Inorg. Chem. **2007**, *46*, 1440–1450

Synthetic and X-ray Structural and Reactivity Studies of Cp*Ru^{IV} Complexes Containing Bidentate Dithiocarbonate, Xanthate, Carbonate, and Phosphinate Ligands (Cp* = η^5-C_5Me_5)

Elaine Phuay Leng Tay, Seah Ling Kuan, Weng Kee Leong,* and Lai Yoong Goh*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 117543, Singapore

Received September 20, 2006

The reaction of $[Cp^*RuCl_2]_2$ (**1**; Cp* = η^5-C_5Me_5) with tetraalkyldithiuram disulfides ($R_2NC(S)SS(S)CNR_2$, 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}Cl$_2$(η^2-dithiolate) complexes [dithiolate = S_2CNR_2, DTC_R (**2a**, R = Me; **2b**, R = Et), S_2CO^iPr (**3**), and $S_2P(^iPrO)_2$ (**4**)]. Dichlorido substitution in **2** and **3** with DTC_{Et} and S_2CO^iPr 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) ligands[2] 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 $[Ru(DTC_{Me})(CO)(PPh_3)(\mu\text{-SPh})]_2^{4+}$ [4a] and $Ru(DTC_{Et})_2(Ts_2N_4)$ (Ts_2N_4 = ditosyltetrazene).[4b] Non-DTC Ru^{IV} compounds are rare, with examples being Ru(chbae)(PPh_3)(py) [H_4(chbae) = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane],[5a] and Ru(bipy)$(NHCMe_2CMe_2NH)_2$[5b] reported by Che and coworkers, Ru(PCy_3)("S_2N_2") ["S_2N_2"$^{4-}$ = 1,2-ethanediamide-

* To whom correspondence should be addressed. E-mail: chmlwk@nus.edu.sg (W.K.L.), chmgohly@nus.edu.sg (L.Y.G.).

(1) (a) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, The Netherlands, 1984. (b) Bruce, M. I. *Comprehensive Organometallic Chemistry (I)*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 661−690 and 843−929. Bennett, M. A.; Bruce, M. I.; Matheson, T. W. *Comprehensive Organometallic Chemistry (I)*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 4, pp 691−841. (c) See the following chapters in Vol. 7 in *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Shriver, D. F., Bruce, M. I., Eds.; Pergamon: Oxford, U.K., 1995 and references cited therein: (i) Chapter 5, pp 291−298 (Bruce, M. I.); (ii) Chapter 7, pp 441−472 (Bennett, M. A.); (iii) Chapter 8, pp 473−548 (Bennett, M. A.; Khan, K.; Wenger, E.); (iv) Chapter 9, pp 549−602 (Bennett, M. A.).

(2) (a) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362. (b) Millar, M.; O'Sullivan, T.; deVries, N.; Koch, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3714. (c) Soong, S.-L.; Hain, J. H.; Millar, M.; Koch, S. A. *Organometallics* **1988**, *7*, 556. (d) Satsangee, S. P.; Hain, J. H., Jr.; Cooper, P. T.; Koch, S. A. *Inorg. Chem.* **1992**, *31*, 5160. (e) See the following chapters in Vol. 5 in *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Constable, E. C., Dilworth, J. R., Vol. Eds.; Pergamon: Oxford, U.K., 2004 and references cited therein: (i) Chapter 5, pp 555−731 (Housecroft, C. E.); (ii) Chapter 6, pp 733−847 (Che, C.-M.; Lau, T.-C.).

(3) See, for instance, the following and references cited therein: (a) Duffy, D. J.; Pignolet, L. H. *Inorg. Chem.* **1974**, *13*, 2045. (b) Mattson, B. M.; Heiman, J. R.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 564. (c) Wheeler, S. H.; Mattson, B. M.; Miessler, G. L.; Pignolet, L. H. *Inorg. Chem.* **1978**, *17*, 340. (d) Miessler, G. L.; Pignolet, L. H. *Inorg. Chem.* **1979**, *18*, 210.

(4) (a) Kawano, M.; Uemura, H.; Watanabe, T.; Matsumoto, K. *J. Am. Chem. Soc.* **1993**, *115*, 2068. (b) Leung, W.-H.; Chim, J. L. C.; Hou, H.; Hun, T. S. M.; Willams, I. D.; Wong, W.-T. *Inorg. Chem.* **1997**, *36*, 4432.

(5) (a) Che, C.-M.; Cheng, W.-K.; Leung, W.-H.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1987**, 418. (b) Chiu, W.-H.; Peng, S.-M.; Che, C.-M. *Inorg. Chem.* **1996**, *35*, 3369. (c) Sellmann, D.; Ruf, R.; Knoch, F.; Moll, M. *Inorg. Chem.* ***1995***, *34*, 4745. (d) Maiti, R.; Shang, M.; Lappin, A. G. *Chem. Commun.* **1999**, 2349.

10.1021/ic061781t CCC: $37.00
Published on Web 01/18/2007

N,*N*′-bis(2-benzenethiolate)(4−)] from Sellmann's group,[5c] and [Ru(mnt)$_3$]$^{2-}$ [mnt^{2-} = 1,2-dicyanoethylenedithiolate-(2−)] reported by Lappin et al.[5d]

The first *organo*ruthenium(IV) complex was the μ-dichloridobis(allyl) complex [RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)]$_2$, 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*RuCl$_2$]$_n$, 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-C_3H_5)X$_2$ (X = Cl, Br), which yielded Cp/Cp*Ru(η^3-C_3H_5)(Me)X, Cp/Cp*Ru(Me)L$_2$X in the presence of ligand L (phosphines or dienes),[13a] or [CpRu(η^3-C_3H_5)$_2$]$^+$ when treated with silver(I) triflate in the presence of propene.[13b] The oxidation of [Cp*RuCl$_2$]$_n$ with the ferrocenium ion in the presence of tetrahydrothiophene led to [Cp*RuCl$_2$(SC_4H_8)$_2$]$^+$.[14] The reaction of [RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)]$_2$ with RSH (R = alkyl or aryl) led to the doubly thiolate-bridged complex [Ru^{IV}Cl(μ-SR)(η^3:η^3-$C_{10}H_{16}$)]$_2$.[15] Recently, Leung reported the syntheses of Cp*Ru complexes containing S- and Se-donor ligands from the Ru^{II} complexes [Cp*Ru(NO)Cl$_2$] and [Cp*Ru(MeCN)$_3$]$^+$ [16] and a ruthenium(IV) acetylide complex [Ru(SR)$_3$Cl(C≡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*RuCl$_2$]$_n$ toward disulfides of the [Z(S)S]$_2$ types [Z = R$_2$NC, tetraalkyldithiuram disulfide for R = Me or Et; Z = ^{i}PrOC, isopropylxanthic disulfide; Z = (^{i}PrO)$_2$P, 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 earler 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)(PPh$_3$)(μ-SPh)]$_2$[21] 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 N_2 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 (^{1}H at 300.14 MHz, ^{13}C at 75.43 MHz, and ^{31}P at 121.49 MHz) or a Bruker AMX500 500-MHz FT-NMR spectrometer (^{1}H at 500.13 MHz, ^{13}C at 125.77 MHz, and ^{31}P at 202.45 MHz) if so stated, with chemical shifts referenced to residual solvent peaks in the respective deutero solvents or to external H_3PO_4. 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: $CDCl_3$ using P_2O_5

(6) (a) Lydon, J. E.; Nicholson, J. K.; Shaw, B. L.; Truter, M. R. *Proc. Chem. Soc. London* **1964**, 421. (b) Porri, L.; Gallazzi, M. G.; Colombo, A.; Allegra, G. *Tetrahedron Lett.* **1965**, *47*, 4187. (c) Nicholson, J. K.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 807.

