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Dinuclear ruthenium complexes containing tripodal dithiophosphonate ligands

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ABSTRACT

Treatment of $[(\eta^6-p-cymene)RuCl(\mu-Cl)]_2$ with Lawesson's reagent $[ArP(S)(\mu-S)]_2$ (Ar = $p-C_6H_4OMe$) in the presence of ammonium hydroxide afforded the dinuclear complex $[(\eta^6-p-cymene)Ru\{\mu-\eta^1(S),\eta^2(S,S')-ArP(O)S_2\}]_2$ (1) in which the tripodal $[ArP(O)S_2]^{2-}$ ligands bind to the ruthenium atom in both bridging and chelating modes with two non-coordinating P=O groups. Interaction of $[RuHCl(CO)(PPh_3)_3]$ with $[ArP(S)(\mu-S)]_2$ and bis(diphenylphosphino)methane (dppm) in the presence of ammonium hydroxide gave the dinuclear complex $[Ru(CO)\{\mu_3-\eta^1(O),\eta^2(S,S')-ArP(O)S_2\}(dppm)]_2$ (2) in which the tripodal $[ArPOS_2]^{2-}$ ligands bind the two Ru atoms *via* both sulfur and oxygen atoms. Treatment of $[Ru(PPh_3)_3Cl_2]$ with $[ArP(S)(\mu-S)]_2$ at reflux in the presence of ammonium hydroxide led to the formation of the dinuclear mixed valence complex $[Ru_2(L_2(\mu-S)\{\mu_3-\eta^1(O),\eta^1(S),-\eta^2(S,S')-ArP(O)S_2\}(PPh_3)_3]$ (3), which contains a $[Ru^{II}(PPh_3)_2Cl]^+$ and $[Ru^{V}(PPh_3)Cl]^{3+}$ moieties by the tripodal $[ArPOS_2]^{2-}$ ligand in a $\mu_3-\eta^1(O),\eta^1(S),\eta^2(S,S')$ coordination mode and the $\mu-S^{2-}$ anion. The crystal structures of 1, 2, and 3-CH₂Cl₂ along with their spectroscopic and electrochemical properties are reported.

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1. Introduction

There has been considerable current interest in the chemistry of ruthenium-sulfur complexes, which is primarily due to their industrial applications in hydrodesulfurization (HDS) and related catalytic processes [1,2]. As the high catalytic activity of RuS₂ in various hydrotreating processes is directed by the sulfur-rich coordination environment around the central metal ion, complexation of ruthenium by thiolate ligands of selected types is of significant importance [3]. As a part of this development, many examples of ruthenium-sulfur complexes with thiolate ligands have been reported [4,5]. Quite a few ruthenium complexes with 1,1'-dithio ligands have also isolated recently [6-8]. Although the phosphor-1,1'-dithio ligands with coinage metals such as copper [9–11], silver [12,13], gold [14–19], and nickel [20–22] are well documented, very few ruthenium-dithiophosphonate complexes have been reported to date [23]. The $[ArPS_2(OR)]^ (Ar = p-CH_3OC_6H_4, R = Me,$ Et, *i*-Pr, and *n*-Pr) anions are normally generated from symmetrical bond cleavage of Lawesson's reagent $[ArP(S)(\mu-S)]_2$ in the presence of corresponding sodium alkoxides [24,25]. As expected, the $[ArPS_2(OR)]^-$ as a phosphor-1,1'-dithio ligand binds to metal ions via the sulfur atoms of PS₂ moiety whilst the introduced OR group

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is not involved in coordination [26,27]. It has been noted that the related thio ligands of the types $[ArPS_3]^{2-}$ and $[ArP(O)S_2]^{2-}$ are found to coordinate copper and silver ions via both sulfur and oxygen atoms [28,29]. The versatile bonding and structural features as well as fascinating chemical reactivities of transition-metal complexes have prompted us to make a systematic study of ruthenium-dithiophosphonate complexes with the tripodal $[ArP(O)S_2]^{2-}$ ligands [23]. Here we report results of these efforts and specially demonstrate three different coordination modes $\mu - \eta^{1}(S), \eta^{2}(S,S')$ (**A**), $\mu_{3} - \eta^{1}(O), \eta^{2}(S,S')$ (**B**) and $\mu_{3} - \eta^{1}(O), \eta^{1}(S), \eta^{2}(S,S')$ (C), as shown in Chart 1, existing in the dinuclear ruthenium $[(\eta^{6}-p-\text{cymene})\text{Ru}\{\mu-\eta^{1}(S),\eta^{2}(S,S')-\text{ArP}(O)S_{2}\}]_{2}$ complexes (1). $[Ru(CO){\mu_3-\eta^1(O),\eta^2(S,S')-ArP(O)S_2}(dppm)]_2$ (dppm = bis(diphenylphosphino)methane) (2), and $[\operatorname{Ru}_2\operatorname{Cl}_2(\mu-S)\{\mu_3-\eta^1(0),\eta^1(S),$ $-\eta^2(S,S')$ -ArP(O)S₂}(PPh₃)₂] (**3**), respectively. The syntheses and molecular structures of these ruthenium-dithiophosphonate complexes along with their spectroscopic and electrochemical properties are described in this paper.

