂] that can bind to various metals.^{21,22} With this in mind, [Ru(PPh₃)₃Cl₂] or [RuHCl(CO)(PPh₃)₃] reacted with Na[FcP(OMe)S₂], derived from $[FcP(S)(\mu-S)]_2$ with MeONa in methanol, giving the neutral mononulcear complexes cis-[Ru{Fc(OCH₃)₂PS₂}₂- $(L')(PPh_3)$] (L' = PPh₃ 5, CO 6) isolated as air-stable, orange crystals. The chlorides and one PPh₃ ligand in [Ru(PPh₃)₃Cl₂] and the chloride and hydrogen atoms and two PPh₃ moieties in [RuHCl(CO)(PPh₃)₃] were substituted by [Fc(OCH₃)PS₂]⁻, resulting in six-coordinate ruthenium(II) centers in 5 and 6. The ³¹P{¹H} NMR spectra show two singlets at δ 41.2 and 105.4 ppm for 5 and δ 43.6 and 106.2 ppm for 6 assignable to the PPh₃ and [Fc(OCH₃)PS₂]⁻ ligands, respectively. The C=O stretching vibration mode was found at 1946 cm^{-1} in the IR spectrum of 6. The FAB⁺ mass spectra of complexes 5 and 6 exhibit molecular ions corresponding to $[M^+]$ and $[M^+ - L']$ (L' = PPh₃ and CO) with the characteristic isotopic distribution patterns.

Interaction of $[Ru(PPh_3)_3Cl_2]$ or $[RuHCl(CO)(PPh_3)_3]$ with dimeric $[FcP(S)(\mu-S)]_2$ in the presence of $NH_3 \cdot H_2O$ in THF followed by recrystallization from CH_2Cl_2 /hexane gave $[Ru{Fc(OH)_2PS_2}_2(L')(PPh_3)]$ (L' = PPh₃ 7, CO 8). Complexes 7 and 8 are stable in the solid state but readily air oxidized in solutions to give paramagnetic green species, presumably ruthenium(III) complexes. The formation of $[FcP(OH)S_2]^-$ is due to the hydrolysis of $[Fc(S)(\mu-S)]_2$ by the treatment of $NH_3 \cdot H_2O$. The ³¹P{¹H} NMR spectra show two intense singlets at δ 29.0 and 43.2 ppm for 7 and δ 31.3 and 44.3 ppm for **8**, assignable to [Fc(OH)PS₂]⁻ and PPh₃, respectively. The characteristic (P)O-H protons were observed at δ 8.14 and 8.21 ppm in the ¹H NMR spectra for 7 and 8, respectively, which were also confirmed by medium broad peaks at 3139 and 3216 cm^{-1} in the IR spectra of 7 and 8, respectively. The IR spectra of 7 and 8 clearly show two sets of bands at 1020-1110 and 680-750 cm⁻¹, which may be attributed to $\nu(P-O)$ and $\nu(P-S)$ absorptions, respectively. The ν (C=O) stretching vibration was found at 1948 cm⁻¹ in the IR spectrum of 8. The positive ion FAB mass spectra show the molecular ions at m/z 1268, 1006, and 744, which correspond to the molecular ions $[M^+]$, $[M^+ - PPh_3]$, and $[M^+ -$ 2PPh₃], respectively, and m/z 985, 957, and 695, which correspond to the molecular ions $[M^+]$, $[M^+ - CO]$, and $[M^+ PPh_3 - CO$, respectively, with the characteristic isotopic distribution patterns.

The [Fc(OH)PS(SH)] may be prepared in situ by the hydrolysis of $[FcP(S)(\mu - S)]_2$ in the presence of an appropriate amount of NH₃·H₂O. Interaction of $[(\eta^6-p-\text{cymene})\text{RuCl}(\mu-$ Cl)]2 with in situ [Fc(OH)S(SH)] in the presence of excess NaHCO₃ under heating conditions followed by recrystallization from CH₂Cl₂/hexane gave $[(\eta^6 - p - \text{cymene})\text{Ru}\{\eta^1(S),$ $\eta^2(S,S')$ -FcPS₂OP(S)SFc]] (9) in 41% yield. It seems that treatment of [FcP(OH)S(SH)] with NaHCO₃ at 60 °C resulted in formation of $Na_2[(FcPS_2)_2O]$ probably due to elimination of the water molecule.^{14,15} Further support for this speculation comes from the X-ray crystallographic analysis of 9. The ${}^{31}P{}^{1}H$ NMR spectrum of 9 displayed two intense singlets at δ 107.1 and 110.8 ppm, which may be tentatively assigned to the [FcP(S)SO-] and [FcPS₂O-] moieties, respectively. The ¹H NMR spectrum of **9** shows the *p*-cymene and ferrocenyl resonances with the expected relative intensities and multiplicities. The IR spectrum of 9 clearly showed three sets of strong bands at 1024 and 875, 781 and 757, and 673 and 561 cm⁻¹, which may be attributed to ν (P–O), ν (P=S), and ν (P-S) absorptions, respectively. The positive ion FAB mass spectrum of 9 displays the expected peak at m/z 811, which corresponds to the molecular ion [M⁺] with the characteristic isotopic distribution pattern.