(7) (a) Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1970**, *92*, 3011. (b) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705. (c) Wilzcynski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* **1983**, *105*, 2066. (d) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278.

(8) (a) Nowell, I. W.; Tabatabaian, K.; White, C. *J. Chem. Soc., Chem. Commun.* **1979**, 547. (b) Bruce, M. I.; Tomkins, I. B.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 687.

(9) Balch, A. L.; Sohn, Y. S. *J. Organomet. Chem.* **1971**, *30*, C31.

(10) (a) Nagashima, H.; Mukai, K.; Itoh, K. *Organometallics* **1984**, *3*, 1314. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 645.

(11) (a) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

(12) (a) Nagashima, H.; Mukai, K.; Shiota, Y.; Ara, K.; Itoh, K.; Suzuki, H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1985**, *4*, 1314. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y.; Nagashima, H.; Itoh, K. *J. Organomet. Chem.* **1986**, *314*, C46.

(13) (a) Nagashima, H.; Yamaguchi, K.; Mukai, K.; Itoh, K. *J. Organomet. Chem.* **1985**, *291*, C20. (b) Itoh, K.; Masuda, K.; Ikeda, H. *Organometallics* **1993**, *12*, 2752.

(14) Manzano, B. R.; Jalon, F. A.; Lahoz, F. J.; Chaudret, B.; de Montauzon, D. *J. Chem. Soc., Dalton Trans.* **1992**, 977.

(15) Blechem, G.; Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1994**, *13*, 1949.

(16) Zhang, Q.-F.; Cheung, F. K. M.; Wong, W.-Y.; Williams, I. D.; Leung, W.-H. *Organometallics* **2001**, *20*, 3777.

(17) Zhang, Q.-F.; Lai, C.-Y.; Wong, W.-Y.; Leung, W.-H. *Organometallics* **2002**, *21*, 4017.

(18) Victoriano, L. I. *Coord. Chem. Rev.* **2000**, *196*, 383 (review) and references cited therein.

(19) (a) Goh, L. Y.; Weng, Z.; Leong, W. K.; Leung, P. H. *Angew. Chem.* **2001**, *40*, 3236. (b) Goh, L. Y.; Weng, Z.; Leong, W. K.; Leung, P. H. *Organometallics* **2002**, *21*, 4398. (c) Goh, L. Y.; Weng, Z.; Leong, W. K.; Leung, P. H.; Haiduc, I. *J. Organomet. Chem.* **2000**, *607*, 64. (d) Goh, L. Y.; Weng, Z.; Leong, W. K.; Haiduc, I.; Lo, K. M.; Wong, R. C. S. *J. Organomet. Chem.* **2001**, *631*, 67.

(20) See, for instance, the following and the references cited therein: (a) Mùller, A., Krebs, B., Eds. *Sulfur—Its Significance for Chemistry; for the Geo-, Bio- and Cosmosphere and Technology*; Elsevier: Amsterdam, The Netherlands, 1984. (b) Stiefel, E. I., Matsumoto, K., Eds. *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996. (c) Dai, S.; Schwendmayer, C.; Schürmann, P.; Ramaswamy, S.; Eklund, H. *Science* **2000**, *287*, 655. (d) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460. (e) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109.

(21) Kawano, M.; Uemura, H.; Watanabe, T.; Matsumoto, K. *J. Am. Chem. Soc.* **1993**, *115*, 2068.

and CD_3CN using CaH_2. Silica gel (Merck Kieselgel 60, 230−400 mesh) was dried at 140 °C overnight before use. The tetraalkyldithiuram disulfides $[R_2NC(S)S]_2$ (R = Me, Et), isopropylxanthic disulfide $[^iPrOC(S)S]_2$, and $RuCl_3 \cdot nH_2O$ were purchased from Merck and used as supplied. $[Cp^*RuCl_2]_n$ (**1**),[22] $[Cp^*RuCl_2(S_2CNMe_2)]$ (**2a**),[23] and bis(thiophosphoryl) disulfide $[(^iPrO)_2P(S)S]_2$[24] were prepared according to published procedures.

Reactions of $[Cp^*RuCl_2]_2$ (1). (a) With $[Et_2NC(S)S]_2$. Synthesis of $[Cp^*RuCl_2(S_2CNEt_2)]$ (2b). To an orange-red solution of **1** (0.54 g, 0.88 mmol) in acetonitrile (10 mL) was added $[Et_2NC(S)S]_2$ (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 $C_{15}H_{25}Cl_2NRuS_2$: 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, $2CH_2$). $^{13}C\{^1H\}$ 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 $[M - Et - Me + 2H]^+$ 385 $[M - 2Cl]^+$, 370 $[M - 2Cl - Me]^+$, 352 $[M - 2Cl - 2Me - 3H]^+$, 313 $[M - 2Cl - NEt_2]^+$, 300 $[Cp^*RuS_2]^+$, 268 $[Cp^*RuS]^+$, 236 $[M - 2Cl - SCNEt_2 = Cp^*Ru]^+$, and higher mass fragments, the significant ones of which are 492 $[M + Cl]^+$ and 522 $[M + Cl + 2Me]^+$. 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 $[^iPrOC(S)S]_2$. Synthesis of $[Cp^*RuCl_2(S_2CO^iPr)]$ (3). Similarly, from the reaction of **1** (0.40 g, 0.66 mmol) with $[^iPrOC(S)S]_2$ (0.18 g, 0.66 mmol) was obtained microcrystalline **3** (0.53 g, 1.20 mmol, 89%). Anal. Calcd for $C_{14}H_{22}Cl_2ORuS_2$: 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, $^3J_{HH}$ = 6.0 Hz, 6H, $CH(CH_3)_2$), 5.64 (septet, 1H, $CH(CH_3)_2$). ^1H NMR (CD_3CN): δ 1.37 (s, 15H, Me_5C_5), 1.49 (d, $^3J_{HH}$ = 6.0 Hz, 6H, $CH(CH_3)_2$), 5.69 (septet, 1H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ 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 $[M - 2H]^+$, 407 $[M - 2H - Cl]^+$, 372 $[M - 2H - 2Cl]^+$, 329 $[M - 2H - 2Cl - (^iPr)]^+$, 300 $[M - 2Cl - (CO^iPr) = Cp^*RuS_2]^+$, 268 $[Cp^*RuS]^+$, 234 $[Cp^*Ru - 2H]^+$, and higher mass fragments, the significant ones of which are 479 $[M + Cl]^+$, 511 $[M + Cl + S]^+$, 539 $[M + Cl + SCO]^+$, 610 $[M + 3Cl + SCO]^+$, and 851. The complex is similar to **2** in solubility and stability.

