

Synthetic and X-ray Structural and Reactivity Studies of Cp^{*}Ru^{IV} Complexes Containing Bidentate Dithiocarbonate, Xanthate, Carbonate, and Phosphinate Ligands (Cp^{*} = η^5 -C₅Me₅)

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The reaction of [Cp^{*}RuCl₂]₂ (**1**; Cp^{*} = η^5 -C₅Me₅) with tetraalkyldithiuram disulfides (R₂NC(S)SS(S)CNR₂, R = Me, Et), isopropylxanthic disulfide ([ⁱPrOC(S)S]₂), and bis(thiophosphoryl) disulfide ([(ⁱPrO)₂P(S)S]₂) led to the isolation of dark-red crystalline solids of Cp^{*}Ru^{IV}Cl₂(η^2 -dithiolate) complexes [dithiolate = S₂CNR₂, DTC_R (**2a**, R = Me; **2b**, R = Et), S₂COⁱPr (**3**), and S₂P(ⁱPrO)₂ (**4**)]. Dichlorido substitution in **2** and **3** with DTC_{Et} and S₂COⁱPr anions yielded Ru^{IV} derivatives containing bis(DTC) and mixed DTC–dithiocarbonate ligands. These are the first *organoruthenium* complexes of such ligands. The reaction of monophosphines with **2a** resulted in monochlorido substitution, whereas the analogous reaction with **3** resulted in displacement of both chlorido ligands and reduction of the metal center to Ru^{II}. Reduction at Ru was also observed in the reaction of **2a** with [CpCr(CO)₃]₂. Of these complexes, only **2** and **3** are air-stable in the solid state for an extended period. All of the complexes have been spectrally characterized, and selected compounds are also crystallographically characterized.

Introduction

The lower (2+ to 0) oxidation states dominate the organometallic chemistry of Ru.¹ Higher oxidation states are still uncommon, though inorganic compounds of Ru^{III} and Ru^{IV} are found quite frequently in the coordination environment of thiolate (–SR) ligands² and 1,1′-dithiolate ligands like dithiocarbamate (DTC). Ru^{IV}(DTC) coordination compounds were extensively studied in the 1970s by Pignolet, who reported examples of both the “binary” and “mixed-ligand” types, with halogeno coligands.³ Other Ru^{IV}(DTC) complexes with various types of coligands include dimeric

[Ru(DTC_{Me})(CO)(PPh₃)(μ -SPh)]₂^{4a} and Ru(DTC_{Et})(Ts₂N₄)(Ts₂N₄ = ditosyltetrazene).^{4b} Non-DTC Ru^{IV} compounds are rare, with examples being Ru(chbae)(PPh₃)(py) [H₄(chbae) = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane],^{5a} and Ru(bipy)(NHCMe₂CMe₂NH)₂^{5b} reported by Che and co-workers, Ru(PCy₃)(“S₂N₂”) [“S₂N₂”⁴⁻ = 1,2-ethanediamide-

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N,N'-bis(2-benzenethiolate)(4-)] from Sellmann's group,^{5c} and [Ru(mnt)₃]²⁻ [mnt²⁻ = 1,2-dicyanoethylenedithiolate-(2-)] reported by Lappin et al.^{5d}

The first organoruthenium(IV) complex was the μ -dichloridobis(allyl) complex [RuCl(μ -Cl)(η^3 : η^3 -C₁₀H₁₆)₂], formed by oxidative trimerization of butadiene or dimerization of isoprene at Ru^{II} in the mid-1960s.⁶ The following 2 decades saw sporadic reports of other organoruthenium(IV) complexes commonly obtained from Ru^{II} species by oxidative addition of hydrogen,⁷ halogens,⁸ quinones,⁹ and allylic halides.¹⁰ The use of the ruthenium(III) halide [Cp*RuCl₂]_n, first synthesized by Bercaw and Suzuki and their co-workers in 1984,¹¹ was exploited by Itoh as a new precursor to Cp*Ru^{IV} complexes via treatment with allylic halides, alcohol, ether, acetate or sulfides,^{12a} and halogens.^{12b} Other routes to Cp/Cp*Ru^{IV} complexes include alkylation, for instance, of Cp/Cp*Ru(η^3 -C₃H₅)X₂ (X = Cl, Br), which yielded Cp/Cp*Ru(η^3 -C₃H₅)(Me)X, Cp/Cp*Ru(Me)L₂X in the presence of ligand L (phosphines or dienes),^{13a} or [CpRu(η^3 -C₃H₅)₂]⁺ when treated with silver(I) triflate in the presence of propene.^{13b} The oxidation of [Cp*RuCl₂]_n with the ferrocenium ion in the presence of tetrahydrothiophene led to [Cp*RuCl₂(SC₄H₈)₂]⁺.¹⁴ The reaction of [RuCl(μ -Cl)(η^3 : η^3 -C₁₀H₁₆)₂] with RSH (R = alkyl or aryl) led to the doubly thiolate-bridged complex [Ru^{IV}Cl(μ -SR)(η^3 : η^3 -C₁₀H₁₆)₂].¹⁵ Recently, Leung reported the syntheses of Cp*Ru complexes containing S- and Se-donor ligands from the Ru^{II} complexes [Cp*Ru(NO)Cl₂] and [Cp*Ru(MeCN)₃]⁺¹⁶ and a ruthenium(IV) acetylide complex [Ru(SR)₃Cl(C \equiv CPh/tol)]⁻ (R = 2,6-dimethylphenyl, tol = 4-tolyl) from [Ru(SR)₃(MeCN)Cl].¹⁷

We were interested in exploring the reactivity of [Cp*RuCl₂]_n toward disulfides of the [Z(S)S]₂ types [Z = R₂NC, tetraalkyldithiuram disulfide for R = Me or Et; Z = ⁱPrOC, isopropylxanthic disulfide; Z = (ⁱPrO)₂P, bis(thiophosphoryl) disulfide]. It has been established that these disulfides readily undergo oxidative addition at transition-metal moieties, leading to complexes with dithio derivatives, of which the most common are the DTCs.¹⁸ In earlier work with some of these disulfides, we had isolated CpCr complexes containing DTC, dithiocarboxamide, and dithiophosphinate ligands.¹⁹ Other possible outcomes may include adduct formation and disulfide ligand oxidation.¹⁸ In this present study, it is anticipated that further variation of products can arise from no, partial, or total substitution of the chlorido ligands by the derivative dithio ligands, with or without oxidation state changes at the metal center. The resultant S-containing complexes of Cp*Ru will be of interest with regard to industrial and biochemical/biological processes.²⁰ The observation of reversible one-step four-electron redox reactions in the Ru^{II} complex [Ru(DTC)(CO)(PPh₃)(μ -Sph)]₂²¹ indicates that electron-rich Ru(DTC) complexes are potential candidates as multielectron catalysts.

Our studies resulting in Cp*Ru^{IV}(dithiolato) complexes are described in this paper.

Experimental Section

All manipulations were carried out under purified N₂ using conventional Schlenk techniques or under an inert atmosphere of Ar in an M. Braun Labmaster 130 Inert Gas System glovebox.

NMR spectra were measured on a Bruker 300-MHz Fourier transform (FT)-NMR spectrometer (¹H at 300.14 MHz, ¹³C at 75.43 MHz, and ³¹P at 121.49 MHz) or a Bruker AMX500 500-MHz FT-NMR spectrometer (¹H at 500.13 MHz, ¹³C at 125.77 MHz, and ³¹P at 202.45 MHz) if so stated, with chemical shifts referenced to residual solvent peaks in the respective deuterio solvents or to external H₃PO₄. IR spectra were measured in the range 4000–350 cm⁻¹ on a BioRad FTS-165 FTIR machine. Mass spectra were obtained on a Finnigan Mat 95XL-T (fast atom bombardment, FAB) or Finnigan-MAT LCQ (electrospray ionization, ESI) spectrometer, and elemental analyses were performed in the microanalytical laboratory in-house.

All solvents were of analytical grade and were dried and freshly distilled before use according to standard techniques. Deutero solvents were vacuum-transferred after drying: CDCl₃ using P₂O₅

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and CD_3CN using CaH_2 . Silica gel (Merck Kieselgel 60, 230–400 mesh) was dried at 140°C overnight before use. The tetraalkylidithiuram disulfides $[\text{R}_2\text{NC}(\text{S})\text{S}]_2$ ($\text{R} = \text{Me}, \text{Et}$), isopropylxanthic disulfide $[\text{iPrOC}(\text{S})\text{S}]_2$, and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ were purchased from Merck and used as supplied. $[\text{Cp}^*\text{RuCl}_2]_n$ (**1**),²² $[\text{Cp}^*\text{RuCl}_2(\text{S}_2\text{CNMe}_2)]$ (**2a**),²³ and bis(thiophosphoryl) disulfide $[(\text{iPrO})_2\text{P}(\text{S})\text{S}]_2$ ²⁴ were prepared according to published procedures.