2. Experimental

2.1. General

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Lawesson's reagent, $[ArP(S)(\mu-S)]_2$ (Ar = p-CH₃OC₆H₄), and the ligand bis(diphenylphosphino)methane (dppm) were purchased from Aldrich and used without further



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purification. $[(\eta^6-p-\text{Cymene})\text{RuCl}(\mu-\text{Cl})]_2$ [30], $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ [31], and [Ru(PPh₃)₃Cl₂] [32] were prepared according to the 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 H₃PO₄ (³¹P). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. Cyclic voltammetry was performed with on a CHI 660 electrochemical analyzer. A standard three-electrode cell was used with glassy carbon working electrode, a platinum counter electrode and Ag/AgCl reference electrode under an nitrogen atmosphere at 25 °C. Formal potentials (E°) were measured in CH₂Cl₂ solutions with 0.1 M [^{*n*}Bu₄N]PF₆ as supporting electrolyte and reported with reference to the ferrocenium-ferrocene couple ($Cp_2Fe^{+/0}$). In the -0.5 to +1.2 V region, a potential scan rate of 100 mV s⁻¹ was used. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. Synthesis of $[(\eta^6 - p - cymene)Ru\{\mu - \eta^1(S), \eta^2(S, S') - ArP(O)S_2\}]_2$ (1)

To a slurry of Lawesson's reagent (82 mg, 0.20 mmol) and 17% NH₃·H₂O (0.2 mL) in THF (10 mL) was added a solution of $[(\eta^6-p-\text{cymene})\text{RuCl}(\mu-\text{Cl})]_2$ (108 mg, 0.20 mmol) in THF (10 mL). The mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo. The solid residue was washed with hexane and further dissolved in 10 mL CH₂Cl₂. The white solid was removed by the filtration. The filtrate was carefully layered with hexane, needle red crystals of 1 suitable for X-ray diffraction were obtained in four days. Yield: 93 mg, 51% (based on Ru). ¹H NMR (300 MHz, CDCl₃): δ ppm) 1.32 (d, 6H, CH(CH₃)₂), 2.14 (s, 3H, PhCH₃), 3.01 (septet, 1H, CH(CH₃)₂), 3.72 (s, 6H, OCH₃), 5.42 and 5.69 (dd, 4H, J = 8.2 Hz, aryl H in cymene), 6.82 (d, 4H, J = 7.8 Hz, aryl H), 7.75–7.97 (dd, 4H, J = 7.9 Hz, aryl H). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ (ppm) 63.5 (s). Selected IR (KBr, cm⁻¹): 1585 (s), 1430 (s), 1244 (s), 689 (s), 556 (s), 531 (m), 503 (s). MS (FAB): *m*/*z* 907 [M⁺], 455 [½M⁺+1]. Anal. Calc. for C₃₄H₄₂O₄P₂S₄Ru₂: C, 45.03; H, 4.67. Found: C, 44.74; H, 4.63%.

2.3. Synthesis of $[Ru(CO)\{\mu-\eta^1(O),\eta^2(S,S')-ArP(O)S_2\}(dppm)]_2$ (**2**)

To a slurry of Lawesson's reagent (41 mg, 0.10 mmol) and 17% $NH_3 \cdot H_2O$ (0.2 mL) in THF (10 mL) was added a solution of [RuHCl(-CO)(PPh_3)_3] (190 mg, 0.20 mmol) in THF (10 mL). The mixture was stirred for 1 h at room temperature and dppm (78 mg, 0.20 mmol) was added, then the mixture was further stirred for additional 3 h. The solvent was removed in vacuo. The solid residue was washed with hexane and further dissolved in 10 mL CH₂Cl₂. The white solid was removed by the filtration. The filtrate was carefully layered with hexane, yellow crystalline solids of **2** in three days at room

