

Carbon–sulfur bond cleavage in $\text{CpRu}(\eta^5\text{-thiophene})^+$ and subsequent reactions of the butadiene-thiolate product *

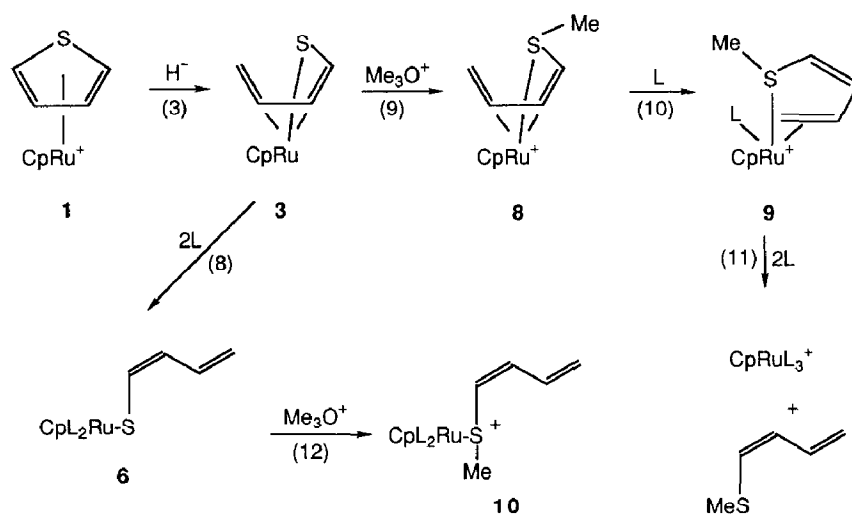
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Abstract

The complexes $\text{CpRu}(\eta^5\text{-Th})^+$ (**1**), where Th is thiophene or a methyl-substituted thiophene, react with hydrides such as $\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2^-$ to give (eq. 3) the C–S cleaved butadiene-thiolate product **3**. Subsequent reactions of **3** are shown:



$\text{L} = \text{PPh}_2\text{Me}$

This scheme is not intended to indicate that all reactions were performed on the thiophene complex; many were carried out using the methyl-substituted thiophene analogs. Structures of complexes of the types **6** and **9** were established by X-ray diffraction studies. Possible mechanisms for reaction 3 are considered, and stereo-

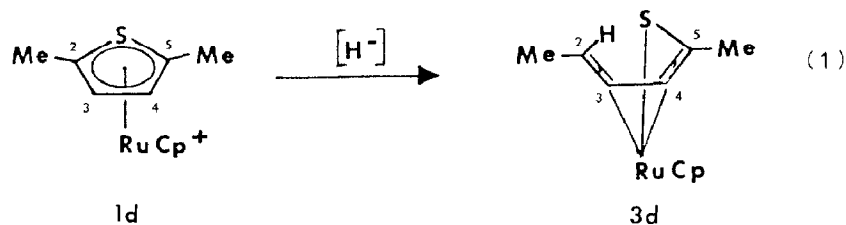
* With many thanks and sincere best wishes to Professor E.O. Fischer on the occasion of his 70th birthday.

chemistries of all complexes are established by ^1H NMR spectrometry. Implications for the mechanism of the catalytic hydrodesulfurization of thiophene are discussed.

Catalytic hydrodesulfurization (HDS), the process by which sulfur is removed from crude oils by treatment with H_2 over a $\text{Mo-Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst, is one of the largest-scale chemical processes practiced in the world [1,2]. Because of its commercial importance, many studies have been directed toward understanding the mechanism of the HDS of thiophene, a model compound typical of the organosulfur compounds which are most difficult to desulfurize in petroleum [3]. Despite this effort, most features of the mechanism, including the mode of thiophene binding to the catalyst surface and the nature of the first steps in the process, are still not established. Our approach to learning more about the HDS process is to prepare transition metal complexes of thiophenes and compare their reactivities with that of thiophenes in reactor studies. The complexes $\text{CpRu}(\text{Th})^+$ (where Th is an η^5 -thiophene or methyl-substituted thiophene and Cp is $\eta\text{-C}_5\text{H}_5$) are of particular interest because the coordinated thiophene undergoes several reactions which may be related to its reactivity on HDS catalysts, and Ru is an excellent HDS catalyst [4].