Reactions of $[\text{Cp}^*\text{RuCl}_2]_2$ (1**). (a) With $[\text{Et}_2\text{NC}(\text{S})\text{S}]_2$. **Synthesis of $[\text{Cp}^*\text{RuCl}_2(\text{S}_2\text{CNEt}_2)]$ (**2b**)**. To an orange-red solution of **1** (0.54 g, 0.88 mmol) in acetonitrile (10 mL) was added $[\text{Et}_2\text{NC}(\text{S})\text{S}]_2$ (0.26 g, 0.88 mmol) with stirring. The solution turned purple instantly. The resultant solution was filtered through a disc (2 cm) of silica gel. Concentration of the filtrate in vacuo to ca. 3 mL, followed by the addition of ether (5 mL) and subsequent cooling at -30°C for 30 min, gave a microcrystalline solid of **2b** (0.67 g, 1.46 mmol, 85%). Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{Cl}_2\text{NRuS}_2$: C, 39.6; H, 5.5; N, 3.1; S, 14.1; Cl, 15.6. Found: C, 39.7; H, 5.7; N, 3.3; S, 14.4; Cl, 16.4. ^1H NMR (CDCl_3): δ 1.30 (t, $J = 7.2$ Hz, 6H, 2CH_3), 1.41 (s, 15H, Me_5C_5), 3.73 (q, $J = 7.2$ Hz, 4H, 2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.2 (Me_5C_5), 12.5 (CH_3), 42.7 (CH_2), 106.3 (Me_5C_5), 204.3 (CS). IR (KBr, cm^{-1}): ν 1517vs (C–N), 1089s, 1010m (NC_2), 859m, 783m (C–S). FAB⁺-MS: m/z 415 $[\text{M} - \text{Et} - \text{Me} + 2\text{H}]^+$, 385 $[\text{M} - 2\text{Cl}]^+$, 370 $[\text{M} - 2\text{Cl} - \text{Me}]^+$, 352 $[\text{M} - 2\text{Cl} - 2\text{Me} - 3\text{H}]^+$, 313 $[\text{M} - 2\text{Cl} - \text{NEt}_2]^+$, 300 $[\text{Cp}^*\text{RuS}_2]^+$, 268 $[\text{Cp}^*\text{RuS}]^+$, 236 $[\text{M} - 2\text{Cl} - \text{SCNEt}_2 = \text{Cp}^*\text{Ru}]^+$, and higher mass fragments, the significant ones of which are 492 $[\text{M} + \text{Cl}]^+$ and 522 $[\text{M} + \text{Cl} + 2\text{Me}]^+$. The complex is sparingly soluble in toluene and ether, moderately soluble in tetrahydrofuran, and highly soluble in acetonitrile and chloro solvents. Solid samples are air-stable, and solutions in CD_3Cl were found unchanged when checked after 3 days at room temperature.**

(b) With $[\text{iPrOC}(\text{S})\text{S}]_2$. **Synthesis of $[\text{Cp}^*\text{RuCl}_2(\text{S}_2\text{COPr})]$ (3**)****. Similarly, from the reaction of **1** (0.40 g, 0.66 mmol) with $[\text{iPrOC}(\text{S})\text{S}]_2$ (0.18 g, 0.66 mmol) was obtained microcrystalline **3** (0.53 g, 1.20 mmol, 89%). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{Cl}_2\text{ORuS}_2$: C, 38.0; H, 5.0; S, 14.5; Cl, 16.0. Found: C, 37.6; H, 4.7; S, 14.9; Cl, 16.4. ^1H NMR (CDCl_3): δ 1.45 (s, 15H, Me_5C_5), 1.50 (d, $^3J_{\text{HH}} = 6.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 5.64 (septet, 1H, $\text{CH}(\text{CH}_3)_2$). ^1H NMR (CD_3CN): δ 1.37 (s, 15H, Me_5C_5), 1.49 (d, $^3J_{\text{HH}} = 6.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 5.69 (septet, 1H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.4 (Me_5C_5), 21.9 (CH_3), 107.2 (Me_5C_5), 222.8 (CS), CH not observed (presumably obscured by the solvent peaks at δ 77.0). IR (KBr, cm^{-1}): ν 1460s, 1372vs, 1280vs (C–O), 1094s 1041m, 900m (C–S), 811m (C–S). FAB⁺-MS: m/z 442 $[\text{M} - 2\text{H}]^+$, 407 $[\text{M} - 2\text{H} - \text{Cl}]^+$, 372 $[\text{M} - 2\text{H} - 2\text{Cl}]^+$, 329 $[\text{M} - 2\text{H} - 2\text{Cl} - (\text{iPr})]^+$, 300 $[\text{M} - 2\text{Cl} - (\text{CO}^i\text{Pr}) = \text{Cp}^*\text{RuS}_2]^+$, 268 $[\text{Cp}^*\text{RuS}]^+$, 234 $[\text{Cp}^*\text{Ru} - 2\text{H}]^+$, and higher mass fragments, the significant ones of which are 479 $[\text{M} + \text{Cl}]^+$, 511 $[\text{M} + \text{Cl} + \text{S}]^+$, 539 $[\text{M} + \text{Cl} + \text{SCO}]^+$, 610 $[\text{M} + 3\text{Cl} + \text{SCO}]^+$, and 851. The complex is similar to **2** in solubility and stability.

(c) With $[(\text{iPrO})_2\text{P}(\text{S})\text{S}]_2$. **Synthesis of $\text{Cp}^*\text{RuCl}_2(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)$ (4**)****. To an orange-red solution of **1** (50 mg, 0.081 mmol) in acetonitrile (4 mL) was added $[(\text{iPrO})_2\text{P}(\text{S})\text{S}]_2$ (35 mg, 0.081 mmol) with stirring. The solution gradually turned maroon in color. After 1 h, the resultant solution was filtered through a disc (2 cm) of silica gel. Concentration of the filtrate in vacuo to ca. 1 mL, followed by the addition of ether (2 mL) and subsequent cooling

at -30°C for 30 min, did not give any solid product. Then the solution was evacuated to dryness and redissolved in 1 mL of toluene. The addition of hexane (1 mL) gave microcrystalline **4** (50 mg, 0.096 mmol, 59%). Anal. Calcd for $\text{C}_{16}\text{H}_{29}\text{Cl}_2\text{O}_2\text{P}_2\text{RuS}_2$: C, 36.9; H, 5.6; S, 12.3; P, 6.0. Found: C, 37.4; H, 5.7; S, 12.0; P, 5.8. ^1H NMR (500 MHz, CD_3CN): δ 1.31 (s, 15H, Me_5C_5), 1.34 (d, $^3J_{\text{HH}} = 6.3$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 4.76 (d of septet, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{PH}} = 10.7$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$) and 5.00 (d of septet, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{PH}} = 13.3$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CD_3CN): δ 9.0 (Me_5C_5), 24.1 and 24.2 (each d, $^3J_{\text{PC}} = 4.6$ Hz, CH_3), 75.7 and 76.1 (each d, $^2J_{\text{PC}} = 7.3$ and 5.0 Hz, respectively, CH), 108.8 (Me_5C_5). ^{31}P NMR (500 MHz, CD_3CN): δ 95.2 (dd, $^3J_{\text{PH}} = 10.4$ and 12.4 Hz). IR (KBr, cm^{-1}): ν 2979m, 2930w, 2909w, 2868vw, 1475mbr, 1376s, 1173w, 1143w, 1097m, 983vs, 961vs, 890wsh, 771s, 640m (P=S). FAB⁺-MS: m/z 480 $[\text{M} - \text{iPr} + 3\text{H}]^+$, 449 $[\text{M} - 2\text{Cl}]^+$, 366 $[\text{M} - \text{S}_2\text{P}(\text{O}^i\text{Pr})]^+$, 351 $[\text{M} - \text{S}_2\text{P}(\text{O}^i\text{Pr}) - \text{Me}]^+$, 300 $[\text{Cp}^*\text{RuS}_2]^+$, 268 $[\text{Cp}^*\text{RuS}]$, 234 $[\text{Cp}^*\text{Ru} - 2\text{H}]^+$, and significant unassigned higher mass fragments, 557, 588, and 663. The compound is very soluble in all organic solvents and, unlike **2** and **3**, is very air-sensitive even in the solid state.

Dichlorido Substitution. (a) Using $\text{Et}_2\text{NC}(\text{S})\text{S}^-$. **Synthesis of $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]\text{Cl}$ (5a**)****. To a purple solution of **2a** (46 mg, 0.11 mmol) in acetonitrile (4 mL) was added $\text{Na}(\text{S})\text{SCNEt}_2$ (24 mg, 0.11 mmol) with stirring. The solution turned red in 1 h. The resultant solution was filtered through a disc (2 cm) of Celite. Concentration of the filtrate in vacuo to ca. 1 mL, followed by the addition of ether (2 mL) and subsequent cooling at -30°C for 30 min, gave a microcrystalline solid of **5a** (40 mg, 0.074 mmol, 69%). Anal. Calcd for $\text{C}_{18}\text{H}_{31}\text{ClIN}_2\text{RuS}_4$: C, 40.0; H, 5.8; N, 5.2; S, 23.7. Found: C, 39.9; H, 6.1; N, 5.0; S, 23.9. ^1H NMR (CDCl_3): δ 1.60 (s, 15H, Me_5C_5), 1.31 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_2CH_3), 3.37 (s, 6H, CH_3), 3.76 and 3.73 (each dq, $^2J_{\text{HH}} = 14.4$ Hz, 2H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.8 (Me_5C_5), 12.3 (CH_3), 38.0 (CH_2CH_3), 43.8 (CH_2CH_3), 105.7 (Me_5C_5), 204.3 and 205.2 (each CS). IR (KBr, cm^{-1}): ν 1560vs, 1527vs (C–N), 1156m, 1086m, 1018m (NC_2), 851w, 784w (C–S). FAB⁺-MS: m/z 505 $[\text{M} - \text{Cl}]^+$, 477 $[\text{M} - \text{Cl} - \text{Et}]$, 385 $[\text{M} - \text{Cl} - (\text{S}_2\text{CNMe}_2)]^+$, 357 $[\text{M} - \text{Cl} - (\text{S}_2\text{CNEt}_2)]^+$, 300 $[\text{Cp}^*\text{RuS}_2]$, 281 $[\text{M} - \text{Cp}^* - \text{Cl} - \text{CNEt}_2 - 5\text{H}]^+$, 268 $[\text{Cp}^*\text{RuS}]$, 236 $[\text{Cp}^*\text{Ru}]$, and a higher mass fragment 533 $[\text{M} - \text{Cl} + \text{Et} - \text{H}]^+$.