2.4. Synthesis of $[Ru_2Cl_2(\mu-S)\{\mu_3-\eta^1(O),\eta^1(S),-\eta^2(S,S')-ArP(O)S_2\}-(PPh_3)_3]\cdot CH_2Cl_2$ (**3**·CH_2Cl_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 reflux for 12 h. The solvent was removed in vacuo. The solid residue was washed with hexane and further dissolved in 10 mL CH₂Cl₂. The white solid was removed by the filtration. The filtrate was carefully layered with hexane, blocky black crystals of 3 CH₂Cl₂ suitable for X-ray diffraction were obtained in a week. Yield: 64 mg, 46% (based on Ru). ¹H NMR (300 MHz, CDCl₃): δ ppm 3.71 (s, 3H, OCH₃), 5.32 (s, 2H, CH₂Cl₂), 6.73 (d, 2H, J = 7.6 Hz, aryl H), 7.16–7.53 (m, 45H, PPh₃), 7.81–8.06 (dd, 2H, J = 7.8 Hz, aryl H). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ ppm 22.6 (d, J = 203 Hz, 2P, PPh₃), 30.1 (s, 1P, PPh₃), 43.4 (s, 1P, ArPS₂O). Selected IR (KBr, cm⁻¹): 1581 (s), 1430 (s), 1019 (s), 679 (s), 557 (s), 534 (m), 502 (s). MS (FAB): m/z 1310 [M⁺], 1275 [M⁺-Cl], 1240 $[M^+-2Cl]$. Anal. Calc. for $C_{61}H_{52}O_2Cl_2P_4S_3Ru_2$ (CH₂Cl₂): C, 53.34; H, 3.90. Found: C, 52.71; H, 3.84%.

2.5. X-ray crystallography

Found: C, 54.07; H, 3.95%.

A summary of crystallographic data and experimental details for $[(\eta^6 - p - cymene) - Ru\{\mu - \eta^1(S), \eta^2(S, S') - ArP(O)S_2\}]_2$ (1), $[Ru(CO)\{\mu - \eta^2(S, S') - ArP(O)S_2\}]_2$ $\eta^{1}(O), \eta^{2}(S,S') - ArP(O)S_{2}(dppm)]_{2}$ (**2**), and $[Ru_{2}Cl_{2}(\mu-S)\{\mu_{3}-\eta^{1}(O), \mu_{3}-\eta^{2}(O)\}]_{2}$ $\eta^{1}(S), -\eta^{2}(S,S')$ -ArP(O)S₂}(PPh₃)₃]·CH₂Cl₂ (**3**·CH₂Cl₂) are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 293(2) K. The collected frames were processed with the software SAINT [33]. The data was corrected for absorption using the program sADABS [34]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [35,36]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3} -H = 0.96 and C_{sp2} -H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of least-squares refinement.

3. Results and discussion

Preliminary results showed that treatment of Lawesson's reagent $[ArP(S)(\mu-S)]_2$ with ammonium hydroxide $(NH_3 \cdot H_2O)$ in a THF solution resulted in a homogeneous solution [23]. Actually, the $[ArP(O)S_2]^{2-}$ as a major component exists in the solution in the presence of base. Accordingly, reaction of the mixture with the ruthenium starting materials led to the isolation of diruthenium–dithiophosphonate complexes. The tripodal ligands bind to the ruthenium atom in three different coordination modes (Chart 1 and Scheme 1).

It has been noted that treatment of $[(\eta^6-p\text{-cymene})\text{RuCl}(\mu\text{-Cl})]_2$ with $[\text{ArP}(S)(\mu\text{-S})]_2$ in the absence of NH₃·H₂O at reflux afforded the dinuclear complex $[(\eta^6-p\text{-cymene})\text{Ru}\{\mu-\eta^1(S),\eta^2(S,S')\text{-ArP}(S)S_2]]_2$ with two terminal P=S bonds [23]. However, reaction of $[(\eta^6-p\text{-})\text{-}$

Table 1

Crystallographic data and experimental details for $[(\eta^6-p-cymene)Ru{\{\mu-\eta^1(S),\eta^2(S,S')-ArP(O)S_2\}]_2(1), [Ru(CO){\{\mu_3-\eta^1(O),\eta^2(S,S')-ArP(O)S_2\}}(dppm)]_2(2), and [Ru_2Cl_2(\mu-S){\{\mu_3-\eta^1(O),\eta^1(S),-\eta^2(S,S')-ArP(O)S_2\}}(PPh_3)_2]-CH_2Cl_2(3-CH_2Cl_2).$