Crystal structures of 1, 2, $3 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{THF}$, $4 \cdot \text{CH}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$, 6, $7 \cdot \text{CH}_2\text{Cl}_2 \cdot 3/4\text{C}_6\text{H}_{14}$, and $9 \cdot \text{CH}_2\text{Cl}_2$ have been determined by single-crystal X-ray diffraction. In all seven structures, the distances within dithiophosphonate ligands agree well with those found in structurally characterized dithiophosphonate complexes with other metal ions,^{11–22} which will not be discussed further. Selected bond lengths and angles for 1, 2, $3 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{THF}$, $4 \cdot \text{CH}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$, 6, $7 \cdot \text{CH}_2\text{Cl}_2 \cdot 3/4\text{C}_6\text{H}_{14}$, and $9 \cdot \text{CH}_2\text{Cl}_2$ are collected in Tables 2–8, respectively.

Complex 1 crystallized in the monoclinic space group $P2_1/n$, and the molecular structure of 1 is illustrated in Figure 1. The neutral complex 1 comprises two $[(\eta^6-p\text{-cymene})\text{Ru}]^{2+}$ fragments bridged by two $[\text{ArP}(\text{S})\text{S}_2]^{2-}$ moieties via the sulfur atoms. The molecular structure of 1 consists of discrete dimeric molecules with distorted octahedral geometry around the ruthenium atom, having a *p*-cymene ring at one face. One of the sulfur atoms of the dithiophosphato

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^6-p\text{-}cymene)\text{Ru}\{\mu-\eta^1(S),\eta^2(S,S')-\text{ArP}(S)S_2)]_2$ (1)

			- ()
Ru(1)-S(2)	2.410(7)	Ru(1)-S(4)	2.414(8)
Ru(1) - S(5)	2.433(8)	Ru(2) - S(1)	2.433(8)
Ru(2) - S(2)	2.425(8)	Ru(2) - S(4)	2.408(7)
P(1) - S(1)	2.040(12)	P(1) - S(2)	2.106(10)
P(1) - S(3)	1.831(16)	P(2) - S(4)	2.120(10)
P(2) - S(5)	2.047(12)	P(2) - S(6)	1.845(16)
S(2) - Ru(1) - S(4)	81.2(2)	S(2) - Ru(1) - S(5)	83.1(3)
S(4) - Ru(1) - S(5)	79.8(3)	S(2) - Ru(2) - S(1)	79.6(3)
S(4) - Ru(2) - S(1)	82.9(3)	S(4) - Ru(2) - S(2)	81.0(2)
Ru(1)-S(2)-Ru(2)	98.7(3)	Ru(2) - S(4) - Ru(1)	99.1(3)
P(1)-S(1)-Ru(2)	86.1(3)	P(1)-S(2)-Ru(1)	108.8(4)
P(1)-S(2)-Ru(2)	84.8(3)	P(2)-S(4)-Ru(2)	108.7(4)
P(2)-S(4)-Ru(1)	85.1(3)	P(2)-S(5)-Ru(1)	86.2(4)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[\operatorname{Ru}(\mu-\eta^1(O),\eta^1(S),\eta^2(S,S')-\operatorname{ArPOS}_2)(\operatorname{PPh}_3)_2]_2$ (2)^{*a*}