Synthesis of $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CNEt}_2)_2]\text{Cl}$ (5b**)**. A similar reaction of **2b** (50 mg, 0.11 mmol) with $\text{Na}(\text{S})\text{SCNEt}_2$ (25 mg, 0.11 mmol), followed by a similar workup, gave microcrystalline **5b** (60 mg, 0.11 mmol, 96%). Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{ClIN}_2\text{RuS}_4 \cdot \text{CH}_3\text{Cl}$: C, 40.8; H, 6.2; N, 4.5; S, 20.7. Found: C, 41.0; H, 6.2; N, 4.8; S, 20.2. ^1H NMR (500 MHz, CD_3CN): δ 1.52 (s, 15H, Me_5C_5), 1.24 (t, $^3J_{\text{HH}} = 6.9$ Hz, 12H, CH_3), 3.73 and 3.69 (each dq, $^2J_{\text{HH}} = 14.5$ Hz, 4H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.9 (Me_5C_5), 12.4 (CH_3), 43.8 (CH_2), 105.8 (Me_5C_5), 204.4 (CS). IR (KBr, cm^{-1}): ν 1532vs, 1443s (C–N), 1075m, 1014w (NC_2), 857w, 786w (C–S). FAB⁺-MS: m/z 533 $[\text{M} - \text{Cl}]^+$, 385 $[\text{M} - \text{Cl} - (\text{S}_2\text{CNEt}_2)]^+$.

Synthesis of $\text{Cp}^*\text{Ru}(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{CO})$ (6b**)**. A similar reaction of **3** (30 mg, 0.068 mmol) with $\text{Na}(\text{S})\text{SCNEt}_2$ (15 mg, 0.068 mmol), followed by a similar workup, gave microcrystalline **6b** (30 mg, 0.063 mmol, 93%). Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{NORuS}_4$: C, 40.3; H, 5.3; N, 2.9; S, 26.9. Found: C, 39.9; H, 5.4; N, 2.8; S, 27.5. ^1H NMR (CD_3CN): δ 1.49 (s, 15H, Me_5C_5), 1.23 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_2CH_3), 3.78–3.59 (overlapping dq, resembling ABX₃ spectrum of **5a**, total 4H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.5 (Me_5C_5), 12.4 (CH_2CH_3), 43.0 (CH_2CH_3), 102.9 (Me_5C_5), 202.7 and 206.8 (CS, S_2CO). IR (KBr, cm^{-1}): ν 1704m (C=O), 1593vs, 1513vs (C–N), 1076s, 1018s (NC_2), 850s (C–S). FAB⁺-MS: m/z 478 $[\text{MH}]^+$, 417 $[\text{M} - 2\text{Et} - 2\text{H}]^+$, 385 $[\text{M} - (\text{S}_2\text{CO})]^+$, 300

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Table 1. Crystal Structure and Refinement Data

compound formula	2b	3	5a	6a	6b	8a	8c	9	10
fw	C ₁₅ H ₂₅ Cl ₂ NRuS ₂ 455.45	C ₁₄ H ₂₂ Cl ₂ ORuS ₂ 442.41	C ₂₀ H ₃₃ Cl ₃ N ₃ RuS ₄ 778.94	C ₁₄ H ₂₁ NORuS ₄ 448.63	C ₁₅ H ₂₅ NORuS ₄ 476.68	C ₃ H ₄ Cl ₅ N ₂ S ₂ O _{0.3} PRuS ₂ 760.26	C ₄₀ H ₅₀ BCINPRuS ₂ 787.23	C ₃₂ H ₃₇ OPRuS ₂ 633.78	C ₁₄ H ₂₁ NORuS ₂ 384.51
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>Pnma</i>	<i>P2₁/c</i>	<i>P1</i>	<i>P2₁/n</i>	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P1</i>
<i>a</i> , Å	15.3251(8)	17.9211(11)	11.1679(4)	8.8077(3)	15.5154(6)	23.7047(5)	11.5644(3)	11.6555(2)	9.3769(5)
<i>b</i> , Å	13.9017(7)	7.0721(4)	12.8682(5)	24.5807(10)	29.6852(12)	17.9199(4)	28.4673(8)	11.1636(2)	11.4486(6)
<i>c</i> , Å	8.7026(5)	15.0124(9)	13.0374(5)	8.8818(4)	10.0847(4)	20.3108(4)	11.9610(3)	18.7075(3)	15.4189(3)
<i>a</i> , deg	90	90	64.5000(10)	90	90	90	90	90	87.4270(10)
<i>β</i> , deg	90	90	78.2670(10)	113.7110(10)	122.3520(10)	123.456(1)	93.9210(10)	101.6760(10)	81.3520(10)
<i>γ</i> , deg	90	90	80.5640(10)	1760.58(12)	90	90	90	90	86.4160(10)
<i>V</i> , Å ³	1854.04	1779.89(18)	1649.56(11)	1760.58(12)	3923.8(3)	7198.2(3)	3928.43(3)	2997.37(8)	1632.18(15)
<i>Z</i>	4	4	2	4	8	8	4	4	4
<i>D</i> (calc), Mg cm ⁻³	1.632	1.651	1.568	1.693	1.614	1.403	1.331	1.404	1.565
<i>μ</i> (Mo Kα), mm ⁻¹	1.352	1.408	1.310	1.362	1.227	0.773	0.642	0.739	1.208
<i>F</i> (000)	928	896	788	912	1952	3136	1640	1312	784
cryst size, mm ³	0.14 × 0.14 × 0.14	0.03 × 0.22 × 0.40	0.30 × 0.24 × 0.16	0.40 × 0.24 × 0.06	0.10 × 0.26 × 0.32	0.22 × 0.22 × 0.10	0.28 × 0.20 × 0.12	0.34 × 0.34 × 0.24	0.40 × 0.36 × 0.32
<i>θ</i> range, deg	2.66–30.53	1.21–30.02	2.36–26.37	2.64–29.93	2.15–30.50	2.22–26.37	2.23–24.71	2.14–28.99	2.19–29.90
reflns collcd	14 849	26 631	23 588	20 229	29 963	27 578	48 864	24 465	22 275
indep reflns	2850	5106	6714	4723	5806	7345	6690	7316	8578
data/restraints/param	2850/0/103	5106/0/188	6714/0/316	4723/0/197	5806/0/215	7345/6/417	6690/0/434	7316/0/314	8578/0/357
GOF on <i>F</i> ²	1.057	1.408	1.098	1.124	1.133	1.092	1.352	1.156	1.034
final <i>R</i> indices	<i>R</i> 1 = 0.0383, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0365, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0435, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0410, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0369, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0593, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0723, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0459, [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0295, [<i>I</i> > 2σ(<i>I</i>)]
<i>R</i> indices (all data)	<i>wR</i> 2 = 0.0797, <i>R</i> 1 = 0.0491, <i>wR</i> 2 = 0.0839	<i>wR</i> 2 = 0.0807, <i>R</i> 1 = 0.0492, <i>wR</i> 2 = 0.0946	<i>wR</i> 2 = 0.1049, <i>R</i> 1 = 0.0471, <i>wR</i> 2 = 0.1074	<i>wR</i> 2 = 0.0927, <i>R</i> 1 = 0.0469, <i>wR</i> 2 = 0.0955	<i>wR</i> 2 = 0.0827, <i>R</i> 1 = 0.0428, <i>wR</i> 2 = 0.0859	<i>wR</i> 2 = 0.1567, <i>R</i> 1 = 0.0745, <i>wR</i> 2 = 0.1661	<i>wR</i> 2 = 0.1499, <i>R</i> 1 = 0.0792, <i>wR</i> 2 = 0.1530	<i>wR</i> 2 = 0.1026, <i>R</i> 1 = 0.0505, <i>wR</i> 2 = 0.1052	<i>wR</i> 2 = 0.0736, <i>R</i> 1 = 0.0343, <i>wR</i> 2 = 0.0758
largest diff peak and hole, e Å ⁻³	1.019 and –0.635	1.084 and –0.404	0.870 and –0.499	1.112 and –0.372	0.795 and –0.457	1.849 and –0.498	1.324 and –1.205	1.059 and –0.390	0.663 and –0.334
<i>T</i> , K	223(2)	223(2)	223(2)	193(2)	223(2)	183(2)	223(2)	223(2)	223(2)

[Cp*RuS₂]⁺, 268 [Cp*RuS]⁺, 234 [Cp*Ru – 2H]⁺, and an intense higher mass fragment at 533 [M – (S₂CO) + S₂CNET₂]⁺.

(b) Using ¹PrOC(S)S[–]. Synthesis of Cp*Ru(S₂CNMe₂)(S₂CO) (6a). To a purple solution of **2a** (50 mg, 0.12 mmol) in acetonitrile (4 mL) was added K(S)SCOⁱPr (20 mg, 0.12 mmol) with stirring. The solution turned red in 1 h. The resultant solution was filtered through a disc (2 cm) of Celite. Concentration of the filtrate in vacuo to ca. 1 mL, followed by the addition of ether (2 mL) and subsequent cooling at –30 °C for 30 min, gave microcrystalline **6a** (43 mg, 0.10 mmol, 82%). Anal. Calcd for C₁₄H₂₁NORuS₄: C, 37.5; H, 4.7; N, 3.1; S, 28.6. Found: C, 37.7; H, 4.7; N, 3.0; S, 28.4. ¹H NMR (CDCl₃): δ 1.54 (s, 15H, Me₅C₅), 3.24 (s, 6H, CH₃). ¹H NMR (CD₃CN): δ 1.49 (s, 15H, Me₅C₅), 3.27 (s, 6H, CH₃). ¹³C{¹H}NMR (CDCl₃): δ 8.6 (Me₅C₅), 37.5 (CH₃), 103.0 (Me₅C₅), 205.7 and 208.1 (CS, CO). IR (KBr, cm⁻¹): ν 1701m (C=O), 1598vs, 1548s (C–N), 1158m (NC₂), 845s (C–S). ESI⁺-MS: *m/z* 450 [MH]⁺, 390 [MH – (SCO)]⁺, 356 [M – (S₂CO)]⁺, and higher mass fragments at 492 [M + CO + Me]⁺ and 477 [M + CO]⁺.

The product **6b** (32 mg, 0.067 mmol, 68%) isolated above was also formed by reacting **2b** (45 mg, 0.099 mmol) in acetonitrile (4 mL) with K(S)SCOⁱPr (17 mg, 0.099 mmol).