In basic CD_3OD solution, fast exchange with deuterium of the 2,5-protons of the π -bound thiophene of $\text{CpRu}(\text{Th})^+$ is observed [5]; preferential exchange occurs in the same positions when thiophene is passed with D_2 over HDS catalysts [6]. Equilibrium studies of the replacement of thiophene (T) in $\text{CpRu}(\text{T})^+$ with methyl-substituted thiophenes show that thiophene coordination to the Ru increases with an increasing number of methyl groups in the thiophene [7]; adsorption on HDS catalysts also increases as the number of methyl groups in the thiophene increases [8].

The thiophene ligand in $\text{CpRu}(\text{Th})^+$ is activated in such a way that upon addition of nucleophiles (OMe^- , SEt^- , $\text{CH}(\text{COOMe})_2^-$ [9], H^- [10]) S-C bond cleavage occurs to give a butadiene thiolate ligand as in eq. 1. The structure of the



$\text{CpRu}(\eta^5\text{-SC}(\text{Me})=\text{CHCH}=\text{CH}(\text{Me}))$ (**3d**) product has been determined by an X-ray structure analysis [10]. In a slow reaction the olefin groups of the butadiene are displaced from the metal center by phosphines to yield the complexes $\text{CpRu}(\text{PPh}_2\text{Me})_2(\eta^1\text{-SCH}=\text{CHCH}=\text{CH}(\text{Nuc}))$ [9]. In this paper, we describe in more detail the addition of nucleophiles to the coordinated thiophene and further reactions of the novel butadiene-thiolate ligand, which finally result in cleavage of the second S-C bond. The overall conversion of thiophenes to hydrocarbons in these Ru complexes suggests a reasonable pathway for the catalytic HDS of thiophenes.

Experimental

Throughout this paper, the compounds are labeled as given in Table 1.

General procedures. ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks and standards (C_6D_6 : 7.15 ppm; CD_2Cl_2 : 5.34 ppm; CD_3COCD_3 : 2.04 ppm). ^2H NMR spectra were recorded on a Bruker WM 300 spectrometer, using the proton signal of the benzene solvent as the internal lock and the naturally occurring D-content of benzene as the standard. The ^{31}P NMR spectra were also obtained on the WM 300 spectrometer with acetone- d_6 as the internal lock and 85% H_3PO_4 as the external standard. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. Reaction mixtures were analyzed with a Varian 3400 gas chromatograph and 4270 integrator.

All reactions were performed under N_2 in reagent grade solvents. Methylene chloride and hexanes were dried over CaH_2 and distilled; diethyl ether and tetrahydrofuran (THF) were dried and distilled from Na/benzophenone . Acetone was dried over 4 Å-molecular sieves. 1,2-Dichloroethane and acetonitrile were used as received from commercial sources. LiAlD_4 , $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ ("Red Al"), PPh_2Me , Ti_2SO_4 , $\text{C}_5\text{Me}_5\text{H}$, and CpTi were purchased from Aldrich Chemical