(c) With $[(^iPrO)_2P(S)S]_2$. Synthesis of $Cp^*RuCl_2(S_2P(O^iPr)_2)$ (4). To an orange-red solution of **1** (50 mg, 0.081 mmol) in acetonitrile (4 mL) was added $[(^iPrO)_2P(S)S]_2$ (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 $C_{16}H_{29}Cl_2O_2P_1Ru_1S_2$: 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, $^3J_{HH}$ = 6.3 Hz, 12H, $CH(CH_3)_2$), 4.76 (d of septet, $^3J_{HH}$ = 6.3 Hz, $^3J_{PH}$ = 10.7 Hz, 1H, $CH(CH_3)_2$) and 5.00 (d of septet, $^3J_{HH}$ = 6.3 Hz, $^3J_{PH}$ = 13.3 Hz, 1H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (500 MHz, CD_3CN): δ 9.0 (Me_5C_5), 24.1 and 24.2 (each d, $^3J_{PC}$ = 4.6 Hz, CH_3), 75.7 and 76.1 (each d, $^2J_{PC}$ = 7.3 and 5.0 Hz, respectively, CH), 108.8 (Me_5C_5). ^{31}P NMR (500 MHz, CD_3CN): δ 95.2 (dd, $^3J_{PH}$ = 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 $[M - {}^iPr + 3H)]^+$, 449 $[M - 2Cl]^+$, 366 $[M - S_2P(O^iPr)]^+$, 351 $[M - S_2P(O^iPr) - Me]^+$, 300 $[Cp^*RuS_2]^+$, 268 $[Cp^*RuS]$, 234 $[Cp^*Ru - 2H]^+$, 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 $Et_2NC(S)S^-$. Synthesis of $[Cp^*Ru(S_2CNMe_2)(S_2CNEt_2)]Cl$ (5a). To a purple solution of **2a** (46 mg, 0.11 mmol) in acetonitrile (4 mL) was added $Na(S)SCNEt_2$ (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 $C_{18}H_{31}ClN_2RuS_4$: 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, $^3J_{HH}$ = 7.2 Hz, 6H, CH_2CH_3), 3.37 (s, 6H, CH_3), 3.76 and 3.73 (each dq, $^2J_{HH}$ = 14.4 Hz, 2H, CH_2CH_3). $^{13}C\{^1H\}$ 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 $[M - Cl]^+$, 477 $[M - Cl - Et]$, 385 $[M - Cl - (S_2CNMe_2)]^+$, 357 $[M - Cl - (S_2CNEt_2)]^+$, 300 $[Cp^*RuS_2]$, 281 $[M - Cp^* - Cl - CNEt_2 - 5H]^+$, 268 $[Cp^*RuS]$, 236 $[Cp^*Ru]$, and a higher mass fragment 533 $[M - Cl + Et - H]^+$.

Synthesis of $[Cp^*Ru(S_2CNEt_2)_2]Cl$ (5b). A similar reaction of **2b** (50 mg, 0.11 mmol) with $Na(S)SCNEt_2$ (25 mg, 0.11 mmol), followed by a similar workup, gave microcrystalline **5b** (60 mg, 0.11 mmol, 96%). Anal. Calcd for $C_{20}H_{35}ClN_2RuS_4 \cdot CH_3Cl$: 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, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3), 3.73 and 3.69 (each dq, $^2J_{HH}$ = 14.5 Hz, 4H, CH_2CH_3). $^{13}C\{^1H\}$ 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 $[M - Cl]^+$, 385 $[M - Cl - (S_2CNEt_2)]^+$.

Synthesis of $Cp^*Ru(S_2CNEt_2)(S_2CO)$ (6b). A similar reaction of **3** (30 mg, 0.068 mmol) with $Na(S)SCNEt_2$ (15 mg, 0.068 mmol), followed by a similar workup, gave microcrystalline **6b** (30 mg, 0.063 mmol, 93%). Anal. Calcd for $C_{16}H_{25}NORuS_4$: 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, $^3J_{HH}$ = 7.2 Hz, 6H, CH_2CH_3), 3.78−3.59 (overlapping dq, resembling ABX_3 spectrum of **5a**, total 4H, CH_2CH_3). $^{13}C\{^1H\}$ 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 $[MH]^+$, 417 $[M - 2Et - 2H]^+$, 385 $[M - (S_2CO)]^+$, 300

(22) Koelle, U.; Kossakowski, J. *Inorg. Synth.* **1992**, *29*, 225.
(23) Kuan, S. L.; Tay, E. P. L.; Leong, W. K.; Goh, L. Y.; Lin, C. Y.; Gill, P. M. W.; Webster, R. D. *Organometallics* **2006**, *25*, 6134.
(24) (a) Kuchen, W.; Mayatepek, H. *Chem. Ber.* **1968**, *101*, 3454. (b) Higgins, Wm. A.; Vogel, P. W.; Craig, W. G. *J. Am. Chem. Soc.* **1955**, *77*, 1864.