	(2),-1 (2),-1 (2),	<i>S</i>) 1111 (<i>S</i>)2)(1 1 13)2].	2 (-)
Ru(1)-S(1)	2.4717(5)	Ru(1)-S(1)#1	2.4844(5)
Ru(1) - S(2)	2.4253(5)	Ru(1)-O(1)#1	2.2309(14)
Ru(1) - P(2)	2.3257(6)	Ru(1) - P(3)	2.3344(5)
P(1) - S(1)	2.0649(7)	P(1) - S(2)	2.0203(7)
P(1) - O(1)	1.5424(15)		
S(1) - Ru(1) - S(2)	81.123(17)	S(1)-Ru(1)-S(1)#1	82.071(17)
S(2)-Ru(1)-S(1)#	1 89.964(18)	P(2)-Ru(1)-S(1)	83.626(18)
P(2)-Ru(1)-S(1)#	1 162.968(19)	P(3) - Ru(1) - S(1)	170.974(19)
P(3)-Ru(1)-S(1)#	1 94.464(18)	P(2) - Ru(1) - S(2)	96.93(2)
P(3) - Ru(1) - S(2)	90.574(19)	P(2)-Ru(1)-P(3)	101.00(2)
O(1)#1-Ru(1)-S(1) 89.32(4)	O(1)#1-Ru(1)-S(1)#1	73.96(4)
O(1)#1-Ru(1)-S(2)	2) 162.35(4)	O(1)#1-Ru(1)-P(2)	96.72(4)
O(1)#1-Ru(1)-P(2)	3) 97.76(4)	Ru(1)-S(1)-Ru(1)#1	97.929(17)
P(1)-S(1)-Ru(1)	85.59(2)	P(1)-S(1)-Ru(1)#1	80.14(2)
P(1)-S(2)-Ru(1)	87.80(2)	P(1) - O(1) - Ru(1) # 1	101.08(7)
<i>a c i i i</i>	c .:	1	1

^{*a*}Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y + 2, -z + 1.

moiety is essentially symmetrically bonded to two ruthenium atoms with distances Ru(1)-S(2) = 2.410(7) and Ru(2)-S(2) = 2.425(8) Å, Ru(1)-S(4) = 2.414(8) and Ru(2)-S(4) = 2.408(7) Å, while S1 and S5 are bonded to the corresponding ruthenium atoms with Ru–S distances of 2.433(8) and 2.433(8) Å. Thus the two sulfur atoms of the bidentate dithiophosphato ligands act as tricoordinate atoms in both bridging and chelating modes.

Complex 2 crystallized in the triclinic space group $P\overline{1}$, and in the solid state 2 exists as a centrosymmetric dimer, as shown in Figure 2. The neutral complex 2 comprises two [Ru-(PPh₃)₂]²⁺ fragments symmetrically bridged by two [ArPOS₂]²⁻ moieties via the sulfur and oxygen atoms. Two ruthenium environments are identical, that is, each is surrounded by two μ_3 -S, one μ -O, and two P atoms, forming a highly distorted octahedral arrangement. The average Ru- μ_3 -S bond distance of 2.4780(5) Å is slightly longer than the average Ru- μ -S bond distance of 2.4253(5) Å. The Ru-O and Ru-P bond lengths in 2 are 2.2309(14) (av) and 2.3300(5) (av) Å, respectively. Four-membered ring Ru₂S₂ is coplanar, and the Ru···Ru nonbonding distance is 3.738 Å.

Complex $3 \cdot CH_2Cl_2 \cdot THF$ crystallized in the triclinic space group $P\overline{1}$ with centrosymmetry. The unit cell of $3 \cdot CH_2Cl_2 \cdot THF$ contains a molecule of 3 and disordered solvent molecules in the crystal lattice. There are two perpendicular arrangements of the molecules in the crystal with slightly different conformations. No significant differences in bonding parameters between these two molecules (A and B) were found (see Table 4). The structure of one of the two crystallographic independent molecules is shown in Figure 3.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for
$[\operatorname{Ru}(\operatorname{CO})(\mu - \eta^1(O), \eta^2(S, S') - \operatorname{ArPOS}_2)(\operatorname{PPh}_3)]_2 \cdot \operatorname{CH}_2\operatorname{Cl}_2 \cdot \operatorname{THF}$
$(3 \cdot CH_2 Cl_2 \cdot THF)^a$