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Table 1

Compound numbering system

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- | | |
|----|---|
| 1 | $[\text{CpRu}(\eta^5\text{-R}^5\text{-} \begin{array}{c} \text{R}^4 \quad \text{R}^3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{-R}^2)] \text{PF}_6$ |
| 2 | $\text{CpRu}(\eta^5\text{-SCR}^2=\text{CR}^3\text{CR}^4=\text{CH}(\text{CH}(\text{COOMe})_2))$ |
| 3 | $\text{CpRu}(\eta^5\text{-SCR}^5=\text{CR}^4\text{CR}^3=\text{CR}^2\text{H})$ |
| 4 | $[\text{Cp}^*\text{Ru}(\eta^5\text{-R}^5\text{-} \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{-R}^2)] \text{PF}_6$ |
| 5 | $\text{Cp}^*\text{Ru}(\eta^5\text{-SCR}^5=\text{CHCH}=\text{CR}^2\text{H})$ |
| 6 | $\text{CpRu}(\text{PPh}_2\text{Me})_2(\eta^1\text{-SCR}^5=\text{CHCH}=\text{CR}^2\text{H})$ |
| 7 | $\text{CpRu}(\text{CO})_2(\eta^1\text{-SCR}^5=\text{CHCH}=\text{CR}^2\text{H})$ |
| 8 | $[\text{CpRu}(\eta^5\text{-S}(\text{Me})\text{CR}^5=\text{CHCH}=\text{CR}^2\text{H})]\text{BF}_4$ |
| 9 | $[\text{CpRu}(\text{PPh}_2\text{Me})(\eta^3\text{-S}(\text{Me})\text{CR}^5=\text{CHCH}=\text{CR}^2\text{H})]\text{BF}_4$ |
| 10 | $[\text{CpRu}(\text{PPh}_2\text{Me})_2(\eta^1\text{-S}(\text{Me})\text{CR}^5=\text{CHCH}=\text{CR}^2\text{H})]\text{BF}_4$ |
-

where the R groups are as follows:

- a $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}$
 - b $\text{R}^2 = \text{Me}; \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}$
 - c $\text{R}^3 = \text{Me}; \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{H}$
 - d $\text{R}^2 = \text{R}^5 = \text{Me}; \text{R}^3 = \text{R}^4 = \text{H}$
 - e $\text{R}^2 = \text{R}^3 = \text{Me}; \text{R}^4 = \text{R}^5 = \text{H}$
 - f $\text{R}^2 = \text{R}^3 = \text{R}^5 = \text{Me}; \text{R}^4 = \text{H}$
 - g $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Me}; \text{R}^5 = \text{H}$
-

Table 2
¹H NMR data for the complexes ^a

Compound	Chemical shift (δ)		Coupling constants (Hz)							Others		
	Cp	H2z	H2e	H3	H4	H5	H2z-H2e	H2z-H3	H2e-H3		H3-H4	H4-H5
2a ^b	4.51s	3.67dd		4.58dd	5.38dd	6.16d		8.6		6.2	5.0	3.29 ^ε ; 3.26, 3.40 (OMe)
2b ^b	4.48s	3.78dd		4.63dd	5.43d	[2.17s]		8.5		6.4		3.31 ^ε ; 3.29, 3.40 (OMe)
2c ^b	4.53s	3.62dd		4.66dd	[1.74s]	6.20d		8.6				<i>J</i> (H3-H5) = 1.2; 3.32 ^ε ; 3.30; 3.42 (OMe)
2e ^b	4.46s	3.69dd		4.74d	[1.81s]	[2.27s]		8.4				3.35 ^ε ; 3.30, 3.41 (OMe)
2g ^b	4.45s	3.88d		[1.64s]	[1.79s]	[2.38s]						3.22 ^ε ; 3.32, 3.43 (OMe)
3a ^b	4.43s	2.62d	3.29d	4.42m	5.50dd	6.30d		10.3	8.8	6.1	5.0	
3b ^b	4.40s	3.48dq	[1.38d]	4.33m	5.40dd	6.21d	[6.2]	8.8		6.2	5.3	
3c ^b	4.40s	2.47s	3.43s	[1.43s]	5.50d	6.33d					5.2	
3d ^b	4.33s	3.58dq	[1.48d]	4.36m	5.42d	[2.29s]	[6.1]	9.2		6.2		
3e ^b	4.37s	3.16q	[1.49d]	[1.51s]	5.44d	6.23d	[6.4]				5.4	
3f ^b	4.30s	3.31q	[1.50d]	[1.59s]	5.61s	[2.35s]	[6.4]					
5a ^b	[1.65s]	2.84d	2.77d	4.04m	5.02dd	5.85d		10.3	8.5	6.3	5.3	
5d ^b	[1.54s]	3.66dq	[1.42d]	4.15dd	4.91d	[2.15s]	[6.3]	9.6		6.4		