Table 1. Crystal Structure and Refinement Data

compound	**2b**	**3**	**5a**	**6a**	**6b**	**8a**	**8c**	**9**	**10**
formula	$C_{15}H_{25}Cl_2NRuS_2$	$C_{14}H_{22}Cl_2ORuS_2$	$C_{20}H_{33}Cl_7N_2RuS_4$	$C_{14}H_{21}NORuS_4$	$C_{16}H_{25}NORuS_4$	$C_{34}H_{41.5}Cl_2N_{2.5}O_{0.5}PRuS_2$	$C_{40}H_{50}BClNPRuS_2$	$C_{32}H_{37}OPRuS_2$	$C_{14}H_{21}NORuS_2$
fw	455.45	442.41	778.94	448.63	476.68	760.26	787.23	633.78	384.51
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*Pnma*	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	15.3251(8)	17.9211(11)	11.1679(4)	8.8077(3)	15.5154(6)	23.7047(5)	11.5644(3)	14.6555(2)	9.3769(5)
b, 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)
c, 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)
α, deg	90	90	64.5000(10)	90	90	90	90	90	87.4270(10)
β, deg	90	110.6960(10)	78.2670(10)	113.7110(10)	122.3520(10)	123.456(1)	93.9210(10)	101.6760(10)	81.3520(10)
γ, deg	90	90	80.5640(10)	90	90	90	90	90	86.4160(10)
V, 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)
Z	4	4	2	4	8	8	4	4	4
D(calc), Mg cm^{-3}	1.632	1.651	1.568	1.693	1.614	1.403	1.331	1.404	1.565
μ(Mo Kα), mm^{-1}	1.352	1.408	1.310	1.362	1.227	0.773	0.642	0.739	1.208
F(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
θ range, deg	2.66−30.53	1.21−30.02	2.36−26.37	2.64−29.93	2.15−30.50	2.06−26.37	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 F^2	1.057	1.408	1.098	1.124	1.133	1.092	1.352	1.156	1.034
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0383,	R1 = 0.0365,	R1 = 0.0435,	R1 = 0.0410,	R1 = 0.0369,	R1 = 0.0593,	R1 = 0.0723,	R1 = 0.0459,	R1 = 0.0295,
	wR2 = 0.0797	wR2 = 0.0807	wR2 = 0.1049	wR2 = 0.0927	wR2 = 0.0827	wR2 = 0.1567	wR2 = 0.1499	wR2 = 0.1026	wR2 = 0.0736
R indices (all data)	R1 = 0.0491,	R1 = 0.0492,	R1 = 0.0471,	R1 = 0.0469,	R1 = 0.0428,	R1 = 0.0745,	R1 = 0.0792,	R1 = 0.0505,	R1 = 0.0343,
	wR2 = 0.0839	wR2 = 0.0946	wR2 = 0.1074	wR2 = 0.0955	wR2 = 0.0859	wR2 = 0.1661	wR2 = 0.1530	wR2 = 0.1052	wR2 = 0.0758
largest diff peakand 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
T, K	223(2)	223(2)	223(2)	193(2)	223(2)	183(2)	223(2)	223(2)	223(2)

$[Cp^*RuS_2]^+$, 268 $[Cp^*RuS]^+$, 234 $[Cp^*Ru - 2H]^+$, and an intense higher mass fragment at 533 $[M - (S_2CO) + S_2CNEt_2]^+$.

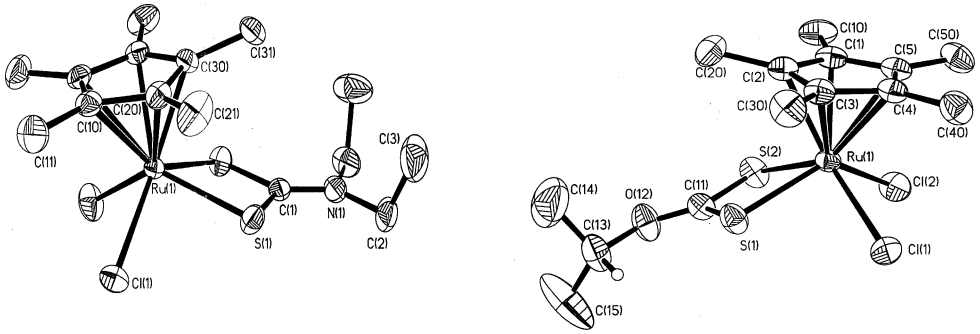
(b) Using ^{i}PrOC(S)S$^-$. Synthesis of Cp*Ru(S_2CNMe_2)(S_2CO) (6a). To a purple solution of **2a** (50 mg, 0.12 mmol) in acetonitrile (4 mL) was added K(S)SCO^{i}Pr (20 mg, 0.12 mmol) with stirring. The solution turned red in 1 h. The resultant solution was filtered through a disc (2 cm) of Celite. 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 $C_{14}H_{21}NORuS_4$: 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. ^{1}H NMR ($CDCl_3$): δ 1.54 (s, 15H, Me_5C_5), 3.24 (s, 6H, CH_3). ^{1}H NMR (CD_3CN): δ 1.49 (s, 15H, Me_5C_5), 3.27 (s, 6H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 8.6 (*Me*$_5$C$_5$), 37.5 (*C*H$_3$), 103.0 (Me$_5$*C*$_5$), 205.7 and 208.1 (*C*S, *C*O). IR (KBr, cm^{-1}): ν 1701m (C═O), 1598vs, 1548s (C−N), 1158m (NC_2), 845s (C−S). ESI$^+$-MS: *m*/*z* 450 $[MH]^+$, 390 $[MH - (SCO)]^+$, 356 $[M - (S_2CO)]^+$, 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)SCO^{i}Pr (17 mg, 0.099 mmol).

Synthesis of Cp*Ru(S_2CO^iPr)(S_2CO) (7). To a purple solution of **3** (50 mg, 0.11 mmol) in acetonitrile (4 mL) was added K(S)-SCO^{i}Pr (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 $C_{15}H_{22}O_2RuS_4$: C, 38.9; H, 4.8; S, 27.7. Found: C, 38.6; H, 4.8; S, 27.9. ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 15H, Me_5C_5), 1.46 (d, $^3J_{HH}$ = 6.4 Hz, 6H, (CH(*C*H$_3$)$_2$), 5.55 (septet, $^3J_{HH}$ = 6.4 Hz, 1H, (C*H*(CH$_3$)$_2$). ^{13}C{H} NMR ($CDCl_3$): δ 8.8 (*Me*$_5$C$_5$), 21.4 (CH-(*C*H$_3$)$_2$), 103.5 (*C*H(CH$_3$)$_2$), 107.3 (Me$_5$*C*$_5$), 201.7 (*C*S), 225.0 (*C*O). IR (KBr, cm^{-1}): 1695m (C═O), 1606s (C−O), 842w (C−S). FAB$^+$-MS: *m*/*z* 463 $[M]^+$, 404 $[M - O^iPr]^+$, 328 $[M - (S_2CO^i$-$Pr)]^+$, 300 $[Cp^*RuS_2]^+$, 268 $[Cp^*RuS]^+$, 234 $[Cp^*Ru - 2H]^+$, and significant higher mass fragments at 537 $[Cp^*_2Ru_2S_2H]$, 568 $[Cp^*_2$-$Ru_2S_3]$, 775 $[M_2 - O - (S_2CO^iPr)]$, 807 $[(M - O^iPr)_2H]^+$, and 869 $[M_2 - O^iPr + 2H]$.

To detect all components of the product mixture, an NMR tube reaction was carried out as follows: $CDCl_3$ (0.50 mL) was added to a mixture of **3** (5 mg, 0.011 mmol) and K(S)SCO^{i}Pr (2 mg, 0.011 mmol) in an NMR tube. After the tube was shaken for 30 min, the ^{1}H NMR spectrum of the red mixture was scanned.