	molecule A	molecule B
Ru(1)-S(1)	2.4297(10)	2.4302(10)
Ru(1) - S(2)	2.4459(10)	2.4459(10)
Ru(1) - P(2)	2.3956(10)	2.3910(10)
Ru(1) - P(3)	2.4236(10)	2.4096(11)
Ru(1)-O(3)#1	2.206(2)	2.192(2)
Ru(1) - C(1)	1.801(4)	1.806(4)
P(1) - S(1)	2.0505(13)	2.0383(13)
P(1) - S(2)	2.0467(13)	2.0453(13)
P(1) - O(3)	1.517(2)	1.509(3)
C(1) - O(1)	1.151(5)	1.148(5)
S(1) - Ru(1) - S(2)	79.77(3)	79.75(3)
P(2)-Ru(1)-S(1)	84.72(3)	85.50(3)
P(3)-Ru(1)-S(1)	167.47(3)	166.90(4)
P(2) - Ru(1) - S(2)	164.42(4)	165.20(4)
P(3) - Ru(1) - S(2)	88.12(3)	87.38(4)
P(2) - Ru(1) - P(3)	107.45(4)	107.41(4)
O(3)#1 - Ru(1) - S(1)	90.19(7)	91.45(7)
O(3)#1-Ru(1)-S(2)	88.98(7)	90.48(7)
O(3)#1-Ru(1)-P(2)	92.54(7)	91.02(7)
O(3)#1-Ru(1)-P(3)	86.37(7)	86.23(7)
C(1) - Ru(1) - S(1)	89.33(12)	88.10(13)
C(1) - Ru(1) - S(2)	89.00(13)	87.94(12)
C(1) - Ru(1) - P(2)	89.38(13)	90.47(12)
C(1) - Ru(1) - P(3)	93.68(13)	93.86(13)
C(1)-Ru(1)-O(3)#1	177.98(14)	178.41(14)
P(1)-S(1)-Ru(1)	90.27(4)	90.08(4)
P(1)-S(2)-Ru(1)	89.91(4)	89.48(4)
P(1)-O(3)-Ru(1)#1	144.09(15)	143.32(16)
Ru(1)-C(1)-O(1)	175.1(4)	174.5(4)

^{*a*}Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y, -z + 2.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Cp*Ru{(ArPS₂O)₂H}]·CH₂Cl₂·0.5H₂O (4·CH₂Cl₂·0.5H₂O)

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Ru(1)-S(1)	2.4527(9)	Ru(1) - S(2)	2.4371(9)
Ru(1) - S(3)	2.4404(8)	Ru(1) - S(4)	2.4573(9)
P(1) - S(1)	2.0139(12)	P(1) - S(2)	2.0143(12)
P(2) - S(3)	2.0161(12)	P(2) - S(4)	2.0195(12)
P(1) - O(1)	1.533(3)	P(2) - O(2)	1.522(2)
O(1) - H(1)	0.879(9)	O(2) - H(1)	1.603(9)
S(2) - Ru(1) - S(3)	80.26(3)	S(2) - Ru(1) - S(1)	76.92(3)
S(3) - Ru(1) - S(1)	127.27(3)	S(2) - Ru(1) - S(4)	129.31(3)
S(3) - Ru(1) - S(4)	76.88(3)	S(1) - Ru(1) - S(4)	82.08(3)
P(1)-S(1)-Ru(1)	86.40(4)	P(1)-S(2)-Ru(1)	86.82(4)
P(2)-S(3)-Ru(1)	87.05(4)	P(2)-S(4)-Ru(1)	86.52(4)
$O(1) - H(1) \cdots O(2)$	163.94(2)		

The neutral complex **3** comprises two $[Ru(CO)(PPh_3)_2]^{2+}$ fragments symmetrically bridged by two $[ArPOS_2]^{2-}$ moieties via the sulfur and oxygen atoms. Two sulfur atoms in a $[ArPOS_2]^{2-}$ moiety chelate a ruthenium atom with a bite angle S-Ru-S of 79.76(3)°. Each ruthenium atom is surrounded by two μ -S, one μ -O, one C, and two P atoms, forming a highly distorted octahedral configuration. The Ru–C bond length and Ru–C–O bond angle in **3** are 1.804(4) Å and 174.8(4)°, respectively, which are comparable to those in [RuH(CO)-{S₂P(OEt)₂}(PPh_3)₂] [Ru–C = 1.829(4) Å and Ru–C–O = 175.4(4)°].¹⁰ The average Ru–P bond length of 2.405(1) Å in **3** is also comparable to that of 2.3300(5) Å in **2**, whereas the bent angle P–O–Ru (av 143.70(15)°) in **3** is obviously bigger than that in **2** (101.08(7)°). The Ru···Ru nonbonding distance in **3** is 5.469 Å.