6a ^c	4.46s	5.00dd	4.82dd	<i>f</i>	6.07dd	6.58d	2.4	17.2	10.2	10.1	9.3	1.52 ^g PMe; 7.1–7.4 Ph
6d ^c	4.46s	5.47dq	[1.68d]	<i>f</i>	6.25d	[1.96s]	[6.6]	15.4		10.3		1.53 ^g PMe; 7.1–7.4 PPh
7a ^b	4.36s	5.28dd	5.14dd	7.71m	6.32m	6.32m	2.1	17.1	9.3	^h	^h	
7d ^b	4.46s	5.70dq	[1.73d]	7.45dd	6.45d	[2.16s]	[6.8]	14.3		10.3		
8a ^c	5.57s	0.86dd	4.23dd	5.58m	6.70dd	6.55d	3.9	10.2	8.3	6.0	5.6	2.73s, SMe
8d ^c	5.44s	2.22dq	[1.84d]	5.44m	6.49d	[2.58s]	[6.03]	10.3		5.9		2.79s, SMe
9a ^c	5.27s	1.83d	3.38d	5.91t,br	5.99d	6.51d		~12	9.2		5.4	2.28s, 2.25s, SMe; PMe ⁱ ;
		1.79d				6.50d						7.1–7.5 PPh
9d ^c	5.35s	2.34m	[1.31d]	5.61d	6.21s	[2.89s]	[6.1]	10.7				2.13s, 2.16s, SMe; 1.87br, PMe; 7.1–7.5Ph
10d ^d	4.86s	5.97dq	[1.87d]	6.54dd	6.24d	[2.03s]	[6.7]	14.1		11.2		2.25s SMe; 1.6br, PMe; 7.1–7.5 PPh
11 ^c	5.00s											PMe ⁱ ;
11 ^d	4.88s											7.1–7.5 PPh
12 ^{c,d}		5.61dq	[1.71d]	6.43dd	6.02d	[2.01s]	[6.6]	15.4		10.7		1.96br, PMe; 7.1–7.5 PPh
												2.23s SMe

^a Values given in [] are for the corresponding Me groups. Positions are numbered as in eq. 2. ^b In C₆D₆. ^c In CD₃COCD₃. ^d In CD₂Cl₂. ^e d, *J* 10.1 Hz; CH.
^f Obscured by Ph. ^g Pseudo triplet, ³*J*(pH) 4.4 Hz. ^h Not resolved. ⁱ Obscured by solvent.

Table 3

 ^{13}C NMR data for the complexes

Compound	Cp	C2	C3	C4	C5	Other
3a ^a	78.2	45.9 (t, 162) ^d	85.5 (d, 162)	95.4 (d, 158)	94.4 (d, 179)	
3d ^a	79.1	61.9 (d, 166)	87.7 (d, 162)	91.6 (d, 161)	109.9 (s)	22.6 (q, 121; Me5), 32.8 (q, 127; Me2)
5d ^a	n.o.	30.5	90.1	93.1	n.o.	1.4 (C_5Me_5); 19.4 (Me5); 25.9 (Me2)
8d ^b	84.2	69.4	89.7	92.5	94.7	20.9, 21.9, 25.0 (Me's)
9d ^b	87.7	64.5 (d, 150)	72.3 (d, 155)	^c	^c	16.3, 23.0, Me2 and Me5; 15.7, 16.1, SMe; 18.5, PMe

^a In C_6D_6 . ^b In CD_3COCD_3 . ^c Obscured by Ph. ^d $^1J(\text{CH})$ coupling constants in parentheses.

Table 4

Summary of crystal data for $\text{CpRu}(\text{PPh}_2\text{Me})_2(\eta^1\text{-S-C}(\text{Me})=\text{CH}-\text{CH}=\text{CH}(\text{Me}))$, **6d**, and $[\text{CpRu}(\text{PPh}_2\text{-Me})(\eta^3\text{-S}(\text{Me})-\text{C}(\text{Me})=\text{CH}-\text{CH}=\text{CH}(\text{Me}))]\text{BF}_4$, **9d**