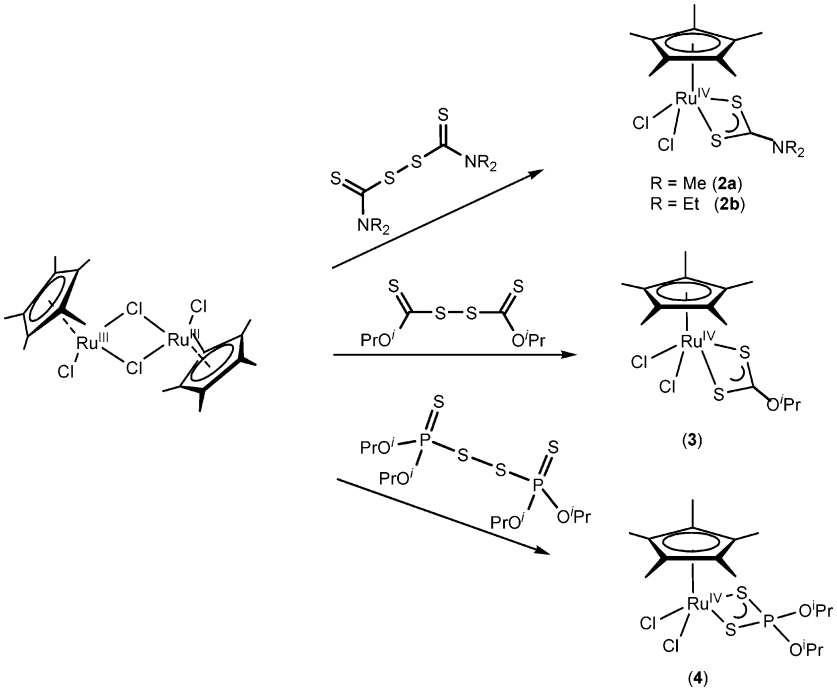
Reaction with Phosphines. (a) Synthesis of [Cp*Ru(S_2CNMe_2)-(PPh_3)Cl]Cl (8a). To a purple solution of **2a** (30 mg, 0.070 mmol) in acetonitrile (12 mL) was added PPh_3 (18 mg, 0.070 mmol) with stirring. The solution turned red after 4 h and was stirred for 17 h. Concentration of the resultant solution 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 $C_{31}H_{36}Cl_2NPRuS_2 \cdot 3H_2O$: 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. ^{1}H NMR (CD_3CN): δ 1.46 (s, 15H, Me_5C_5), 3.03 and 3.17 (each s, 3H, CH_3), 6.8−7.8 (m, 15H, PPh_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 8.9 (s, *Me*$_5$C$_5$), 38.0 and 38.2 (each s, CH_3), 110.6 (s, Me$_5$*C*$_5$), 129.4 (s, br, PPh), 132.2 (s, PPh), 134.4 (s, br, PPh), 201.9 (s, CS). ^{31}P{^{1}H} NMR (CD_3CN): δ 35.2 (s, PPh_3). IR (KBr, cm^{-1}): ν 1559vs (C−N), 1091m (NC_2), 750w, 698s (C−S). FAB$^+$-MS: *m*/*z* 654 $[M - Cl = Cp^*Ru(S_2CNMe_2)(PPh_3)Cl]^+$, 619 $[M - 2Cl]^+$, 497 $[M - 2Cl - (S_2CNMe_2) - 2H]^+$, 392 $[M - Cl - PPh_3]^+$, 357 $[M - 2Cl - PPh_3]^+$, and 297 $[M - 2Cl - PPh_3 - CNMe_2 -$



2b **3**

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



4H]$^+$. HRMS. Calcd for $[C_{31}H_{36}ClNPRuS_2]^+$: 654.0759. Found: 654.0745 (ESI$^+$) and 654.0776 (FAB$^+$).

(b) Synthesis of [Cp*Ru(S$_2$CNMe$_2$)(PPhMe$_2$)Cl][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 $C_{21}H_{32}ClNRuS_2P_2F_6$: 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. ^{1}H NMR (CD_3CN): δ 1.56 (s, 15H, Me_5C_5), 1.82 (d, $^2J_{PH}$ = 8.1 Hz, 3H, PMe), 1.85 (d, $^2J_{PH}$ = 8.8 Hz, 3H, PMe), 3.05 and 3.16 (each s, 3H, Me), 7.3−7.8 (m, 5H, PPh). ^{13}C{^{1}H} NMR (CD_3CN): δ 9.1 (s, C_5Me_5), 12.6 and 13.2 (each d, $^1J_{PC}$ = 38.6 Hz, P*Me*), 37.9 and 38.1 (each s, Me), 109.5 (C_5Me_5), 134.3 (d, $^1J_{PC}$ = 56.2 Hz, *ipso*-C), 132.3 (d, $^3J_{PC}$ = 6.4 Hz, *meta*-C) and 131.6 (s, *para*-C), 128.4 (d, $^2J_{PC}$ = 9.7 Hz, *ortho*-C) (P*Ph*), 202.7 (*CS*). ^{31}P{^{1}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 [M − Cl = Cp*Ru(S_2CNMe_2)($PPhMe_2$)]$^+$.

(c) Synthesis of [Cp*Ru(S$_2$CNMe$_2$)(PMe$_3$)Cl][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 $C_{40}H_{50}BClNPRuS_2$: 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. ^{1}H NMR (CD_3CN): δ 1.56 (s, 15H, Me_5C_5), 1.54 (d, $^2J_{PH}$ = 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}C{^{1}H} NMR (CD_3CN): δ 8.9 (C_5Me_5), 13.4 (d, $^1J_{PC}$ = 40.2 Hz, P*Me*$_3$), 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, B*Ph*$_4$), 202.9 (*CS*). ^{31}P{^{1}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 [M − Cl = Cp*Ru(S_2CNMe_2)(PMe_3)Cl]$^+$, 432 [M − 2Cl]$^+$, 392 [M − Cl − PMe_3]$^+$, 356 [M − 2Cl − PMe_3]$^+$. ESI$^+$-HRMS. Calcd for $[C_{16}H_{30}ClNPRuS_2]^+$: 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(S_2CO^iPr)(PPh_3) (9). To a purple solution of **3** (50 mg, 0.113 mmol) in acetonitrile (12 mL) was added PPh_3 (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 $C_{32}H_{37}OPRuS_2$: 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. ^{1}H NMR (CD_3CN): δ 1.42 (s, 15H, Me_5C_5), 1.12 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$), 4.95 (septet, $^3J_{HH}$ = 6.0 Hz, 1H, CH(CH_3)$_2$), 7.2−7.6 (m, 15H, PPh_3). ^{1}H NMR (C_6D_6): δ 1.55 (s, 15H, Me_5C_5), 0.97 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$), 5.00 (septet, $^3J_{HH}$ = 6.0 Hz, 1H, CH(CH_3)$_2$), 7.0−7.8 (m, 15H, PPh_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 11.0 (C_5Me_5), 22.3 (CH(CH_3)$_2$), 74.5 (CH(CH_3)$_2$), 86.6 (C_5Me$_5$), 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) (PPh), 227.1 (CS). ^{31}P{^{1}H} NMR (CD_3CN): δ 54.5 (PPh_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.2 (PPh_3). IR (KBr, cm^{-1}): ν 1027m, 1097s (C−S), 1227vs (C−O). ESI$^+$-MS: *m*/*z* 634 [M = Cp*Ru(S_2CO^iPr)(PPh_3)]$^+$, 499 [M − (S_2CO^iPr)]$^+$, 372 [M − PPh_3]$^+$, 329 [M − PPh_3 − ^{i}Pr)]$^+$, 300 [Cp*RuS_2]$^+$, 263 [PPh_3H]$^+$.