Compound	1	2	$3 \cdot CH_2Cl_2$
Empirical formula	$C_{34}H_{42}O_4P_2S_4Ru_2$	$C_{66}H_{58}O_6P_6S_4Ru_2$	$C_{62}H_{54}O_2Cl_4P_4S_3Ru_2$
Formula weight	907.00	1463.32	1395.05
Crystal system	monoclinic	triclinic	triclinic
Unit cell dimensions			
a (Å)	12.0589(7)	11.1328(7)	11.0054(1)
b (Å)	10.5437(6)	11.6164(7)	13.4004(2)
c (Å)	14.8083(10)	14.5682(9)	20.8159(3)
α (°)		75.517(1)	86.553(1)
β (°)	106.595(4)	76.385(1)	79.733(1)
γ (°)		61.430(1)	84.064(1)
<i>V</i> (Å ³)	1804.38(19)	1587.09(17)	3001.78(7)
Space group	$P2_1/n$	PĪ	ΡĪ
Ζ	2	1	2
D_{calc} (g cm ⁻³)	1.669	1.531	1.543
T (K)	296(2)	296(2)	296(2)
F(000)	920	744	1412
μ (Mo K α) (mm ⁻¹)	1.194	0.810	0.935
Total reflections	16165	22291	42007
Independent reflections	4106	7267	13809
Parameters	212	380	695
R _{int}	0.0340	0.0288	0.0213
$R_1^{a}, wR_2^{b} (I > 2\sigma(I))$	0.0329, 0.0729	0.0275, 0.0635	0.0325, 0.0796
R_1 , wR_2 (all data)	0.0534, 0.0857	0.0347, 0.0673	0.0419, 0.0856
Goodness-of-fit (GOF) on F^{2c}	1.031	1.043	1.020

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$

^b $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}.$

^c GoF = $[\sum w|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.

cymene)RuCl(μ -Cl)]₂ with [ArP(S(S)(μ -S)]₂ in the presence of NH₃·H₂O at room temperature gave analogous complex $[(\eta^6-p$ cymene)Ru{ μ - $\eta^{1}(S)$, $\eta^{2}(S,S')$ -ArP(O)S₂}]₂ (**1**) with two terminal P=O bonds. The IR spectrum of **1** shows the v (P=O) and v (P-S) stretching vibrations at 1244 and 689 cm⁻¹, respectively. The ³¹P{¹H} NMR spectrum of **1** in CDCl₃ exhibited a single resonance at δ 63.5 ppm which obviously shifts upfield by the comparison of analogous complex $[(\eta^6-p-\text{cymene})\text{Ru}\{\mu-\eta^1(S),-\eta^2(S,S')-\text{ArP}(S)S_2\}]_2$ with same structural type (84.1 ppm) [23]. The positive ion FAB mass spectrum of **1** shows the molecular ions $[M^+]$ and $[\frac{1}{2}M^++1]$ with the characteristic isotopic distribution patterns. As the previous report, interaction of $[RuHCl(CO)(PPh_3)_3]$ with $[ArP(S)(\mu-S)]_2$ in the presence of NH₃·H₂O gave the dinuclear complex $[Ru(CO)(\mu_3 - \eta^1(O), \eta^2(S, S') - ArPOS_2)(PPh_3)_2]_2$ [23] in which the PPh₃ ligands were substituted by stronger σ -donor dppm ligands in the present reaction, leading to isolation of a new dinuclear complex $[Ru(CO){\mu_3-\eta^1(O),\eta^2(S,S')-ArP(O)S_2}(dppm)]_2$ (2). The IR spectrum of **2** shows a strong absorption band at 1025 cm⁻¹ which is assigned to the v (P–O) vibration [37]. The absorption band at 677 cm⁻¹ may be due to the v (P–S) vibration bond. The v (C \equiv O) stretching vibration was found at 1988 cm⁻¹ in the IR spectrum of **2** [37]. The ³¹P{¹H} NMR spectrum of **2** in CDCl₃ shows an intense singlet at δ 14.7 ppm and a weak singlet at δ 58.6 ppm, assignable to dppm and $[ArP(O)S_2]^{2-}$, respectively. The positive ion FAB mass spectrum of **2** displays the expected peaks at m/z 1463, 731 and 703, corresponding to the molecular ions $[M^+]$, $[\frac{1}{2}M^+-1]$ and [½M⁺-CO-1], respectively, with the characteristic isotopic distribution patterns. Contrast to formation of the dinuclear complex [Ru(μ - $\eta^1(O)$, $\eta^2(S)$, $\eta^2(S,S')$ -ArPOS₂)(PPh₃)₂]₂ from reaction of $[Ru(PPh_3)_3Cl_2]$ with $[ArP(S)(\mu-S)]_2$ in the presence of NH₃·H₂O [23], treatment of $[Ru(PPh_3)_3Cl_2]$ with $[ArP(S)(\mu-S)]_2$ at reflux in THF followed by recrystallization from CH₂Cl₂/hexane gave airstable black crystals characterized as $[Ru_2Cl_2(\mu-S){\mu_3-\eta^1(O),\eta^1(S),-\eta^1(S),-\eta^1(O),\eta^1(S),-\eta^$ $\eta^{2}(S,S')$ -ArP(O)S₂}(PPh₃)₃] (**3**). Two [Ru(PPh₃)₂Cl]⁺ and [Ru(PPh₃) Cl]³⁺ fragments were bridged by the tripodal $[ArP(O)S_2]^{2-}$ and μ -S²⁻ ligands, indicative of the mixed-valence octahedral ruthenium(II) and trigonal-bipyramidal ruthenium(IV) centers in the