	6d	9d
formula	$\text{C}_{37}\text{H}_{40}\text{RuSP}_2$	$\text{C}_{25}\text{H}_{30}\text{BF}_4\text{RuSP}$
mol wt, g mol^{-1}	679.8	581.4
cryst size, mm	$0.4 \times 0.3 \times 0.2$	$0.7 \times 0.5 \times 0.3$
color	orange red	yellow
crystal system	orthorhombic	triclinic
space group	$P2_1nb$ (33)	$P\bar{1}$ (2)
a , Å	15.6061(6)	10.6364(23)
b , Å	19.3116(25)	13.3260(21)
c , Å	10.8715(19)	9.6140(18)
α , deg	90.0	108.12(1)
β , deg	90.0	102.11(2)
γ , deg	90.0	90.10(2)
Z	4	2
$\mu(\text{Mo-K}\alpha)$, cm^{-2}	6.5	7.9
D_{calcd} , g cm^{-3}	1.37	1.53
T , K	298	298
reflection measured	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
diffractometer	Datex graphite monochromator, $\text{Mo-K}\alpha$ ($\lambda = 0.70966$ Å)	Enraf-Nonius CAD 4 graphite monochromator, $\text{Mo-K}\alpha$ ($\mu = 0.71073$ Å)
scan limit	$2\theta \leq 50^\circ$	$2\theta \leq 55^\circ$
total data	6608	11578
unique data	1865 with $I \geq 2\sigma(I)$	4882 averaged with $I \geq 3\sigma(I)$
absorption correction	ψ -scan	ψ -scan
refinement	C, Ru, S, P anisotropic H position calculated	C, Ru, S, P anisotropic B, F isotropic (disordered along a 3-fold axis) H position calculated
R, R_w ^a	0.086, 0.075 ^b	0.052, 0.073 ^c
programs	^d , ORTEP	SHELX 76, SHELXS 86, ORTEP

^a $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^b $w = 1/\sigma^2|F_o|$. ^c $w = 1/(\sigma^2|F_o| + 0.001|F_o|^2)$. ^d Ref. 16.

Co. The thiophene complexes $[\text{CpRu(Th)}]\text{PF}_6$ (**1**) [5,7,9] and $[\text{CpRu(SC}_4\text{D}_4)]\text{PF}_6$ [5b] were prepared as described earlier. The ^1H NMR data of all complexes described in this paper are given in Table 2; the ^{13}C NMR data of selected examples are given in Table 3. The crystal structure analysis data are summarized in Table 4. Reactions were conducted at room temperature unless specified otherwise.

Preparation of complexes 2. Complexes **1a–1c**, **1e** and **1g** were allowed to react with an excess of $\text{NaCH}(\text{COOMe})_2$ and were isolated (50–80%) exactly as described earlier [9]. No reaction occurred with complex **1d** within 3 h. All products were characterized by their spectra.

Preparation of complexes 3a–3f. 50 mg of **1** were dissolved in 20 ml of THF and treated with an equimolar amount of $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ ("Red Al", 3.4 M solution in toluene, further diluted with THF). The solution immediately turned yellow. The solvent was removed in vacuo, the residue was dissolved in benzene, and the solution was chromatographed over basic Al_2O_3 (5×50 mm) with benzene as eluant. The product (60% yield) was sublimed under vacuum [10]. $\text{CpRu(SC}_4\text{H}_5)$ (**3a**): EIMS (18 eV), m/e 252 (M^+) overlapping with 251 ($M^+ - \text{H}$), 167 (CpRu^+); Anal. Found: C, 43.13; H, 4.17. $\text{C}_9\text{H}_{10}\text{RuS}$ calcd.: C, 43.01; H, 4.01%. $\text{CpRu(SC}_4\text{Me}_2\text{H}_3)$ (**3d**): EIMS (17 eV), m/e 280 (M^+), 265 ($M^+ - \text{CH}_3$); Anal. Found: C, 47.36; H, 4.91. $\text{C}_{11}\text{H}_{14}\text{RuS}$ calcd.: C, 47.29; H, 5.05%.

The analogous deuterated complex $\text{CpRu(SC}_4\text{H}_4\text{D})$ was prepared by adding a solution of LiAlD_4 (4 mg, 0.1 mmol) in THF (5 ml) to a solution of **1a** (46 mg, 0.11 mmol) in 25 ml of THF.