Synthesis of Cp*Ru(S₂COⁱPr)(S₂CO) (7). To a purple solution of **3** (50 mg, 0.11 mmol) in acetonitrile (4 mL) was added K(S)-SCOⁱPr (20 mg, 0.11 mmol) with stirring. The solution turned red in 1 h. The resultant solution was filtered through a disc (2 cm) of Celite. Concentration of the filtrate in vacuo to ca. 1 mL, followed by the addition of ether (2 mL) and subsequent cooling at –30 °C for 30 min, gave microcrystalline **7** (52 mg, 0.11 mmol, 99%). Anal. Calcd for C₁₅H₂₂O₂RuS₄: C, 38.9; H, 4.8; S, 27.7. Found: C, 38.6; H, 4.8; S, 27.9. ¹H NMR (CDCl₃): δ 1.58 (s, 15H, Me₅C₅), 1.46 (d, ³J_{HH} = 6.4 Hz, 6H, (CH(CH₃)₂), 5.55 (septet, ³J_{HH} = 6.4 Hz, 1H, (CH(CH₃)₂)). ¹³C{¹H} NMR (CDCl₃): δ 8.8 (Me₅C₅), 21.4 (CH(CH₃)₂), 103.5 (CH(CH₃)₂), 107.3 (Me₅C₅), 201.7 (CS), 225.0 (CO). IR (KBr, cm⁻¹): 1695m (C=O), 1606s (C–O), 842w (C–S). FAB⁺-MS: *m/z* 463 [M]⁺, 404 [M – OⁱPr]⁺, 328 [M – (S₂COⁱ-Pr)]⁺, 300 [Cp*RuS₂]⁺, 268 [Cp*RuS]⁺, 234 [Cp*Ru – 2H]⁺, and significant higher mass fragments at 537 [Cp*₂Ru₂S₂H], 568 [Cp*₂-Ru₂S₃], 775 [M₂ – O – (S₂COⁱPr)], 807 [(M – OⁱPr)₂H]⁺, and 869 [M₂ – OⁱPr + 2H].

To detect all components of the product mixture, an NMR tube reaction was carried out as follows: CDCl₃ (0.50 mL) was added to a mixture of **3** (5 mg, 0.011 mmol) and K(S)SCOⁱPr (2 mg, 0.011 mmol) in an NMR tube. After the tube was shaken for 30 min, the ¹H NMR spectrum of the red mixture was scanned.

Reaction with Phosphines. (a) Synthesis of [Cp*Ru(S₂CNMe₂)-(PPh₃)Cl]Cl (8a). To a purple solution of **2a** (30 mg, 0.070 mmol) in acetonitrile (12 mL) was added PPh₃ (18 mg, 0.070 mmol) with stirring. The solution turned red after 4 h and was stirred for 17 h. Concentration of the resultant solution in vacuo to ca. 3 mL, followed by the addition of ether (2 mL) and subsequent cooling at –30 °C for 30 min, gave microcrystalline **8a** (36 mg, 0.052 mmol, 75%). Anal. Calcd for C₃₁H₃₆Cl₂NPRuS₂·3H₂O: C, 50.1; H, 5.7; N, 1.9; S, 8.6; P, 4.2. Found: C, 49.9; H, 5.7; N, 1.8; S, 8.8; P, 4.0. ¹H NMR (CD₃CN): δ 1.46 (s, 15H, Me₅C₅), 3.03 and 3.17 (each s, 3H, CH₃), 6.8–7.8 (m, 15H, PPh₃). ¹³C{¹H} NMR (CD₃CN): δ 8.9 (s, Me₅C₅), 38.0 and 38.2 (each s, CH₃), 110.6 (s, Me₅C₅), 129.4 (s, br, PPh), 132.2 (s, PPh), 134.4 (s, br, PPh), 201.9 (s, CS). ³¹P{¹H} NMR (CD₃CN): δ 35.2 (s, PPh₃). IR (KBr, cm⁻¹): ν 1559vs (C–N), 1091m (NC₂), 750w, 698s (C–S). FAB⁺-MS: *m/z* 654 [M – Cl = Cp*Ru(S₂CNMe₂)(PPh₃)Cl]⁺, 619 [M – 2Cl]⁺, 497 [M – 2Cl – (S₂CNMe₂) – 2H]⁺, 392 [M – Cl – PPh₃]⁺, 357 [M – 2Cl – PPh₃]⁺, and 297 [M – 2Cl – PPh₃ – CNMe₂ –

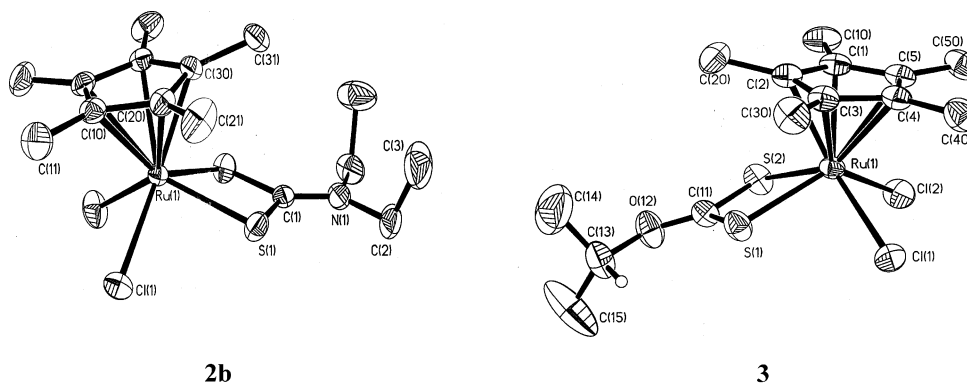
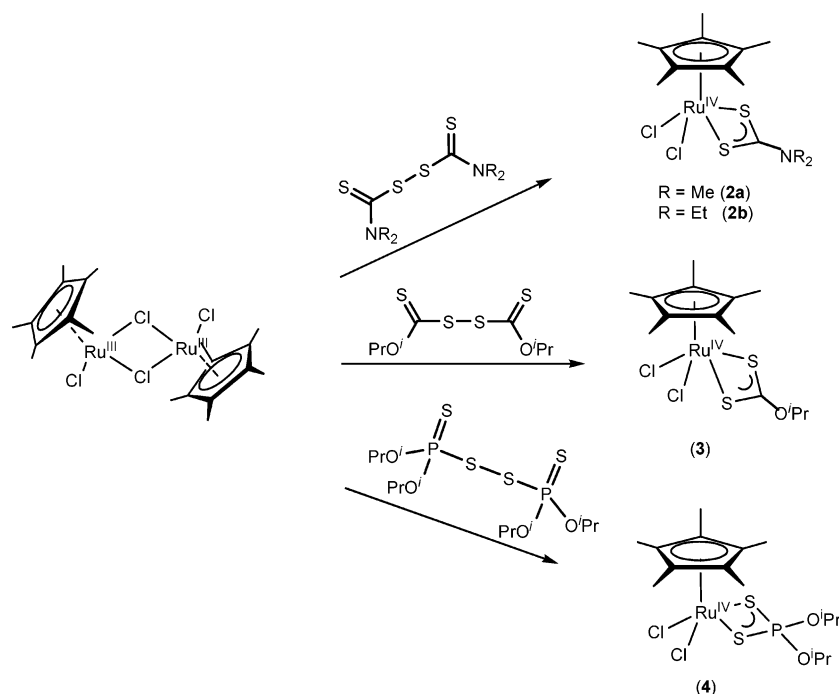


Figure 1. Molecular structures of the dications of **2b** and **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

Scheme 1



$4\text{H}]^+$. HRMS. Calcd for $[\text{C}_{31}\text{H}_{36}\text{ClNPRuS}_2]^+$: 654.0759. Found: 654.0745 (ESI⁺) and 654.0776 (FAB⁺).

(b) Synthesis of $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CNMe}_2)(\text{PPhMe}_2)\text{Cl}][\text{PF}_6]$ (8b**).** To a purple solution of **2a** (30 mg, 0.070 mmol) in acetonitrile (10 mL) was added PPhMe_2 (9.7 mg, 10 μL , 0.070 mmol). The solution turned red after stirring for 2 h. After 17 h, solid NH_4PF_6 (30 mg, 0.184 mmol) was added and the precipitated NH_4Cl was removed by filtration through a disc (2 cm) of Celite. Concentration of the filtrate in vacuo to ca. 3 mL, followed by the addition of ether (2 mL) and subsequent cooling at -30°C for 30 min, gave microcrystalline **8b** (39 mg, 0.058 mmol, 83%). Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{ClNPRuS}_2\text{P}_2\text{F}_6$: C, 37.4; H, 4.8; N, 2.1; S, 9.5; P, 9.2. Found: C, 37.0; H, 4.8; N, 2.0; S, 9.7; P, 9.7. ^1H NMR (CD_3CN): δ 1.56 (s, 15H, Me_5C_5), 1.82 (d, $^2J_{\text{PH}} = 8.1$ Hz, 3H, PMe), 1.85 (d, $^2J_{\text{PH}} = 8.8$ Hz, 3H, PMe), 3.05 and 3.16 (each s, 3H, Me), 7.3–7.8 (m, 5H, PPh). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 9.1 (s, C_5Me_5), 12.6 and 13.2 (each d, $^1J_{\text{PC}} = 38.6$ Hz, PMe), 37.9 and 38.1 (each s, Me), 109.5 (C_5Me_5), 134.3 (d, $^1J_{\text{PC}} = 56.2$ Hz, *ipso*-C), 132.3 (d, $^3J_{\text{PC}} = 6.4$ Hz, *meta*-C) and 131.6 (s, *para*-C), 128.4 (d, $^2J_{\text{PC}} = 9.7$ Hz, *ortho*-C) (PPh), 202.7 (CS). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 9.7 (s, PPhMe_2), -142.9 (septet, $J = 703$ Hz, PF_6). IR (KBr, cm^{-1}): ν 1554m (C–N), 1015w (NC_2), 840s (C–S). ESI⁺-MS: m/z 494 $[\text{M} - \text{Cl} = \text{Cp}^*\text{Ru}(\text{S}_2\text{CNMe}_2)(\text{PPhMe}_2)]^+$.