neutral dinuclear complex 3. Although the mechanism for the formation of **3** has not been well elucidated, it seems likely that the partly decomposition of $[ArP(S)(\mu-S)]_2$ at reflux to the S²⁻ anion is involved. The oxidation of Ru^{II} to Ru^{IV} was probably caused by a Ru disproportionation reaction under thermodynamic conditions [38]. Complex 3 is not a Ru(III)-Ru(III) complex that should be paramagnetic due to an anti-ferromagnetic coupling across the sulfidoligands. The identity of the μ_3 -bridging ligand (S1) can be assigned as either sulfur or oxygen. However, the formulation of **3** as a μ_3 oxo complex will result in the structural refinement with higher R value with unacceptable thermal parameters. The formulation of **3** as a μ_3 -sulfide complex was further supported by microanalytic and NMR analyses. Notwithstanding, we still puzzled why the ruthenium(II) center could be bound to the hard oxygen atoms of the tripodal $[ArP(O)S_2]^{2-}$ ligand in **3**. In the ³¹P{¹H} NMR spectrum of **3**, two singlets at δ 30.1 and 43.4 ppm were tentatively assigned to $[Ru(PPh_3)Cl]^{3+}$ and $[ArP(O)S_2]^{2-}$ moieties, respectively, one doublet at δ 22.6 ppm may be reasonably assigned to two phosphorous atoms in the [Ru(PPh₃)₂Cl]⁺ fragment. The P–P coupling constant was determined to be $J({}^{31}P, {}^{31}P) = 203$ Hz with a clear resolution of the doublet signal. The FAB⁺ mass spectrum of complex **3** exhibits molecular ions corresponding to [M⁺], [M⁺-Cl] and [M⁺-2Cl] with the characteristic isotopic distribution patterns. Although the parent molecular ions of complex 3 are detected at very low intensity, a series of intense peaks assigned to ions which are formed by the subsequent loss of the chloride ligands were observed.

Complex **1** crystallized in the monoclinic space group $P2_1/n$, and the molecular structure of **1** is illustrated in Fig. 1 and selected bond lengths and angles are given in Table 2. The neutral complex **1** comprises two $[(\eta^6-p\text{-cymene})\text{Ru}]^{2+}$ fragments bridged by the sulfur atoms of two $[\text{ArP}(\text{O})\text{S}_2]^{2-}$ moieties with two non-coordinative P=O groups. 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 dithiophosphonato moiety is essentially symmetrically bonded to two ruthenium atoms with distances [Ru(1)-S(2) = 2.4169(8) and Ru(1)-S(2a) = 2.4227(8) Å, symmetric



Scheme 1. Synthetic route for three diruthenium–dithiophosphonate complexes. Reagents and conditions: (i) NH₃·H₂O, THF, rt; (ii) $[(\eta^6-p-cymene)RuCl(\mu-Cl)]_2$, THF, rt; (iii) $[RuHCl(CO)(PPh_3)_3]$, dppm, THF, rt; (iv) $[Ru(PPh_3)_3Cl_2]$, THF, reflux.



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

code: a -x + 2, -y, -z.] while the S(1) atom is bonded to the corresponding ruthenium atom with Ru(1)–S(1) distance of 2.4308(9) Å, which is compatible to bonding characters in the similar complex $[(\eta^6-p-cymene)Ru\{\mu-\eta^1(S),\eta^2(S,S')-ArP(S)S_2\}]_2$ [23] Accordingly,

Table 2								
Selected	bond	lengths	(Å)	and	angles	(°)	for	$[(\eta^{6}-p-cymene)Ru\{\mu-\eta^{1}(S),\eta^{2}(S,S')\}$
$ArP(0)S_2$	}] ₂ (1).							

(-)-2)]2 (-).			
Ru(1)-S(1)	2.4308(9)	Ru(1)-S(2)	2.4169(8)
Ru(1)-S(2)#1	2.4227(8)	P(1)-S(1)#1	2.0270(12)
P(1)-S(2)	2.1246(12)	P(1)-O(1)	1.488(2)
S(2)-Ru(1)-S(1)	85.46(3)	S(2)#1-Ru(1)-S(1)	81.21(3)
P(1)#1-S(1)-Ru(1)	86.72(4)	P(1)-S(2)-Ru(1) = 1	106.93(4)
P(1)-S(2)-Ru(1)#1 O(1)-P(1)-S(1)#1	84.82(4) 117.26(11)	S(1)#1-P(1)-S(2) O(1)-P(1)-S(2)	99.05(5) 117.18(11)

Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y, -z.

two the sulfur atoms of the tripodal dithiophosphonato $[ArP(O)S_2]^{2-}$ ligands act as tri-coordinate atoms in both bridging and chelating modes. The P–O bond length of 1.488(2) Å in **1** is obviously typical for the double-bond character.