Preparation of the complexes $[\text{Cp}^*\text{Ru(Th)}]\text{PF}_6$ (4**) ($\text{Th} = \text{T}$ (**4a**); 2,5- Me_2T (**4d**) and $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$).** Cp^*Ti was produced by treating Cp^*H (4.9 ml, 30 mmol), dissolved in 75 ml of THF, with 12.5 ml of $n\text{-BuLi}$ (2.4 M in hexanes) for 15 h and then addition of 11.4 g (45 mmol) of Ti_2SO_4 [11]. Complexes **4a** and **4d** were prepared by the method used for the analogous Cp complexes [5] by treating the intensely yellow Cp^*Ti (9.4 g, 28 mmol) with $[\text{BzRuCl}_2]_2$ (1.0 g, 2.0 mmol) ($\text{Bz} = \eta^6\text{-C}_6\text{H}_6$) in 75 ml of acetonitrile. The reaction solution rapidly turned red-brown. After 1 h NH_4PF_6 (1.0 g, 6.1 mmol) was added. The solution was filtered, evaporated and the residue extracted with CH_2Cl_2 . The complex $[\text{Cp}^*\text{RuBz}]\text{PF}_6$ was precipitated by adding Et_2O ; the yield was 300 mg (0.65 mmol, 16%). This complex, prepared previously by another route [12], was then photolyzed in order to obtain the complex $[\text{Cp}^*\text{Ru(CH}_3\text{CN)}_3]\text{PF}_6$, which was not isolated but reacted directly with an excess of thiophene to give **4** (yield 30%) as in the preparations of complexes **1** [5b,7,9]. $[\text{Cp}^*\text{Ru(T)}]\text{PF}_6$ (**4a**): ^1H NMR (acetone- d_6): 2.07 (s; Cp^*), 6.19 (m; H2,5), 6.22 (m; H3,4); FAB-MS: 321 (M^+). $[\text{Cp}^*\text{Ru(2,5-Me}_2\text{T)}]\text{PF}_6$ (**4d**): ^1H NMR (acetone- d_6): 2.01 (s; Cp^*), 2.27 (s; Me2,5), 5.93 (s; H3,4).

Preparation of complexes 5a and 5b. These complexes were obtained in a similar way as complexes **3**. $[\text{Cp}^*\text{Ru}(\eta^5\text{-SC}_4\text{Me}_2\text{H}_3)]$ (**5d**): EIMS (15 eV), m/e 350 (M^+), 335 ($M^+ - \text{Me}$), 268 ($\text{Cp}^*\text{RuS}^+ - \text{H}$). Elemental analyses could not be obtained because the product decomposes slowly to Cp^*_2Ru , which was observed in the MS and ^1H NMR spectra [13].

Preparation of complexes 6a and 6d. About 0.04 mmol of **3** were dissolved in 0.5 ml of acetone- d_6 and placed in an NMR tube; 20 μl (2.6 equivalent) of PPh_2Me were added and the NMR tube was glass-sealed under vacuum and placed in a constant temperature bath at 50°C . The reaction solution turned orange. The

reaction was complete after 4 days, no decomposition or side products could be observed. The NMR tube was opened, the solvent evaporated and the residue washed several times with small amounts of Et₂O in order to remove the excess phosphine. Crystals of **6d** were obtained for the X-ray diffraction studies by slow evaporation of the solvent from an acetone solution. [CpRu(PPh₂Me)₂(η^1 -SC₄Me₂H₃)] (**6d**): ³¹P NMR (acetone-*d*₆): δ 33.7 ppm. EIMS (17 eV), *m/e* 480 (*M*⁺ – PPh₂Me), 367 (CpRu(PPh₂Me)⁺), 280 (*M*⁺ – 2PPh₂Me); Anal. Found: C, 65.15; H, 6.05. C₃₇H₄₀P₂SRu calcd.: C, 65.37; H, 5.93%.