(c) Synthesis of $[\text{Cp}^*\text{Ru}(\text{S}_2\text{CNMe}_2)(\text{PMe}_3)\text{Cl}][\text{BPh}_4]$ (8c**).** To a purple solution of **2a** (30 mg, 0.070 mmol) in acetonitrile (10 mL) was added PMe_3 (5.3 mg, 7 μL , 0.070 mmol) with stirring. The solution turned red after 1 h. After 17 h, solid NaBPh_4 (40 mg, 0.136 mmol) was added and the precipitated NaCl was removed by filtration through a disc (2 cm) of Celite. Concentration of the solution in vacuo to ca. 3 mL, followed by the addition of ether (2 mL) and subsequent cooling at -30°C for 30 min, gave microcrystalline **8c** (43 mg, 0.055 mmol, 78%). Anal. Calcd for $\text{C}_{40}\text{H}_{50}\text{BClNPRuS}_2$: C, 61.0; H, 6.4; N, 1.8; S, 8.2; P, 3.9. Found: C, 61.0; H, 6.4; N, 1.3; S, 7.9; P, 3.9. ^1H NMR (CD_3CN): δ 1.56 (s, 15H, Me_5C_5), 1.54 (d, $^2J_{\text{PH}} = 9.6$ Hz, 9H, PMe_3), 3.24 (s, 3H, Me), 3.25 (s, 3H, Me), 6.8–7.3 (m centered at 6.85, 7.00, and 7.28 (1:2:2), total 20H, BPh_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 8.9 (C_5Me_5), 13.4 (d, $^1J_{\text{PC}} = 40.2$ Hz, PMe_3), 38.1 and 38.4 (each s, Me), 109.0 (C_5Me_5), 122.6, 126.4, and 136.6, with one peak probably obscured by δ 118.1 of CD_3CN (each s, BPh_4), 202.9 (CS). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.3 (PMe_3). IR (KBr, cm^{-1}): ν 1558s (C–N), 1159m (NC_2), 948s, 846m (C–S). ESI⁺-MS: m/z 468 $[\text{M} - \text{Cl} = \text{Cp}^*\text{Ru}(\text{S}_2\text{CNMe}_2)(\text{PMe}_3)\text{Cl}]^+$, 432 $[\text{M} - 2\text{Cl}]^+$, 392 $[\text{M} - \text{Cl} - \text{PMe}_3]^+$, 356 $[\text{M} - 2\text{Cl} - \text{PMe}_3]^+$. ESI⁺-HRMS. Calcd for $[\text{C}_{16}\text{H}_{30}\text{ClNPRuS}_2]^+$: 468.0289. Found: 468.0276.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of **2** and **3**

2a		2b		3	
Ru(1)–S(1)	2.3706(12)	Ru(1)–S(1)	2.3644(7)	Ru(1)–S(1)	2.3554(8)
Ru(1)–S(2)	2.3681(10)	Ru(1)–S(1)#1	2.3644(7)	Ru(1)–S(2)	2.3639(8)
S(1)–C(11)	1.712(5)	S(1)–C(1)	1.704(2)	S(1)–C(11)	1.682(3)
S(2)–C(11)	1.724(4)	C(1)–S(1)#1	1.704(2)	S(2)–C(11)	1.685(3)
N(11)–C(11)	1.304(5)	N(1)–C(1)	1.323(4)	O(12)–C(11)	1.300(4)
S(2)–Ru(1)–S(1)	71.16(4)	S(1)–Ru(1)–S(1)#1	70.70(3)	S(1)–Ru(1)–S(2)	71.23(3)
S(1)–C(11)–S(2)	106.7(2)	S(1)#1–C(1)–S(1)	106.78(19)	S(1)–C(11)–S(2)	109.40(17)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of **5a** and **6a,b**

5a		6a		6b	
Ru(1)–S(1)	2.3852(9)	Ru(1)–S(1)	2.3793(7)	Ru(1)–S(1)	2.3967(6)
Ru(1)–S(2)	2.3851(9)	Ru(1)–S(2)	2.3947(7)	Ru(1)–S(2)	2.3842(6)
Ru(1)–S(3)	3.3942(9)	Ru(1)–S(3)	2.3869(8)	Ru(1)–S(3)	2.3792(6)
Ru(1)–S(4)	2.3960(8)	Ru(1)–S(4)	2.3824(7)	Ru(1)–S(4)	2.3855(6)
S(1)–C(1)	1.709(4)	S(1)–C(1)	1.711(3)	S(1)–C(10)	1.712(2)
S(2)–C(1)	1.709(4)	S(2)–C(1)	1.711(3)	S(2)–C(10)	1.711(2)
S(3)–C(2)	1.709(3)	S(3)–C(4)	1.755(3)	S(3)–C(20)	1.754(3)
S(4)–C(2)	1.711(3)	S(4)–C(4)	1.758(3)	S(4)–C(20)	1.744(3)
N(1)–C(1)	1.317(5)	N(1)–C(1)	1.315(4)	N(10)–C(10)	1.322(3)
N(2)–C(2)	1.313(4)	O(1)–C(4)	1.217(4)	O(20)–C(20)	1.211(3)
S(2)–Ru(1)–S(1)	71.24(3)	S(1)–Ru(1)–S(2)	71.19(2)	S(2)–Ru(1)–S(1)	71.03(2)
S(3)–Ru(1)–S(4)	71.22(3)	S(4)–Ru(1)–S(3)	72.04(3)	S(3)–Ru(1)–S(4)	71.37(3)
S(1)–C(1)–S(2)	108.77(19)	S(2)–C(1)–S(1)	108.60(15)	S(2)–C(10)–S(1)	108.49(12)
S(3)–C(2)–S(4)	109.27(18)	S(3)–C(4)–S(4)	105.94(17)	S(4)–C(20)–S(3)	105.24(14)

(d) **Synthesis of Cp*Ru(S₂COⁱPr)(PPh₃) (9).** To a purple solution of **3** (50 mg, 0.113 mmol) in acetonitrile (12 mL) was added PPh₃ (59 mg, 0.226 mmol). The solution was stirred for 4 h. The resultant red solution was evacuated to dryness and the residue redissolved in toluene (ca. 2 mL) and cooled at –30 °C for 30 min, giving microcrystalline **9** (43 mg, 0.068 mmol, 60%). Anal. Calcd for C₃₂H₃₇OPRuS₂: C, 60.6; H, 5.9; S, 10.1; P, 4.9. Found: C, 60.8; H, 5.9; S, 10.3; P, 5.3. ¹H NMR (CD₃CN): δ 1.42 (s, 15H, Me₅C₅), 1.12 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 4.95 (septet, ³J_{HH} = 6.0 Hz, 1H, CH(CH₃)₂), 7.2–7.6 (m, 15H, PPh₃). ¹H NMR (C₆D₆): δ 1.55 (s, 15H, Me₅C₅), 0.97 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 5.00 (septet, ³J_{HH} = 6.0 Hz, 1H, CH(CH₃)₂), 7.0–7.8 (m, 15H, PPh₃). ¹³C{¹H} NMR (C₆D₆): δ 11.0 (C₅Me₅), 22.3 (CH(CH₃)₂), 74.5 (CH(CH₃)₂), 86.6 (C₅Me₅), 138.0 (d, ¹J_{PC} = 35.3 Hz, *ipso*-C), 135.3, 135.2 (each s) and 134.8 (d, ²J_{PC} = 19.3 Hz, *ortho*-C) (PPh₃), 227.1 (CS). ³¹P{¹H} NMR (CD₃CN): δ 54.5 (PPh₃). ³¹P{¹H} NMR (C₆D₆): δ 54.2 (PPh₃). IR (KBr, cm^{–1}): ν 1027m, 1097s (C–S), 1227vs (C–O). ESI⁺-MS: *m/z* 634 [M = Cp*Ru-(S₂COⁱPr)(PPh₃)]⁺, 499 [M – (S₂COⁱPr)]⁺, 372 [M – PPh₃]⁺, 329 [M – PPh₃ – ⁱPr]⁺, 300 [Cp*RuS₂]⁺, 263 [PPh₃H]⁺.

Reaction of 2a with [CpCr(CO)₃]₂. Synthesis of Cp*Ru-(S₂CNMe₂)(CO) (10). To a green solution of [CpCr(CO)₃]₂ (24 mg, 0.059mmol) in toluene (10 mL) was added **2a** (50 mg, 0.12 mmol). The solution was stirred for 2 h at room temperature. The resultant greenish-blue solution was evacuated to dryness and the residue extracted with hexane. The extract was concentrated to ca. 3 mL, and subsequent cooling at –30 °C for 30 min gave microcrystalline moderately air-stable **10** (43 mg, 0.11 mmol, 92%). Anal. Calcd for C₁₄H₂₁NORuS₂: C, 43.7; H, 5.5; N, 3.6; S, 16.7. Found: C, 44.0; H, 5.6; N, 3.3; S, 16.9. ¹H NMR (CDCl₃): δ 1.81 (s, 15H, Me₅C₅), 3.18 (s, 6H, 2CH₃). ¹H NMR (CD₃CN): δ 1.78 (s, 15H, Me₅C₅), 3.14 (s, 6H, 2CH₃). ¹³C{¹H} NMR (CDCl₃): δ 10.0 (Me₅C₅), 38.1 (CH₃), 93.1 (Me₅C₅), 201.9 (CS) and 215.6 (CO). IR (KBr, cm^{–1}): ν 1901vs (C–O), 1529s (C–N), 1153m (NC₂), 980m (C–S). FAB⁺-MS: *m/z* 385.0 [MH]⁺, 357.0 [MH – CO]⁺.