The solid-state structure of **2** has been confirmed by X-ray crystallography. Complex **2** crystallized in the triclinic space group $P\bar{1}$ with centro-symmetry. Fig. 2 shows a perspective view of **2**; selected bond lengths and angles are given in Table 3. The neutral complex **2** comprises two $[Ru(CO)(dppm)_2]^{2+}$ 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 ruthenium atom with a bite angle S–Ru–S of 80.62(2)°. Each ruthenium atom



Fig. 2. Perspective view of $[Ru(CO){\mu_3-\eta^1(O),\eta^2(S,S')-ArP(O)S_2}(dppm)]_2$ **2**.



Ru(1)-S(1)	2.4483(5)	Ru(1)-S(2)	2.4492(5)
Ru(1)-P(2)	2.3197(6)	Ru(1) - P(3)	2.3201(5)
Ru(1)-C(1)	1.811(2)	Ru(1)-O(2)#1	2.1729(13)
P(1)-S(1)	2.0396(7)	P(1)-S(2)	2.0471(7)
P(1)-O(2)	1.5130(14)	C(1)-O(1)	1.157(2)
S(1)-Ru(1)-S(2)	80.619(18)	P(2)-Ru(1)-S(1)	171.826(19)
P(3)-Ru(1)-S(1)	104.52(2)	C(1)-Ru(1)-S(1)	89.91(7)
C(1)-Ru(1)-S(2)	89.90(7)	O(2)#1-Ru(1)-S(2)	93.27(4)
P(2)-Ru(1)-S(2)	101.641(19)	P(3)-Ru(1)-S(2)	174.562(19)
C(1)-Ru(1)-O(2)#1	176.71(7)	C(1)-Ru(1)-P(2)	97.91(7)
O(2)#1-Ru(1)-P(2)	80.60(4)	C(1)-Ru(1)-P(3)	91.86(7)
O(2)#1-Ru(1)-P(3)	84.90(4)	P(2)-Ru(1)-P(3)	73.02(2)
P(1)-S(1)-Ru(1)	88.26(2)	P(1)-S(2)-Ru(1)	88.07(2)
P(1)-O(2)-Ru(1)#1	146.70(9)	Ru(1)-C(1)-O(1)	177.6(2)

Symmetry transformations used to generate equivalent atoms: #1 -x + 2, -y + 1, -z + 1.

is surrounded by two μ -S, one μ -O, one C and two P atoms, forming a highly distorted octahedral geometry. The Ru–C bond length and Ru–C–O bond angle in **2** are 1.811(2) Å and 177.6(2)°, respectively, which are comparable to those in [Ru(CO){ μ_3 - $\eta^1(O)$, $\eta^2(S,S')$ -ArP(O)S₂}(PPh₃)₂]₂ [Ru–C = 1.804(4) Å and Ru–C–O = 174.8(4)°] [23] and [RuH(CO){S₂P(OEt})₂}(PPh₃)₂] [Ru–C = 1.829(4) Å and Ru–C–O = 175.4(4)°] [39]. The average Ru–P bond length of 2.3320(1) Å in **2** is normal in the ruthenium complexes with Ru–P(dppm) bonds [40], whereas the bent angle P–O–Ru (av. 146.70(9)°) in **2** is obviously larger than those in [Ru(CO)-{ μ_3 - $\eta^1(O)$, $\eta^2(S,S')$ -ArP(O)S₂}(PPh₃) _2]₂ (av. 143.70(15)°) and [Ru(μ - $\eta^1(O)$, $\eta^2(S)$, $\eta^2(S,S')$ -ArPOS₂)(PPh₃)₂]₂ (av. 101.08(7)°) [23], an indicative of the bulky of the dppm ligands in complex **2**.

X-ray structural analysis revealed that **3**·CH₂Cl₂ crystallized in the triclinic space group $P\bar{1}$, consists of one neutral complex and one CH₂Cl₂ solvent molecule. The molecular structure of **3** is shown in Fig. 3, selected bond lengths and angles of **3**·CH₂Cl₂ are listed in Table 4. The mixed-valence ruthenium atoms are bridged by the tripodal [ArPOS₂]²⁻ ligand in a μ_3 - $\eta^1(O)$, $\eta^1(S)$, $\eta^2(S,S')$ coordination mode and the μ -S²⁻ anion. The geometry around Ru^{II} in **3**·CH₂Cl₂ is a highly distorted octahedron whereas the Ru^{IV}-containing moiety has a distorted trigonal {RuS₂Cl} core with the μ_3 -S and PPh₃ at the axial positions [S(1)–Ru(2)–P(4) = 177.14(2)°]. The four-



Fig. 3. Perspective view of $[Ru_2Cl_2(\mu-S){\mu_3-\eta^1(O),\eta^1(S),\eta^2(S,S')-ArP(O)S_2}(PPh_3)_2]$ **3.**

Table 4Selected bond lengths (Å) and angles (°) for $[Ru_2Cl_2(\mu-S)\{\mu_3-\eta^1(0),\eta^1(S),\eta^2(S,S')-ArP(O)S_2\}(PPh_{3})_2]\cdot CH_2Cl_2$ (3 · CH₂Cl₂).