Preparation of complexes 7a and 7d. 10 mg of **3** were dissolved in 5 ml of benzene; CO was bubbled several times through the solution during the 8-day reaction. The solution was filtered and the solvent evaporated under vacuum. The ¹H NMR spectra of **7a** and **7d** are similar to those of the phosphine substituted complexes **6**. EIMS (70 eV): **7a** *m/e* 308 (*M*⁺), 280 (*M*⁺ – CO), 252 (*M*⁺ – 2CO), 85 (C₄H₅S⁺); **7d** *m/e* 336 (*M*⁺), 280 (*M*⁺ – 2CO), 265 (*M*⁺ – 2CO – Me), 113 (C₄Me₂H₃S⁺).

Preparation of complexes 8a and 8d. 0.05 mmol of **3** were dissolved in 10 ml of CH₂Cl₂ and 10 mg (0.7 mmol) of [Me₃O]BF₄ were added. The reaction solution turned deep orange immediately and yellow after 30 min. The solution was concentrated under vacuum and passed through a small column of basic alumina (5 × 5 mm) with CH₂Cl₂ as eluant. The product was obtained in high purity and high yield (> 90%). [CpRu(SC₄Me₃H₃)]BF₄ (**8d**): FAB, *m/e* 295 (*M*⁺). Anal. Found: C, 38.37; H, 4.81. C₁₂H₁₇BF₄RuS calcd.: C, 37.81; H, 4.50%.

Preparation of complexes 9a and 9d. 0.025 mmol of **8** were dissolved in 0.5 ml of acetone-*d*₆ and placed in an NMR tube; 5 μ l (0.027 mmol) of PPh₂Me were added and the NMR tube was glass-sealed under vacuum. After one day at 50 °C the reaction was complete giving only small amounts of complex **11**. The solvent was evaporated and the residue washed with Et₂O. Yellow crystals of **9d** were obtained for the X-ray studies by slow diffusion of Et₂O into a solution of **9d** in CH₂Cl₂. [CpRu(PPh₂Me)(η^3 -SC₄Me₃H₃)]BF₄ (**9d**): ³¹P NMR (acetone-*d*₆): δ 37.4 ppm; FAB-MS, *m/e* 495 (*M*⁺, base peak), 367 (CpRu(PPh₂Me)⁺), 295 (*M*⁺ – PPh₂Me).

Preparation of complex [CpRu(PPh₂Me)₃]BF₄ (11). 0.027 mmol of **8d** were treated in a similar manner as described for the preparation of **9d**, but now with 25 μ l (0.135 mmol, 5-fold excess) of PPh₂Me. The reaction takes about two weeks to go to completion. **11** has a pale yellow color. [CpRu(PPh₂Me)₃]BF₄: ³¹P NMR (acetone-*d*₆): δ 25.8 ppm; FAB-MS: 767 (*M*⁺), 567 (*M*⁺ – PPh₂Me).

Preparation of complex 10d. 6 mg (0.009 mmol) of **6d** were dissolved in 5 ml of CH₂Cl₂ and reacted with 6 mg (0.04 mmol) of [Me₃O]BF₄. The solution turned deeper orange. After 1 h the solution was filtered, evaporated and washed with Et₂O. The FAB-MS shows no parent ion but peaks at *m/e* 567 (CpRu(PPh₂Me)₂⁺) and 367 (CpRu(PPh₂Me)⁺).