The solid-state structure of 4 has been established by X-ray crystallography. The crystal of $4 \cdot CH_2Cl_2 \cdot 0.5H_2O$ crystallized

Table 6. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[Ru(CO){Fc(OCH₃)PS₂}₂(PPh₃]] (6)

$CI3-[Ku(CO)(IC(OCII3)IS_2)_2(III3)](0)$					
Ru(1)-S(1)	2.4521(11)	Ru(1) - S(2)	2.5458(11)		
Ru(1) - S(3)	2.5081(10)	Ru(1)-S(4)	2.4356(10)		
Ru(1) - P(3)	2.3203(10)	Ru(1) - C(21)	1.831(5)		
P(1) - O(1)	1.590(3)	P(2) - O(2)	1.591(3)		
C(21)-O(3)	1.146(5)				
S(1) - Ru(1) - S(2)	78 43(3)	S(3) = Ru(1) = S(2)	86 27(3)		
S(4) - Ru(1) - S(2)	91.80(4)	S(1) - Ru(1) - S(3)	92.60(4)		
S(4) - Ru(1) - S(3)	79.84(3)	S(4) - Ru(1) - S(1)	168.09(4)		
P(3) - Ru(1) - S(1)	94.06(4)	P(3) - Ru(1) - S(4)	94.12(3)		
P(3) - Ru(1) - S(2)	98.46(4)	P(3) - Ru(1) - S(3)	172.49(4)		
C(21) - Ru(1) - S(1)	98.67(13)	C(21) - Ru(1) - S(2)	173.08(12)		
C(21) - Ru(1) - S(3)	87.59(12)	C(21) - Ru(1) - S(4)	90.26(13)		
C(21) - Ru(1) - P(3)	87.98(12)	Ru(1) - C(21) - O(3)	176.2(4)		
P(1)-S(1)-Ru(1)	88.87(5)	P(1)-S(2)-Ru(1)	86.76(5)		
P(2)-S(3)-Ru(1)	86.95(4)	P(2)-S(4)-Ru(1)	88.24(4)		
S(1) - P(1) - S(2)	104.34(6)	S(3) - P(2) - S(4)	104.70(6)		
O(1) - P(1) - S(1)	112.69(13)	O(1) - P(1) - S(2)	114.40(12)		
O(2) - P(2) - S(3)	113.31(12)	O(2) - P(2) - S(4)	112.34(11)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for cis-[Ru{Fc(OH)PS₂}₂(PPh₃)₂]·CH₂Cl₂· $^{3}/_{4}C_{6}H_{14}$ (7·CH₂Cl₂· $^{3}/_{4}C_{6}H_{14})$

	(, 0112012	/40014/	
Ru(1)-S(1)	2.4645(14)	Ru(1) - S(2)	2.5534(13)
Ru(1) - S(3)	2.5368(12)	Ru(1)-S(4)	2.4544(13)
Ru(1) - P(3)	2.3046(12)	Ru(1) - P(4)	2.3328(12)
P(1) - S(1)	1.9970(19)	P(1) - S(2)	2.016(2)
P(2) - S(3)	2.019(2)	P(2) - S(4)	2.0042(18)
P(1)-O(1)	1.586(4)	P(2)-O(2)	1.590(4)
S(1) - Ru(1) - S(2)	77.13(5)	S(2) - Ru(1) - S(3)	91.92(4)
S(4) - Ru(1) - S(2)	95.61(4)	S(4) - Ru(1) - S(3)	77.26(4)
S(1) - Ru(1) - S(3)	93.42(5)	S(4) - Ru(1) - S(1)	168.11(4)
P(3)-Ru(1)-S(1)	92.81(4)	P(4) - Ru(1) - S(1)	98.73(5)
P(3)-Ru(1)-S(2)	169.15(5)	P(4) - Ru(1) - S(2)	86.29(4)
P(3) - Ru(1) - S(3)	84.56(4)	P(4) - Ru(1) - S(3)	166.98(5)
P(3) - Ru(1) - S(4)	93.62(4)	P(4) - Ru(1) - S(4)	90.07(4)
P(3)-Ru(1)-P(4)	99.41(4)	P(1) - S(1) - Ru(1)	85.34(6)
P(1)-S(2)-Ru(1)	82.63(6)	P(2)-S(3)-Ru(1)	82.60(6)
P(2)-S(4)-Ru(1)	85.07(6)	S(1) - P(1) - S(2)	102.47(8)
S(3) - P(2) - S(4)	101.53(7)	O(1) - P(1) - S(1)	114.78(18)
O(1) - P(1) - S(2)	111.14(18)	O(2) - P(2) - S(3)	110.42(19)
O(2) - P(2) - S(4)	114.88(18)		