Reaction of 2a with [CpCr(CO)$_3$]$_2$. Synthesis of Cp*Ru(S_2CNMe_2)(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 $C_{14}H_{21}NORuS_2$: 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. ^{1}H NMR ($CDCl_3$): δ 1.81 (s, 15H, Me_5C_5), 3.18 (s, 6H, 2CH_3). ^{1}H NMR (CD_3CN): δ 1.78 (s, 15H, Me_5C_5), 3.14 (s, 6H, 2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.0 (Me_5C_5), 38.1 (CH_3), 93.1 (Me_5C_5), 201.9 (CS) and 215.6 (CO). IR (KBr, cm^{-1}): ν 1901vs (C−O), 1529s (C−N), 1153m (NC_2), 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 $CDCl_3$ 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 F^2.

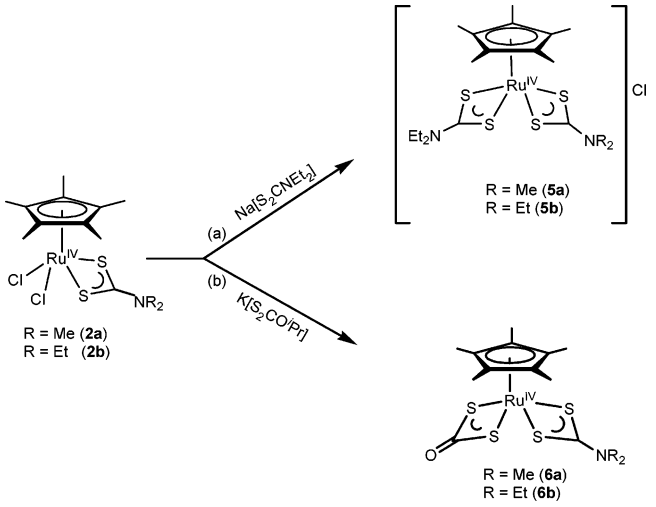
Two chloroform solvent molecules were found in **5a**. For **8a**, there were two acetonitrile molecules, with occupancies of 1.0 and 0.5, respectively, as well as a water molecule. There was disorder of the chloride counterion, which was modeled over three sites, with occupancies of 0.37, 0.37, and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

Results and Discussion

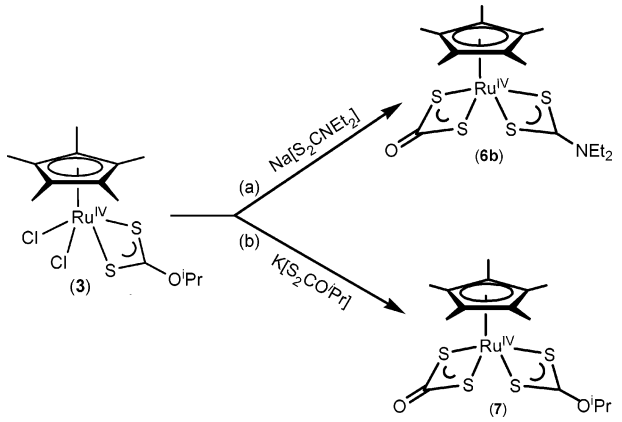
Reactions with Disulfides. Treatment of the Ru^{III} complex **1** with the disulfanes−tetraalkyldithiuram disulfides [R_2NC(S)S]$_2$ (R = Me,[23] Et), isopropylxanthic disulfide [^{i}PrOC(S)S]$_2$, and bis(thiophosphoryl) disulfide [(^{i}PrO)$_2$P(S)S]$_2$− resulted in facile cleavage of the bridging 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.

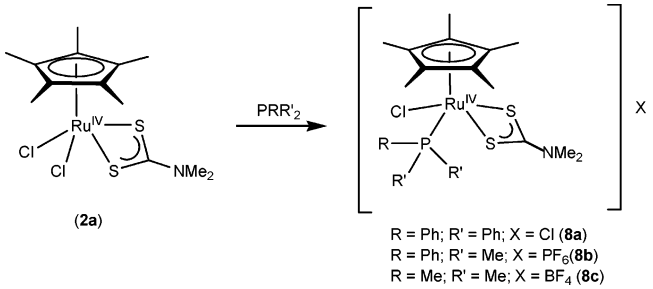
Scheme 2



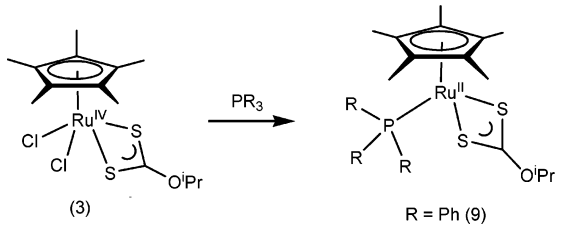
Scheme 3



Scheme 4



Scheme 5



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*, η^2-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 ^{1}H NMR spectra in $CDCl_3$ and at δ 8.2 and 8.4 (methyl C's) and δ 106.3 and 107.2 (ring C's) in their ^{13}C NMR spectra. The proton resonances in $CDCl_3$ of the DTC ligand of **2b** are observed as a triplet at δ 1.30 (CH_3) and a quartet at δ 3.73 (CH_2), consistent with the presence of a plane of symmetry and possibly also rapid free rotation about the C−N bond. The corresponding ^{13}C 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 ^{1}H NMR spectrum in $CDCl_3$ as a doublet at δ 1.50 (CH_3) 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 NC_2 in **2b** and of C−S and C−O in **3**. The mother 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 ^{1}H NMR spectral data at 300 MHz in $CDCl_3$ shows a singlet for Cp* at δ 1.37, a doublet at δ 1.39 (CH_3), and two septets at δ 4.76 and 5.09 (CH) for the two ^{i}Pr groups in the molecule; scanned at 500 MHz in CD_3CN, 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 ^{31}P NMR spectrum shows a doublet of doublet at δ 95.2, indicating coupling to two different CH protons. This is consistent with the ^{13}C 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 ^{1}H NMR spectrum is not clear. The combined inference is the presence of inequivalent O^{i}Pr 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.