$\begin{array}{cccccccccccccccccccccccccccccccccccc$				
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ru(1)-S(3)Ru(2)-S(3)Ru(2)-S(2)Ru(1)-P(2)Ru(2)-P(4)Ru(2)-P(4)S(2)-P(1)	2.1938(6) 2.1415(6) 2.3447(7) 2.3380(6) 2.3174(7) 2.3073(7) 2.0563(9)	$\begin{array}{c} Ru(1)-S(1) \\ Ru(2)-S(1) \\ Ru(1)-O(1) \\ Ru(1)-P(3) \\ Ru(1)-Cl(1) \\ S(1)-P(1) \\ P(1)-O(1) \end{array}$	2.5090(6) 2.4667(6) 2.2325(16) 2.3665(7) 2.4626(7) 2.0615(9) 1.5134(19)
	$\begin{split} & S(3)-Ru(1)-O(1) \\ & O(1)-Ru(1)-P(2) \\ & O(1)-Ru(1)-P(3) \\ & S(3)-Ru(1)-Cl(1) \\ & P(2)-Ru(1)-Cl(1) \\ & P(2)-Ru(1)-S(1) \\ & Cl(1)-Ru(1)-S(1) \\ & Cl(1)-Ru(1)-S(1) \\ & S(3)-Ru(2)-P(4) \\ & S(3)-Ru(2)-P(4) \\ & S(3)-Ru(2)-S(2) \\ & P(4)-Ru(2)-S(2) \\ & P(4)-Ru(2)-S(2) \\ & Cl(2)-Ru(2)-S(1) \\ & S(2)-Ru(2)-S(1) \\ & P(1)-S(2)-Ru(2) \\ & P(1)-O(1)-Ru(1) \\ \end{split}$	93.52(5) 164.72(5) 93.64(5) 167.92(3) 87.46(3) 83.74(2) 95.12(2) 84.37(2) 96.99(2) 104.37(3) 97.13(2) 88.27(2) 88.27(2) 88.27(2) 82.39(2) 78.99(3) 86.12(3) 101.05(9)	$\begin{split} S(3)-Ru(1)-P(2)\\ S(3)-Ru(1)-P(3)\\ P(2)-Ru(1)-P(3)\\ O(1)-Ru(1)-Cl(1)\\ P(3)-Ru(1)-Cl(1)\\ P(3)-Ru(1)-S(1)\\ S(3)-Ru(2)-Cl(2)\\ Cl(2)-Ru(2)-P(4)\\ Cl(2)-Ru(2)-P(4)\\ Cl(2)-Ru(2)-S(1)\\ P(4)-Ru(2)-S(1)\\ P(4)-Ru(2)-S(1)\\ P(1)-S(1)-Ru(2)\\ Ru(2)-S(1)-Ru(1)\\ Ru(2)-S(3)-Ru(1) \end{split}$	95.75(2) 90.73(2) 98.35(2) 81.07(5) 100.35(2) 73.83(5) 165.89(2) 115.23(3) 90.26(3) 138.47(3) 85.86(2) 177.14(2) 82.87(3) 86.24(2) 103.34(2)

membered Ru₂S₂ ring is almost co-planar with deviation (0.068 Å) from the least square plane. Two Ru- μ_3 -S bond lengths [Ru(1)–S(1) = 2.509(1) Å and Ru(2)–S(1) = 2.468(1) Å] are obviously longer than two Ru- μ -S bond lengths [[Ru(1)–S(3) = 2.194(1) Å and Ru(2)–S(3) = 2.142(6) Å] in the Ru₂S₂ ring. The Ru^{IV}–S bond lengths in **3**·CH₂Cl₂ are compared with those in the ruthenium(IV)-thiolate complexes [41,42]. The Ru(1)–Cl(1) bond length of 2.463(1) Å in the octahedral core is slightly longer than the Ru(2)–Cl(2) bond length of 2.307(1) Å in the trigonal–bipyramidal core. The bent angle P–O–Ru of 101.05(9)° in **3**·CH₂Cl₂ is obviously acuter than those in [Ru(CO){ μ - η ¹(O), η ²(S,S')-ArP(O)S₂}(PPh₃)]₂ (av. 143.70(15)°) [23] and **2** (av. 146.70(9)°), but is compared with [Ru(μ - η ¹(O), η ²(S), η ²(S,S')-ArPOS₂)(PPh₃)₂]₂ (av. 101.08(7)°) with two [Ru(PPh₃)₂]²⁺ moieties [23]. The Ru^{II}···Ru^{II} non-bonding separation of 3.738 Å in (μ - η ¹(O), η ²(S), η ²(S,S')-ArPOS₂)(PPh₃)₂]₂ [23].