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^6 - p\text{-cymene})\text{Ru}\{\eta^1(S),\eta^2(S,S')\text{-FcPS}_2\text{OP}(S)\text{SFc}\}]\cdot\text{CH}_2\text{Cl}_2(9\cdot\text{CH}_2\text{Cl}_2)$

Ru(1) - S(1)	2.4640(7)	Ru(1) - S(2)	2.4460(7)
Ru(1) - S(3)	2.4440(6)	P(1) - S(1)	2.0049(9)
P(1) - S(2)	1.9913(9)	P(2) - S(3)	2.0294(9)
P(2) - S(4)	1.9399(10)	P(1) - O(1)	1.6074(18)
P(2) - O(1)	1.6533(18)		
S(1) - Ru(1) - S(2)	79.37(2)	S(1) - Ru(1) - S(3)	87.75(2)
S(2) - Ru(1) - S(3)	95.70(2)	P(1)-S(1)-Ru(1)	82.79(3)
P(1) - S(2) - Ru(1)	83.53(3)	P(2)-S(3)-Ru(1)	113.95(3)
S(1) - P(1) - S(2)	103.37(4)	S(3) - P(2) - S(4)	116.43(5)
O(1) - P(1) - S(1)	111.39(7)	O(1) - P(1) - S(2)	111.47(7)
O(1) - P(2) - S(3)	107.06(7)	O(1) - P(2) - S(4)	107.64(7)
P(1) - O(1) - P(2)	129.48(11)		

in the orthorhombic space group *Pbca*. A perspective view of molecule **4** is shown in Figure 4. Complex **4** exhibits a fourlegged piano-stool configuration for the typical Ru(IV) monocyclopentadienyl complexes, with coordination being to η^5 -Cp* and two dithiophosphonates as bidentate ligands. It should be noted that several non-hydrido Cp*Ru(IV) complexes with dithiolate ligands, such as [Cp*Ru(S₂CNMe₂)₂]-



Figure 1. Perspective view of $[(\eta^6-p-\text{cymene})\text{Ru}\{\mu-\eta^1(S),\eta^2-(S,S')-\text{ArP}(S)S_2\}]_2$, 1.



Figure 2. Perspective view of [Ru(μ - $\eta^1(O)$, $\eta^1(S)$, $\eta^2(S,S')$ -ArPOS₂)-(PPh₃)₂]₂, 2.

 $[N(Ph_2PS)_2]^{34}$ [Cp*Ru-(S₂CNR₂)₂]Cl (R = Me, Et),⁹ [Cp*Ru- $(S_2CNEt_2)(S_2CO)]$,⁹ and $[Cp*RuCl_2(\eta^2-dithiolate)]$ (dithiolate = S_2CNR_2 , R = Me, Et; S_2CO^iPr , $S_2P(O^iPr)_2$),⁹ have been reported to date. Complex 4 appears to be the first example of a Cp*Ru(IV) complex containing dithiophosphonate ligands. The average Ru-S distance (2.4469(9)Å) for **4** is longer than those in [Cp*Ru(S₂CNMe₂)₂][N(Ph₂PS)₂] (av 2.387(1) Å),³⁴ $[Cp*Ru(S_2CNMe_2)_2]Cl (av 2.33901(9) Å),⁹ and <math>[Cp*Ru(S_2CNEt_2)(S_2CO)] (av 2.3858(7) Å).⁹ The dithiophospho$ nate bite angles in 4 [range 76.88(3)-76.92(3)°] are obviously larger than those of the dithiocarbamate [range 71.03(3)-71.24(3)°] and dithiocarbonate [range 71.37(3)-72.04(3)°] in [Cp*Ru(S₂CNEt₂)(S₂CO)].⁹ Two P–O bonds in the dithiophosphonate ligands are 1.533(3) and 1.522(2) Å, which are in the range of the P-O single bond. The hydrogen atom of the hydroxyl moiety is tentatively assigned to the O1 atom because the P(1)-O(1) of 1.533(3) Å is slightly longer than the P(2)-O(2) of 1.522(2) Å. A strong intramolecular hydrogen bond is observed in the dithiophosphonate ligands, as indicated by $O(1) \cdots O(2)$ of 2.459(3) Å with the O(1)-H- $(1) \cdots O(2)$ angle of 163.94(2)°.