Crystal Structure Determinations. Diffraction-quality crystals were obtained as follows: **2b**, **3**, **6b**, **8a**, and **8c** from acetonitrile solutions layered with ether after 2 days at –30 °C, **5a** from a CDCl₃ solution after 2 days at –30 °C, **6a** from acetonitrile–ether after 2 h at 5 °C, and **4**, **9**, and **10** from a solution in toluene layered with hexane after 2–3 days at –30 °C.

The crystals were mounted on glass fibers. X-ray data were collected on a Bruker APEX AXS diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ = 0.710 73 Å), with the SMART suite of programs.^{25a} Data were processed and corrected for Lorentz and polarization effects with SAINT^{25b} and for absorption with SADABS.^{25c} Structural solution and refinement were carried out with the SHELXTL suite of programs.^{25d} The crystal data collection and processing parameters are given in Table 1.

The structures were solved by direct methods or Patterson maps to locate the heavy atoms, followed by difference maps for the light, non-H atoms. All non-H atoms were generally given anisotropic displacement parameters in the final model. Refinements were against F².

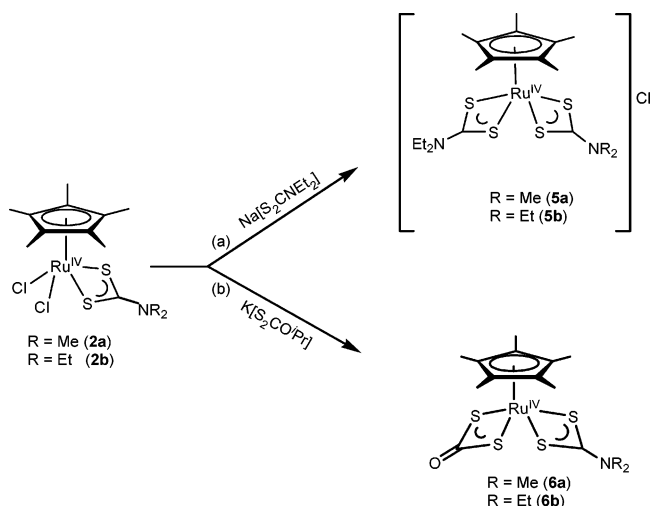
Two chloroform solvent molecules were found in **5a**. For **8a**, there were two acetonitrile molecules, with occupancies of 1.0 and 0.5, respectively, as well as a water molecule. There was disorder of the chloride counterion, which was modeled over three sites, with occupancies of 0.37, 0.37, and 0.26, respectively, with appropriate restraints.

Results and Discussion

Reactions with Disulfides. Treatment of the Ru^{III} complex **1** with the disulfanes—tetraalkyldithiuram disulfides [R₂NC-(S)S]₂ (R = Me,²³ Et), isopropylxanthic disulfide [ⁱPrOC-(S)S]₂, and bis(thiophosphoryl) disulfide [(ⁱPrO)₂P(S)S]₂—resulted in facile cleavage of the bridging Ru–Cl and S–S

(25) (a) SMART, version 5.628; Bruker AXS Inc.: Madison, WI, 2001. (b) SAINT+, version 6.22a; Bruker AXS Inc.: Madison, WI, 2001. (c) Sheldrick, G. M. SADABS; University of Göttingen, Göttingen, Germany, 1996. (d) SHELXTL, version 5.1; Bruker AXS Inc.: Madison, WI, 1997.

Scheme 2

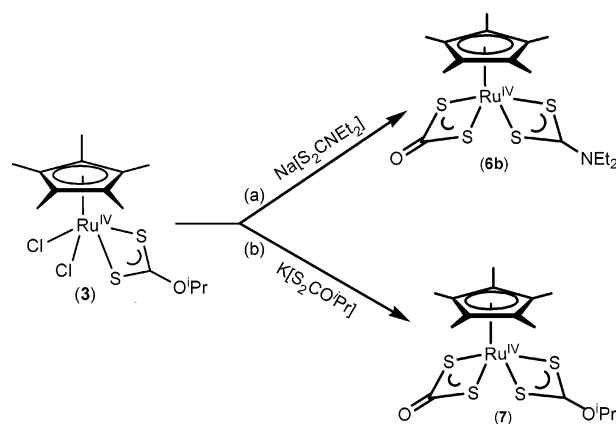


bonds with concomitant oxidation of the metal centers, resulting in the formation of dichlorido-Cp^{*}Ru^{IV} complexes **2**, **3**, and **4**, respectively, which were isolated in high yields as air-stable (**2** and **3**) and very air-sensitive (**4**) crystalline solids (Scheme 1).

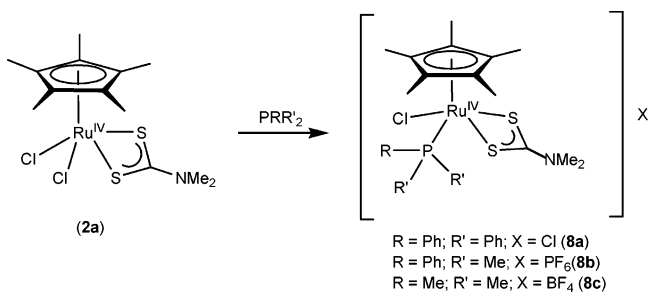
The complexes **2b** and **3** possess similar structures, showing coordination of Ru to Cp^{*}, η²-DTC, and two chlorido ligands, as illustrated in Figure 1 for **2b** and **3**. Assuming that Cp^{*} takes up three coordination sites, the Ru^{IV} center is formally seven-coordinate. Bond parameters of these complexes, together with those of **2a**,²³ are given in Table 2. It is seen that the C–S bond lengths [1.682(3)–1.724(4) Å] fall intermediate between those for the C–S single bond (1.81 Å) and the C=S double bond (1.61 Å). The C–N bond distances [1.300(4)–1.304(5) Å] also fall intermediate between those for a C–N single bond (1.47 Å) and a C=N double bond (1.27 Å). In **3**, the C–O bond length [1.300(4) Å] also lies between those of a C–O single bond (1.43 Å) and a C=O double bond (1.23 Å).²⁶ The presence of a mirror plane through the Ru(1), C(1), and N(1) atoms in **2b**, resulting from symmetrical bonding of the DTC ligand to the Ru center, is reflected in the metric data in Table 2.

The spectral data are consistent with the molecular structures. The Me groups of Cp^{*} rings of **2b** and **3** are seen as singlets at δ 1.41 and 1.45, respectively, in their ¹H NMR spectra in CDCl₃ and at δ 8.2 and 8.4 (methyl C's) and δ 106.3 and 107.2 (ring C's) in their ¹³C NMR spectra. The proton resonances in CDCl₃ of the DTC ligand of **2b** are observed as a triplet at δ 1.30 (CH₃) and a quartet at δ 3.73 (CH₂), consistent with the presence of a plane of symmetry and possibly also rapid free rotation about the C–N bond. The corresponding ¹³C NMR resonances of the DTC ligand are found at δ 12.5 and 42.7, respectively, and that of the CS moiety is found at δ 204.3. The isopropyl group of **3** is observed in the ¹H NMR spectrum in CDCl₃ as a doublet at δ 1.50 (CH₃) and a septet at δ 5.64 (CH). Significant in the IR spectra are the presence of stretching frequencies of C–S, C–N, and NC₂ in **2b** and of C–S and C–O in **3**. The mother

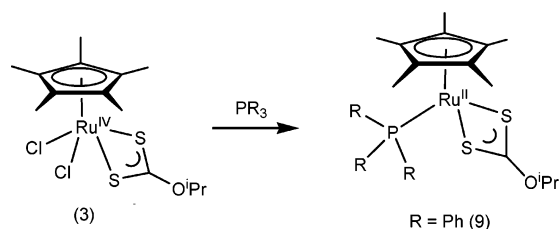
Scheme 3



Scheme 4



Scheme 5



ions of these complexes are not observed; the highest mass fragment of **2b** shows loss of Et and Me groups, while that of **3** shows loss of two H atoms, with subsequent loss of chlorido ligands.

The single-crystal X-ray diffraction analysis of **4** was not obtained. However, a structure conforming to the formulation shown in Scheme 1 is supported by microanalytical and spectral data. Thus, the ¹H NMR spectral data at 300 MHz in CDCl₃ shows a singlet for Cp^{*} at δ 1.37, a doublet at δ 1.39 (CH₃), and two septets at δ 4.76 and 5.09 (CH) for the two ⁱPr groups in the molecule; scanned at 500 MHz in CD₃-CN, these latter resonances are seen as symmetrical 9- and 10-line multiplets, which are comprised of P-coupled doublets of proton-coupled septets. The proton-decoupled ³¹P NMR spectrum shows a doublet of doublet at δ 95.2, indicating coupling to two different CH protons. This is consistent with the ¹³C NMR spectrum, which reveals two CH moieties possessing slightly different P–C coupling constants and two P-coupled doublets pertaining to Me groups in two different environments; indeed, the underlying reason for the absence of this effect in the ¹H NMR spectrum is not clear. The combined inference is the presence of inequivalent OⁱPr moieties in the phosphinate ligand, an expected consequence of a probable tetrahedral geometry at

(26) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

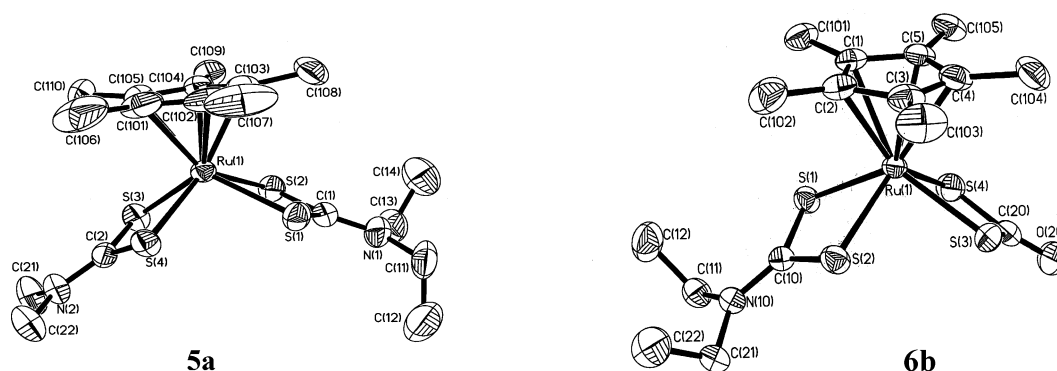


Figure 2. Molecular structures of the cations of **5a** and **6b**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