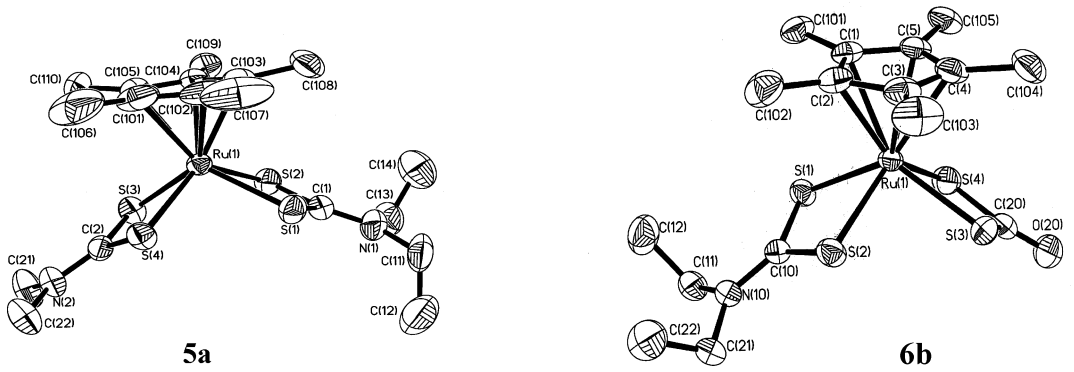


Figure 2. Molecular structures of the cations of **5a** and **6b**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

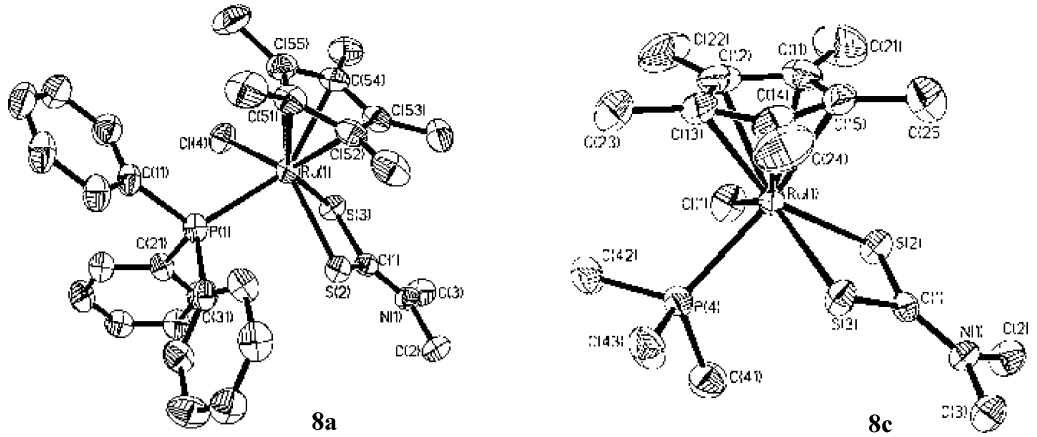


Figure 3. Molecular structures of **8a** and **8c**. Thermal ellipsoids are drawn at the 50% probability level, and the anions of the complexes are omitted. H atoms are omitted for clarity.

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

molecule A						molecule B: **10**			
8a		**8c**		**9**					
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 $Et_2NC(S)S^-$ 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(η^2-S_2CNR_2)(η^2-S_2CO)] **6a** and **6b** (Scheme 2b). While this manuscript was in preparation, complex **5a** was reported to be isolated as the [$N(Ph_2PS)_2$] salt from the oxidation of Cp*Ru{$N(Ph_2PS)_2$} with $[Me_2NC(S)S]_2$.[27]

Complex **6b** was also obtained from the reaction of **3** with $Et_2NC(S)S^-$ (Scheme 3a). The reaction of **3** with $^iPrOC(S)S^-$ results in the formation of a dithiocarbonato complex [Cp*Ru(η^2-S_2CO^iPr)(η^2-S_2C═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 η^5-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 dithiocarbonate [71.37(3)−72.04(3)°].

The spectral data are consistent with the molecular structures. The ^{1}H NMR spectrum of **5a** in $CDCl_3$ shows

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

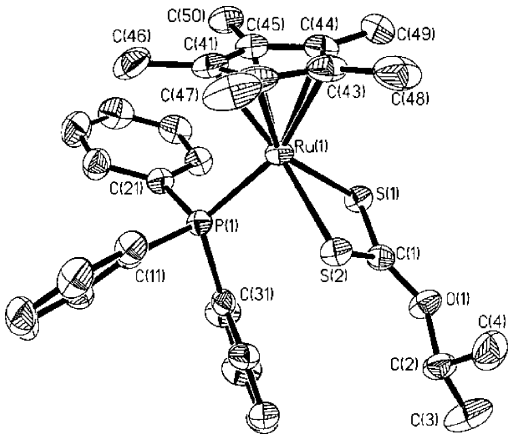


Figure 4. Molecular structure of **9**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

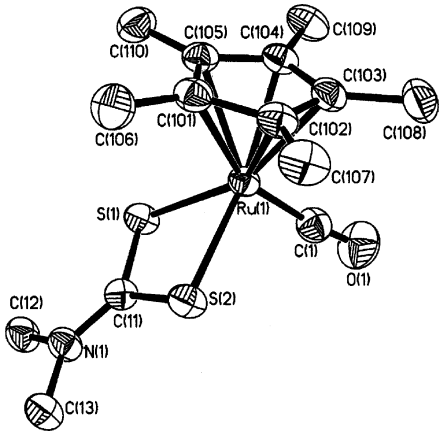


Figure 5. ORTEP diagram for one of the molecules in the unit cell of **10**. Thermal ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

singlets at δ 1.60 for the Cp* Me protons and at δ 3.37 for the six N*Me*$_2$ 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 CH_3 with coupling constants of 14.4 Hz ($^2J_{HH}$) and 7.2 Hz ($^3J_{HH}$). The ^{1}H NMR spectrum of **5b** in CD_3CN 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 CH_3 protons and an overlapping doublet of quartet (dq) at δ 3.77−3.65 for the CH_2 protons, with coupling closely resembling the ABX_3 spectrum of **5a**.

The ^{1}H NMR spectra of **6a** and **6b** in CD_3CN both showed a singlet at δ 1.49 for the Me protons of the Cp* ring. The Me protons of the η^2-S_2CNMe_2 ligand in **6a** are observed as a singlet at δ 3.27, while the η^2-S_2CNEt_2 ligand in **6b** is manifested as a triplet at δ 1.23 for the CH_3 protons and overlapping dq at δ 3.78−3.59 for the CH_2 protons, with a ABX_3 coupling scheme as in **5a**. The presence of $\nu_{C=O}$ stretching frequencies (1701m in **6a** and 1704m 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 ^{1}H NMR spectrum in $CDCl_3$ (a singlet at δ 1.58 for Cp*, a doublet at δ 1.46 for CH_3's, and a septet at δ 5.55 for CH of the isopropyl xanthate ligand), its IR spectrum ($\nu_{C=O}$ 1695 m), and its FAB-MS spectrum (m/z = 463 for the molecular ion).