⁽³⁴⁾ Cheung, W. M.; Zhang, Q. F.; Williams, I. D.; Leung, W. H. Inorg. Chim. Acta 2006, 359, 782–788.



Figure 3. Perspective view of $[\operatorname{Ru}(\operatorname{CO})(\mu - \eta^1(O), \eta^2(S, S') - \operatorname{ArPOS}_2) - (\operatorname{PPh}_3)_2]_2$, 3.



Figure 4. Perspective view of [Cp*Ru{(ArPS₂O)₂H}], 4.

The molecular structure of 6 is shown in Figure 5. The geometry around ruthenium is pseudo-octahedral with two cis-chelating [Fc(OCH₃)PS₂]⁻ ligands. The chelating S-Ru-S angles are considerably reduced [78.43(3)° and $79.84(3)^{\circ}$] due to the small bite of the dithio ligands. The four-membered RuS₂P rings are nonplanar. Each ring contains a pair of long and short Ru-S bonds [Ru(1)-S(2) =2.5458(11)Å ("long") with Ru(1)-S(1) = 2.4521(11)Å ("short"); Ru(1)-S(3) = 2.5081(10) Å ("long") with Ru(1)-S(4) =2.4356(10) Å ("short")]. The average Ru-S bond length in 6 (av 2.4854(11) Å) is comparable to that in $7 \cdot CH_2Cl_2 \cdot 3/4$ - C_6H_{14} (av 2.5023(13) Å). Among the unequal R-S bonds in four-membered RuS_2P rings for 6, the Ru(1)-S(2) bond (2.5458(11) Å) trans to CO in **6** is elongated due to π backbonding from the C≡O bond. The Ru-P bond length of 2.3203(10) Å in 6 agrees well with those in $7 \cdot CH_2Cl_2 \cdot 3/4$ - C_6H_{14} and some other related ruthenium(II) complexes with PPh₃ ligands.^{5,10,35} The Ru–C bond length of 1.831(5) Å in **6** is normal for the ruthenium-carbonyl complexes.^{8,10}

X-ray structural analysis revealed that $7 \cdot CH_2Cl_2 \cdot {}^3/_4$ -C₆H₁₄ crystallized in the monoclinic space group C2/c, consisting of neutral complex and disorder solvent molecules that are consistent with the microanalytical and NMR data. The molecular structure of 7 is shown in Figure 6. Two *cis* PPh₃ ligands bind to the ruthenium center with the P–Ru–P angle of 99.41(4)°, and two chelating [Fc(OH)PS₂]⁻ ligands



Figure 5. Perspective view of cis-[Ru(CO){Fc(OCH₃)PS₂}₂-(PPh₃)], 6.



Figure 6. Perspective view of *cis*-[Ru{Fc(OH)PS₂}₂(PPh₃)₂], 7.

form the basal plane. The four-membered RuS₂P rings are nonplanar and distorted with the average chelating S–Ru–S angle of 77.20(5)°. Each ring contains a pair of long and short Ru–S bonds. A similar case was observed in *cis*-[Ru{S₂P-(OEt)₂}₂(PPh₃)₂].¹⁰ The average Ru–S bond length in 7· CH₂Cl₂·³/₄C₆H₁₄ (av 2.5023(13) Å) is comparable to that in *cis*-[Ru{S₂P(OEt)₂}₂(PPh₃)₂] (av 2.4974(11) Å) with the chelated dithiophosphate ligands,¹⁰ but slightly longer than that in *cis*-[Ru(S₂CNEt₂)₂(PPh₃)₂] (av 2.3952(5) Å) with chelated dithiocarbamate ligands.³⁶ The average Ru–P bond length of 2.3187(12) Å in 7·CH₂Cl₂·³/₄C₆H₁₄ agrees well with those in some related ruthenium(II)-PPh₃ complexes.^{5,10,35,36}

X-ray structural analysis revealed that $9 \cdot CH_2Cl_2$ crystallized in the orthorhombic space group *Pbca*, consisting of one neutral complex and one CH₂Cl₂ solvent molecule. The molecular structure of **9** is shown in Figure 7. The central ruthenium atom in **9** exists in a distorted octahedral coordination environment, with the phenyl ring of the *p*-cymene ligand formally occupying three octahedral sites. The [FcPS₂OP-(S)SFc]²⁻ ligand is bonded to the metal center via three sulfur atoms to complete the coordination sphere. [FcPS₂OP(S)-SFc]²⁻ acts as an unsymmetrical tridentate ligand to form