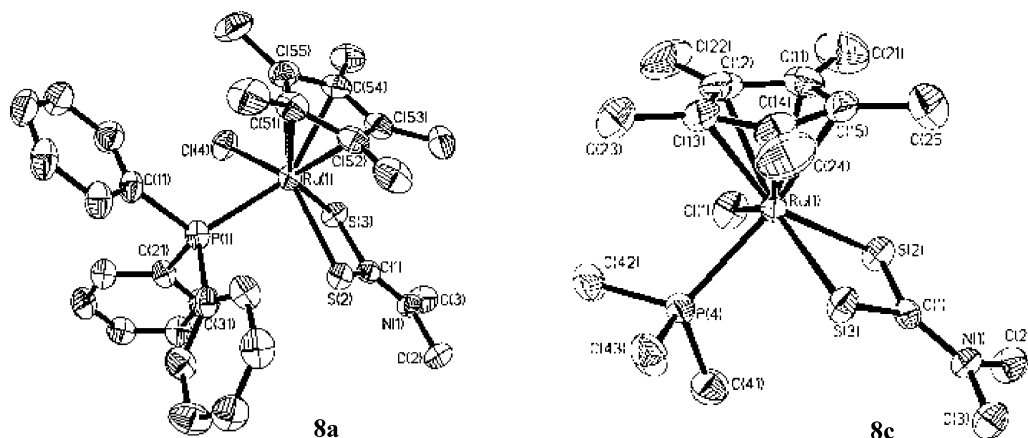


Figure 3. Molecular structures of **8a** and **8c**. Thermal ellipsoids are drawn at the 50% probability level, and the anions of the complexes are omitted. H atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of **8a**, **8c**, **9**, and **10**

molecule A									
8a		8c		9		molecule B: 10			
Ru(1)–S(2)	2.3981(12)	Ru(1)–S(2)	2.3833(14)	Ru(1)–S(1)	2.4102(7)	Ru(1)–S(1)	2.3964(6)	Ru(2)–S(3)	2.3986(6)
Ru(1)–S(3)	2.3807(12)	Ru(1)–S(3)	2.3903(14)	Ru(1)–S(2)	2.3974(7)	Ru(1)–S(2)	2.3925(6)	Ru(2)–S(4)	2.4103(6)
S(2)–C(1)	1.707(5)	S(2)–C(1)	1.705(5)	S(1)–C(1)	1.689(3)	S(1)–C(11)	1.711(2)	S(3)–C(21)	1.714(2)
S(3)–C(1)	1.714(5)	S(3)–C(1)	1.719(5)	S(2)–C(1)	1.692(3)	S(2)–C(11)	1.714(2)	S(4)–C(21)	1.715(2)
N(1)–C(1)	1.304(6)	N(1)–C(1)	1.310(6)	O(1)–C(1)	1.325(3)	N(1)–C(11)	1.321(3)	N(2)–C(21)	1.315(3)
Ru(1)–P(1)	2.3968(13)	Ru(1)–P(4)	2.3562(15)	Ru(1)–P(1)	2.3009(7)	Ru(1)–C(1)	1.841(2)	Ru(2)–C(2)	1.833(2)
Ru(1)–Cl(4)	2.4039(12)	Ru(1)–Cl(1)	2.4141(15)			O(1)–C(1)	1.152(3)	O(2)–C(2)	1.148(3)
S(3)–Ru(1)–S(2)	70.70(4)	S(2)–Ru(1)–S(3)	70.70(5)	S(2)–Ru(1)–S(1)	71.77(2)	S(2)–Ru(1)–S(1)	72.107(19)	S(3)–Ru(2)–S(4)	72.121(19)
S(2)–C(1)–S(3)	107.8(2)	S(2)–C(1)–S(3)	107.5(3)	S(1)–C(1)–S(2)	112.90(16)	S(1)–C(11)–S(2)	110.75(12)	S(3)–C(21)–S(4)	111.28(12)
						O(1)–C(1)–Ru(1)	173.8(2)	O(2)–C(2)–Ru(2)	174.8(2)

P. The mass spectral fragments are also consistent with the proposed formulation. The P=S stretch is identified in the IR spectrum.

Chlorido Substitution in 2 and 3. (a) Reaction with Et₂NC(S)S[−] and ⁱPrOC(S)S[−]. Complexes **2a** and **2b** undergo dichlorido substitution with the DTC_{Et} anion to give bis(DTC) complexes **5a** and **5b**, respectively (Scheme 2a). The similar reaction with isopropyl xanthate is accompanied by loss of the isopropyl group, resulting in thiocarbonate complexes [Cp*Ru(η²-S₂CNR₂)(η²-S₂CO)] **6a** and **6b** (Scheme 2b). While this manuscript was in preparation, complex **5a** was reported to be isolated as the [N(Ph₂PS)₂] salt from the oxidation of Cp*Ru{N(Ph₂PS)₂} with [Me₂NC(S)S]₂.²⁷

Complex **6b** was also obtained from the reaction of **3** with Et₂NC(S)S[−] (Scheme 3a). The reaction of **3** with ⁱPrOC(S)S[−]

results in the formation of a dithiocarbonato complex [Cp*Ru(η²-S₂COⁱPr)(η²-S₂C=O)] (**7**).

The molecular structures of the bis(thiolato) complexes, **5a** and **6a,b**, have been determined. The ORTEP diagrams of **5a** and **6b** are given in Figure 2, and that of **6a** in Figure S1 in the Supporting Information. The molecules all assume a four-legged piano-stool configuration, with coordination being to η⁵-Cp* and two bidentate dithiolate ligands. The metric data are given in Table 3. Like in complexes **2**, the C–S and C–N bonds possess partial double-bond character. The C–O bond lengths [1.217(4) Å in **6a** and 1.211(3) Å in **6b**] in the dithiocarbonate ligands are close to that of the C=O double bond (1.23 Å).²⁶ The DTC bite angles in these complexes [range 71.03(2)–71.24(3)°] are slightly smaller than those of the dithiocarbonato [71.37(3)–72.04(3)°].

The spectral data are consistent with the molecular structures. The ¹H NMR spectrum of **5a** in CDCl₃ shows

(27) Cheung, W.-M.; Zhang, Q.-F.; Williams, I. D.; Leung, W.-H. *Inorg. Chim. Acta* **2006**, 359, 782.

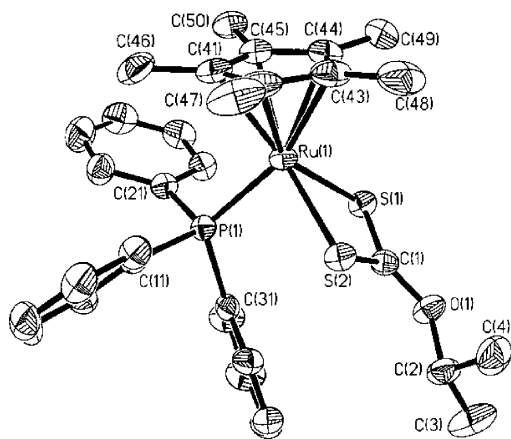


Figure 4. Molecular structure of **9**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

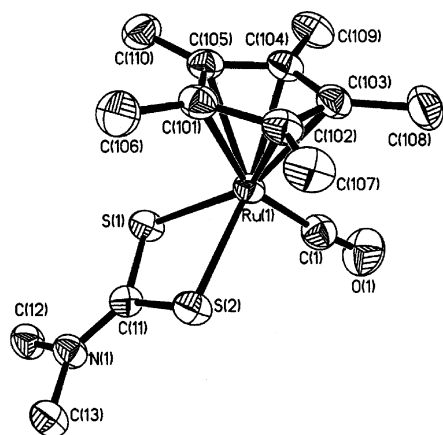


Figure 5. ORTEP diagram for one of the molecules in the unit cell of **10**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

singlets at δ 1.60 for the Cp* Me protons and at δ 3.37 for the six NMe₂ protons on the DTC_{Me} ligand; the nature of the latter is indicative of rapid rotation about the C(1)–N(1) bond. The six Me protons of the DTC_{Et} ligand are seen as a triplet at δ 1.31 and the methylene protons as a doublet of quartets (δ 3.76 and 3.73), in agreement with an AB system coupled to CH₃ with coupling constants of 14.4 Hz ($^2J_{\text{HH}}$) and 7.2 Hz ($^3J_{\text{HH}}$). The ¹H NMR spectrum of **5b** in CD₃CN shows a singlet at δ 1.52 for the Cp* Me protons. The resonances of the DTC_{Et} ligands are observed as a triplet at δ 1.24 for the CH₃ protons and an overlapping doublet of quartet (dq) at δ 3.77–3.65 for the CH₂ protons, with coupling closely resembling the ABX₃ spectrum of **5a**.

The ¹H NMR spectra of **6a** and **6b** in CD₃CN both showed a singlet at δ 1.49 for the Me protons of the Cp* ring. The Me protons of the η^2 -S₂CNMe₂ ligand in **6a** are observed as a singlet at δ 3.27, while the η^2 -S₂CNEt₂ ligand in **6b** is manifested as a triplet at δ 1.23 for the CH₃ protons and overlapping dq at δ 3.78–3.59 for the CH₂ protons, with an ABX₃ coupling scheme as in **5a**. The presence of $\nu_{\text{C=O}}$ stretching frequencies (1701 cm⁻¹ in **6a** and 1704 cm⁻¹ in **6b**) in their IR spectra is indicative of the dithiocarbonate ligand. Their molecular [MH]⁺ ions were observed.