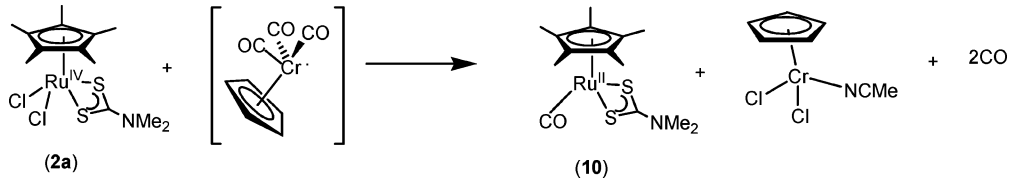
These dithiocarbonate complexes are the first examples of an organoruthenium, and notably of Ru^{IV}. The only other such example among the transition metals was a (phenyl)-rhodium complex reported by Bianchini.[28] *Coordination* compounds of dithiocarbonate are much more common, mainly of Pd^{II} and Pt^{II}, with the first case reported by Fackler and Seidel in 1969[29] 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, $[Ru(S_2CO)(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$), was reported by Wilton-Ely and Hogarth, from a clean facile reaction of *cis*-$[RuCl_2(dppm)_2]$ with CS_2 and NaOH.[35] Other synthetic routes to date have involved the reaction of bromo/isocyanate complexes with CS_2[31] and xanthate anions,[33b,34c] oxidation of η^2-CS_2 complexes with O_2, S_8, or Se_n,[33c] and nucleophilic attack of ligated xanthate (S_2COR) 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 RS_2COR.[30] Indeed, in an NMR-tube reaction of **3** with a stoichiometric amount of K(S)SCO^{i}Pr in $CDCl_3$, we observed in the product solution resonances pertaining to the complex **7**, as well as those assignable to [^{i}PrS_2CO^{i}Pr] (viz., δ 1.44 and 1.46 (each d, $^3J_{HH}$ = 6 Hz, 3H, C*H*$_3$), 3.79 and 5.76 (each septet, $^3J_{HH}$ = 6 Hz, 1H, C*H*$(CH_3)_2$).

(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 PPh_3 resulted in the displacement of both chlorido ligands and the reduction of the metal center to the 2+ oxidation state

(28) Bianchini, C.; Meli, A.; Laschi, F.; Vizza, F.; Zanello, P. *Inorg. Chem.* **1989**, *28*, 227.
(29) Fackler, J. P., Jr.; Seidel, W. C. *Inorg. Chem.* **1969**, *8*, 1631.
(30) (a) Cornock, M. C.; Gould, R. O.; Jones, C. L.; Owen, J. D.; Steele, D. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 496. (b) Alison, J. M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 254.
(31) Werner, K. v.; Beck, W.; Böhner, U. *Chem. Ber.* **1974**, *107*, 2434.
(32) Contreras, R.; Valderrama, M.; Riveros, O.; Moscoso, R.; Boys, D. *Polyhedron* **1996**, *15*, 183.
(33) (a) Perpiñán, M. F.; Ballester, L.; González-Casso, M. E.; Santos, A. *J. Chem. Soc., Dalton Trans.* **1987**, 281. (b) Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton. Trans.* **1996**, 1935. (c) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Orlandini, A. *J. Organomet. Chem.* **1985**, *286*, 259.
(34) (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1024. (b) Bianchini, C.; Meli, A.; Vizza, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 767. (c) Cole-Hamilton, D. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1818.
(35) Wilton-Ely, J. D. E. T.; Solanki, D.; Hogarth, G. *Inorg. Chem.* **2006**, *45*, 5210.

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 ^{1}H 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 CD_3CN). Complexes **8a**−**c** show nonequivalent Me groups of the DTC ligand in their ^{1}H 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 ^{1}H 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 CH_3 and a septet at δ 4.95 for CH. The P atoms of PPh_3 in **8a** and **9**, of $PPhMe_2$ in **8b**, and of PMe_3 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 $CpRu(PPh_3)(S_2COR)$ (R = Me, Et, or Pr), which was formed from the reaction of $CpRu(PPh_3)_2Cl$ 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 PPh_3 and its poorer donor capability resulting from the presence of electron-withdrawing Ph groups, whereas Me substituents in PMe_3 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 $CpCrCl_2$(solvent) with loss of CO ligands (Scheme 6). $CpCrCl_2(CH_3CN)$ was characterized structurally and found to be identical with that which we have reported before.[41]

The ^{1}H NMR spectrum of the Ru^{II} complex **10** in $CDCl_3$ 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 $CDCl_3$ solution under N_2, **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, $[Cp^*RuCl_2]_2$ (**1**), with S−S-bonded substrates, $[R_2NC(S)S]_2$ (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

(36) Coto, A.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 4392.
(37) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.
(38) Goh, L. Y.; Weng, Z.; Hor, A. T. S.; Leong, W. K. *Organometallics* **2002**, *21*, 4408.
(39) See references in: Weng, Z.; Goh, L. Y. *Acc. Chem. Res.* **2004**, *37*, 187.
(40) See, for instance, the following: (a) Ng, V. W. L.; Leong, W. K.; Koh, L. L.; Tan, G. K.; Goh, L. Y. *J. Organomet. Chem.* **2004**, *689*, 3210. (b) Ng, V. W. L.; Kuan, S. L.; Leong, W. K.; Koh, L. L.; Tan, G. K.; Goh, L. Y.; Webster, R. W. *Inorg. Chem.* **2005**, *44*, 5229. (c) Köhler, F. H.; Lachmann, J.; Muller, G.; Zeh, H.; Brunner, H.; Pfauntsch, J.; Wachter, J. *J. Organomet. Chem.* **1989**, *365*, C15. (d) Bräunlein, B.; Köhler, F. H.; Strauss, W.; Zeh, H.; *Z. Naturforsch.* **1995**, *50b*, 1739.
(41) Goh, L. Y.; Hambley, T. W. *J. Organomet. Chem.* **1990**, *395*, 269.

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 $[CpCr(CO)_3]_2$ is strongly influenced by the oxidizing tendency of Ru^{IV} and the halophilicity of the resulting $CpCr^{III}$ moiety.

(42) References 6−8 in: Shin, R. Y. C.; Goh, L. Y. *Acc. Chem. Res.* **2006**, *39*, 301.

Acknowledgment. Support from the National University of Singapore under Academic Research Fund Grants R-143-000-077-112 and R-143-000-209-112 to L.Y.G. and a research scholarship to E.P.L.T. are gratefully acknowledged.

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.

IC061781T