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Figure 7. Perspective view of $[(\eta^6-p\text{-cymene})\text{Ru}\{\eta^1(S),\eta^2(S,S')\text{-}FcPS_2OP(S)SFc}], 9.$

one four-membered chelate ring RuS₂P with a S(1)-Ru-(1)-S(2) bite angle of 79.37(2)° and the two six-membered rings RuS_2P_2O with S(1)-Ru(1)-S(3) angle of 87.75(2)° and S(2)-Ru(1)-S(3) angle of 95.70(2)°. The three Ru-S bonds are approximately equal in length [Ru(1)-S(1) = 2.4640(7),Ru(1)-S(2) = 2.4460(7), and Ru(1)-S(3) = 2.4440(6) Å], and the corresponding three P-S bonds are also equal in length [P(1)-S(1) = 2.0049(9), P(1)-S(2) = 1.9399(10), and P(2)-S(3) = 2.0294(9) A], suggesting that the $[FcPS_2OP(S)SFc]^2$ moiety has a partial π character. The average Ru–S bond length in 9 [av 2.4513(7) Å] is slightly shorter than those in 6 $[av 2.4854(11) \text{ Å}] and 7 \cdot CH_2Cl_2 \cdot \frac{3}{4}C_6H_{14} [av 2.5023(13) \text{ Å}].$ The P(2)-S(4) bond length of 1.9399(10) Å in 9 indicates a considerable double-bond character, which is supported by a strong absorption at 781 cm⁻¹ due to the stretching vibration of the P=S double bond shown in the IR spectrum of 9. The $[FcPS_2OP(S)SFc]^{2-}$ ligand contains a nonlinear P(1)–O-(1)-P(2) linkage with an angle of $129.48(11)^{\circ}$.

In summary, a series of ruthenium complexes containing the dithiophosphonates $[Ar(RO)PS_2]^-$ and $[Fc(RO)PS_2]^-$

ligands were synthesized and characterized structurally and spectroscopically. The dinuclear neutral complexes, $[Ru(\mu \eta^{1}(O), \eta^{1}(S), \eta^{2}(S, S')$ -ArPOS₂)(PPh₃)₂]₂ and [Ru(CO)(μ - η^{1} - $(O), \eta^2(S, S')$ -ArPOS₂)(PPh₃)]₂, were obtained from the reactions of [Ru(PPh₃)₃Cl₂] and [RuHCl(CO)(PPh₃)₃], respectively, with Lawesson's reagent in the presence of ammonium hydroxide. The mononuclear ruthenium(IV) complex [Cp*Ru{(ArPS₂O)₂H}] with a four-legged piano-stool geometry was synthesized from the reaction of dimeric [Cp*Ru-(OMe)]₂ with Lawesson's reagent in the presence of ammonium hydroxide. Similarly, the mononuclear ruthenium(II) complexes $[Ru{Fc(OH)_2PS_2}_2(L')(PPh_3)]$ (L' = PPh₃, CO) were isolated from interaction of [Ru(PPh₃)₃Cl₂] or $[RuHCl(CO)(PPh_3)_3]$ with dimeric $[FcP(S)(\mu-S)]_2$ in the presence of ammonium hydroxide. The mononuclear neutral complex $[(\eta^6-p\text{-cymene})\text{Ru}\{\eta^1(S),\eta^2(S,S')\text{-FcPS}_2\text{OP}(S)\text{SFc}\}]$ was formed via the elimination of water from the [FcP-(OH)S(SH)] intermediate in the presence of NaHCO₃. It is interesting to note that [FcPS₂OP(S)SFc]²⁻ acts as an unsymmetrical tridentate ligand to form one four-membered chelate ring RuS₂P and two six-membered rings RuS₂P₂O. The initial aim of this work was to demonstrate the versatile coordination of the phosphonodithioates formed under different conditions and to study their reactivity as ligands with the typical ruthenium(II) starting complexes. The study of the reactivity of ruthenium-phosphonodithioate complexes toward unsaturated organic substrates is underway in this laboratory.

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Supporting Information Available: Listings of final atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes 1, 2, $3 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{THF}$, 4· CH₂Cl₂·0.5H₂O, 6, $7 \cdot \text{CH}_2\text{Cl}_2 \cdot 3/4\text{C}_6\text{H}_{14}$, and $9 \cdot \text{CH}_2\text{Cl}_2$. This material is available free of charge via the Internet at http:// pubs.acs.org.