Likewise, spectral characterization of complex **7** was via its ¹H NMR spectrum in CDCl₃ (a singlet at δ 1.58 for

Cp*, a doublet at δ 1.46 for CH₃'s, and a septet at δ 5.55 for CH of the isopropyl xanthate ligand), its IR spectrum ($\nu_{\text{C=O}}$ 1695 cm⁻¹), and its FAB-MS spectrum (m/z = 463 for the molecular ion).

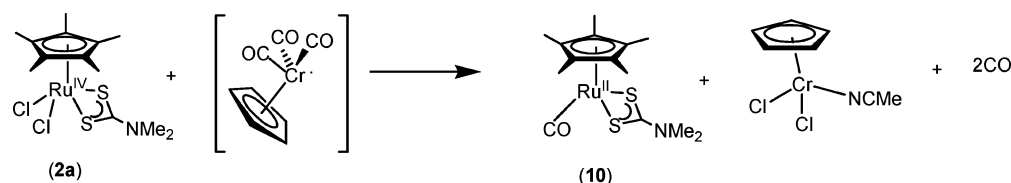
These dithiocarbonate complexes are the first examples of an organoruthenium, and notably of Ru^{IV}. The only other such example among the transition metals was a (phenyl)-rhodium complex reported by Bianchini.²⁸ Coordination compounds of dithiocarbonate are much more common, mainly of Pd^{II} and Pt^{II}, with the first case reported by Fackler and Seidel in 1969²⁹ and subsequent examples from the groups of Stephenson,³⁰ Beck,³¹ and Contreras.³² There are a few dithiocarbonate compounds of Ni^{II},³³ and detailed synthetic and reactivity studies of Rh, reported by the groups of Bianchini and Stephenson.^{28,34} Very recently, the first such Ru^{II} coordination compound, [Ru(S₂CO)(dppm)₂] (dppm = Ph₂PCH₂PPh₂), was reported by Wilton-Ely and Hogarth, from a clean facile reaction of *cis*-[RuCl₂(dppm)₂] with CS₂ and NaOH.³⁵ Other synthetic routes to date have involved the reaction of bromo/isocyanate complexes with CS₂³¹ and xanthate anions,^{33b,34c} oxidation of η^2 -CS₂ complexes with O₂, S₈, or Se_n,^{33c} and nucleophilic attack of ligated xanthate (S₂COR) with Lewis bases, e.g., phosphines,^{29,30,33a} with iodide,³² and with xanthate anions.³⁰

Stephenson and co-workers had postulated that the mechanism of xanthate-promoted formation of dithiocarbonato complexes of Pd and Pt involves the intermediate formation of a tris(dithiocarbonato) complex, followed by intramolecular generation of a dithiocarbonate moiety, upon release of a dithiocarbonate ester RS₂COR.³⁰ Indeed, in an NMR-tube reaction of **3** with a stoichiometric amount of K(S)SCO-Pr in CDCl₃, we observed in the product solution resonances pertaining to the complex **7**, as well as those assignable to [iPrS₂CO⁻Pr] (viz., δ 1.44 and 1.46 (each d, $^3J_{\text{HH}}$ = 6 Hz, 3H, CH₃), 3.79 and 5.76 (each septet, $^3J_{\text{HH}}$ = 6 Hz, 1H, CH(CH₃)₂).

(b) Reaction with Phosphines. The reaction of **2a** with phosphines PRR'₂ resulted in the substitution of one chlorido ligand, giving monocationic complexes **8a–c** in high yields (Scheme 4). By comparison, the reaction of **3** with PPh₃ resulted in the displacement of both chlorido ligands and the reduction of the metal center to the 2+ oxidation state

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Scheme 6



(Scheme 5). The basis for this reactivity difference is probably electronic in origin; DTC ligands are well recognized for their ability to stabilize high oxidation states in transition metals via extensive electron delocalization, which results in delocalization of the positive charge toward the periphery of the complex.¹⁸ It appears that the higher donor capability of the xanthate ligand, arising from more localized electron density at the S atoms, has facilitated a redox reaction in which reduction occurred at Ru, while the chlorido ligands are oxidized, releasing chlorine in the process.

The structural formulation of all of the phosphine derivatives of **2a** and **3** is supported by their ¹H NMR spectra, which show a singlet for Cp* (δ 1.46 for **8a**, δ 1.56 for both **8b** and **8c**, and δ 1.42 for **9**, in CD₃CN). Complexes **8a–c** show nonequivalent Me groups of the DTC ligand in their ¹H NMR spectra (singlets at δ 3.03 and 3.17 in **8a**, δ 3.05 and 3.16 in **8b**, and δ 3.24 and 3.25 in **8c**), suggestive of nonrotation about their C–N bonds. The Me substituents on P are seen as doublets in the ¹H NMR spectra at δ 1.82 and 1.85 in **8b** and δ 1.54 in **8c**, while Ph substituents are found in the aromatic region at δ 6.8–7.8. The isopropyl group of the xanthate ligand in **9** is observed as a doublet at δ 1.12 for CH₃ and a septet at δ 4.95 for CH. The P atoms of PPh₃ in **8a** and **9**, of PPhMe₂ in **8b**, and of PMe₃ in **8c** resonate at δ 35.2, 54.5, 9.7, and 11.6, respectively.

The ORTEP diagrams for the molecular structures of the phosphine derivatives **8a** and **8c** are shown in Figure 3. With coordination to Cp*, bidentate DTC, a monophosphine, and a chlorido ligand, the metal centers assume a four-legged piano-stool configuration. The bond parameters are given in Table 4, which also includes those of the Ru^{II} “three-legged piano-stool” complex **9** (Figure 4), which is coordinated to triphenylphosphine like **8a** but unlike **8a** does not possess a chlorido ligand. **9** is structurally similar to CpRu(PPh₃)(S₂COR) (R = Me, Et, or Pr), which was formed from the reaction of CpRu(PPh₃)₂Cl with the sodium salt of xanthate.³⁶ As in all of the other structurally characterized complexes discussed earlier, the C–S and C–N distances are indicative of partial double-bond character.

The Ru–P distances increase in the order of **9** < **8c** < **8a**. The weaker bond in **8a** as compared to **8c** is probably the combined effect of the steric bulk of PPh₃ and its poorer donor capability resulting from the presence of electron-withdrawing Ph groups, whereas Me substituents in PMe₃ are electron-releasing. The shortest Ru–P distance found in **9** is in agreement with the general observation of slightly shorter Ru–P bonds (by 0.02–0.04 Å) in neutral Ru complexes vis-à-vis those in cationic Ru complexes.³⁷ The Ru–S distances of the Ru^{IV} complexes in this study range

from 2.3554(8) to 2.3981(12) Å, while those of the Ru^{II} complexes, **9** and **10**, are longer [range: 2.3925(6)–2.4103(6) Å].

(c) Reaction of 2a with [CpCr(CO)₃]₂. Complex **2a** was reacted with dimeric [CpCr(CO)₃]₂ to test the ability of its monomeric radical to extract S atoms from the DTC ligand, a reactivity feature that had been demonstrated for DTC ligands^{19a,38} and various other dithiolate- and S-containing ligands in CpCr complexes.³⁹ However, this reaction showed that S abstraction from DTC at Cp*Ru^{IV} did not occur. Rather, the reaction was influenced by the oxidizing tendency of Ru^{IV} in **2a** and the halophilicity of the resulting Cr^{III},⁴⁰ producing the Ru^{II} complex **10** and CpCrCl₂(solvent) with loss of CO ligands (Scheme 6). CpCrCl₂(CH₃CN) was characterized structurally and found to be identical with that which we have reported before.⁴¹

The ¹H NMR spectrum of the Ru^{II} complex **10** in CDCl₃ possesses singlet resonances at δ 1.81 and 3.18 for the Cp* and Me protons of the DTC ligand, respectively. Its IR spectrum in KBr shows a terminal CO stretch at 1901 cm^{–1}. The mass fragment *m/z* 385 in the MS spectrum indicates a protonated mother ion.

Unlike **2a,b** and **3**, solid samples of **10** (Figure 5) lasted only a day in air, those of **5a,b**, **6a,b**, **7**, and **8a–c** ca. 30 min, while those of **4** and **9** are very air-sensitive. In a CDCl₃ solution under N₂, **8a–c** remained unchanged for a day, while **9** only lasted a few hours.

Conclusions

The reaction of the μ -dichloro dinuclear Ru^{III} complex, [Cp*RuCl₂]₂ (**1**), with S–S-bonded substrates, [R₂NC(S)S]₂ (R = Me, Et), [iPrOC(S)S]₂, and [(iPrO)₂P(S)S]₂, resulted in the formation of diamagnetic mononuclear dichloridoruthenium(IV) complexes containing η^2 -dithiolate ligands (DTC, xanthate, and dithiophosphate, respectively). This is the first instance of the oxidative role of disulfides in the formation of Ru^{IV} complexes. The derived DTC and xanthate

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complexes underwent dichlorido substitution with DTC and xanthate anions, with conversion of η^2 -xanthate to η^2 -dithiocarbonate. Chlorido substitution of the DTC complex with phosphines resulted in a monochloridophosphine derivative. The dichloridoxanthate complex reacted with PPh_3 with total displacement of the chlorido ligands and reduction of Ru to the 2+ oxidation state, in agreement with previous observations of the necessary donation of at least two negative charges from anionic coligands for stabilization of higher oxidation states of Ru.⁴² The reaction of the dichlorido-DTC complex with $[\text{CpCr}(\text{CO})_3]_2$ is strongly influenced

by the oxidizing tendency of Ru^{IV} and the halophilicity of the resulting CpCr^{III} moiety.

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Supporting Information Available: Complete crystallographic data in CIF format for **2a**, **2b**, **3**, **5a**, **6a**, **6b**, **8a**, **8c**, **9**, and **10** and an ORTEP diagram of **6a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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