Formal redox potentials of the present ruthenium– dithiophosphonate complexes **1–3** have been determined by cyclic voltammetry. The cyclic voltammograms of complexes **1** and **2** in CH₂Cl₂ show a reversible couple at ca. 0.10–0.23 V, versus Cp₂Fe^{+/} ^o, which is assigned as the metal-centered Ru^{III}–Ru^{II} couple because tripodal [ArPOS₂]^{2–} ligand is redox inactive at this potential, another irreversible couples at 0.44 V for **1** and 0.51 V for **2** are tentatively attributed to Ru^{III}–Ru^{IV} oxidation. The cyclic voltammogram of **3** in CH₂Cl₂ shows two reversible couples at 0.21 and 0.85 V which are tentatively attributed to the metal-centered Ru^{III}–Ru^{II} and Ru^{III}–Ru^{IV} couples, respectively. The one-electron nature of these responses has been confirmed by comparing their current heights with the standard Cp₂Fe^{+/0} under identical experimental conditions [43]. The irreversibility of Ru^{III}–Ru^{IV} oxidation for **1** and **2** suggests that the ruthenium(II) state in two complexes is well stabilized by the combination of σ -donor phosphine and electron-rich sulfur ligands [44].

In summary, we have synthesized and structurally characterized three dinuclear ruthenium complexes containing tripodal dithiophosphonato $[ArP(O)S_2]^{2-}$ (Ar = *p*-CH₃OC₆H₄) ligands which exhibit three different coordination modes. Complex $[(n^6-p-cvme$ ne)Ru{ μ - $\eta^1(S)$, $\eta^2(S,S')$ -ArP(O)S₂}]₂ (1) displays two the sulfur atoms of the tripodal [ArP(O)S₂]²⁻ as tri-coordinate atoms in both bridging and chelating modes, leaving two non-coordinative P=O groups. Complex $[Ru(CO){\mu_3-\eta^1(O),\eta^2(S,S')-ArP(O)S_2}(dppm)]_2$ (**2**) comprises two $[Ru(CO)(dppm)_2]^{2+}$ fragments symmetrically bridged by two tripodal $[ArPOS_2]^{2-}$ ligands *via* the sulfur and oxygen atoms. Complex $[Ru_2Cl_2(\mu-S)\{\mu_3-\eta^1(0),\eta^1(S),-\eta^2(S,S')-\eta^2(S,S')\}$ $ArP(O)S_2(PPh_3)_2$ (3) contains two mixed-valence ruthenium-containing species [Ru^{II}(PPh₃)₂Cl]⁺ and [Ru^{IV}(PPh₃)Cl]³⁺ bridged by the tripodal [ArPOS₂]^{2–} ligand in a μ_3 - $\eta^1(O)$, $\eta^1(S)$, $\eta^2(S,S')$ coordination mode and the μ -S^{2–} anion. The geometry around Ru^{II} is a highly distorted octahedron whereas the Ru^{IV}-containing moiety has a distorted trigonal {RuS₂Cl} core with the μ_3 -S and PPh₃ at the axial positions. The initial aim of this work was to demonstrate the versatile coordination modes of the tripodal dithiophosphonato $[ArP(O)S_2]^{2-}$ ligands and to study their reactivity as ligands with the typical ruthenium(II) starting complexes. The study of the reactivity of ruthenium-dithiophosphonate complexes toward unsaturated organic substrates is underway in this laboratory.

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Appendix A. Supplementary material

CCDC 800317, 800317 and 800319 contain the supplementary crystallographic data for $[(\eta^6-p\text{-cymene})\text{Ru}\{\mu-\eta^1(S),\eta^2(S,S')-\text{ArP}(O)S_2\}]_2$ (1), $[\text{Ru}(\text{CO})\{\mu_3-\eta^1(O),\eta^2(S,S')-\text{ArP}(O)S_2\}(\text{dppm})]_2$ (2), and $[\text{Ru}_2\text{Cl}_2(\mu-S)\{\mu_3-\eta^1(O),\eta^1(S),-\eta^2(S,S')-\text{ArP}(O)S_2\}(\text{PPh}_3)_3]\cdot\text{CH}_2\text{Cl}_2$ (3·CH₂Cl₂), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.044.

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