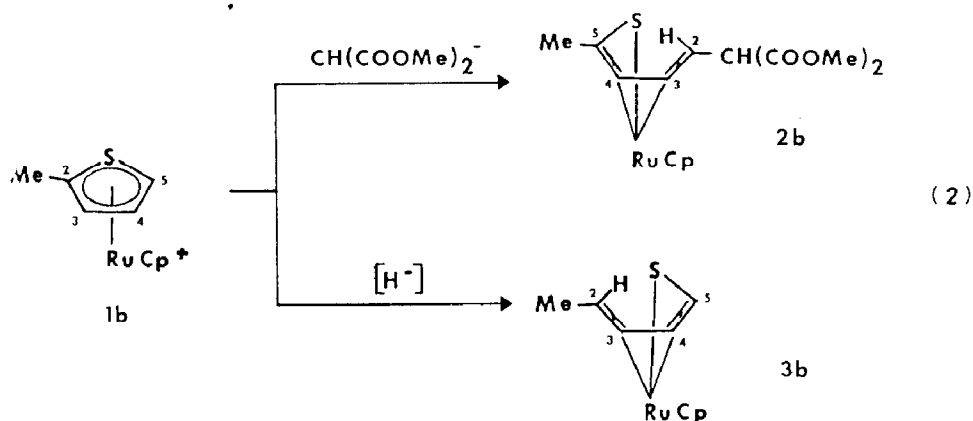
Reaction of 3d with H₂. 10 mg (0.036 mmol) of **3d** were dissolved in 3 ml of benzene and placed in a high pressure reactor (Parr Instruments) and pressurized to 27 atm of H₂. The reactor was heated for 5 h at the desired temperature. After cooling to room temperature, the solution was transferred to a flask; and the solvent was evaporated into a cold trap; both the trapped volatiles and the residue were studied. At room temperature no reaction occurred. At 80 °C, only a small amount of another compound could be seen in the residue besides the starting complex. At 110 °C all of the starting complex had reacted. The black powder residue was

soluble in common organic solvents, even hexanes, and showed several peaks in the ^1H NMR spectrum (benzene- d_6) in the region 4.3–5 ppm, with different relative intensities in different reactor runs. Its elemental analyses (C, 40.97; H, 4.57; S, 10.24) did not correspond to a simple composition. Mass spectra: EIMS (70 eV, 300°C) m/e 591, 564 ($\text{Cp}_3\text{Ru}_3\text{S}_2^+$), 531 ($\text{Cp}_2\text{Ru}_3\text{S}_3^+$), 499 ($\text{Cp}_2\text{Ru}_3\text{S}_2^+$), 398 ($\text{Cp}_2\text{Ru}_2\text{S}_2^+$), 333 ($\text{CpRu}_2\text{S}_2^+$). Direct exposure probe-MS (20 eV) m/e 591, 564, 531, 398. GC-MS of the trapped volatiles: besides the reaction solvent benzene, the parent m/e 86 ($\text{C}_6\text{H}_{14}^+$), and the fragmentation peaks identical to those of n-hexane (n- C_6H_{14}) [14] were observed. Integration of the C_6H_{14} peaks as compared with the benzene solvent showed that the butadiene thiolate ligand in **3d** was quantitatively converted to n-hexane. There is no reaction between benzene and H_2 under these conditions.

In a reaction at 200°C , n- C_6H_{14} was also observed in the volatiles. The black residue from this reaction was insoluble in all organic solvents and generated H_2S with acid. This residue was partly crystalline, but the X-ray powder pattern showed broad lines (d -spacing: 2.10; 2.08; 2.03; 1.80; 1.76) which did not correspond to Ru or RuS_2 [15].

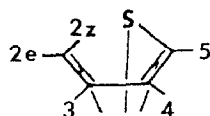
Results and discussion

Nucleophilic addition to CpRu(Th)^+ . As described earlier, both $\text{CH}(\text{COOMe})_2^-$ [9] and H^- [10] (eq. 1), add in a fast reaction to the complex CpRu(T)^+ causing S–C bond cleavage and formation of complexes of the type $\text{CpRu}(\eta^5\text{-SCH=CH-CH=CH(Nuc)})$. Additions of $\text{CH}(\text{COOMe})_2^-$ and H^- (from $[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{-OMe})_2^-]$) to the 2-MeT complex (**1b**), however, occur at different sites (eq. 2); the large malonate nucleophile attacks the carbon atom not bearing the Me group, whereas the H^- donor transfers H^- to the methylated carbon atom. The same is seen in NMR spectra (Table 2) of products **2** and **3** from reactions of CpRu(Th)^+ complexes of higher methylated thiophenes, 2,3-Me₂T and 2,3,4-Me₃T, where $\text{CH}(\text{COOMe})_2^-$ adds to a carbon adjacent to S which is not methylated, whereas H^- adds to the methylated site. Consequently, H^- adds to the 2,5-Me₂T complex (**1d**), while there is no reaction with $\text{CH}(\text{COOMe})_2^-$. The lack of reaction with



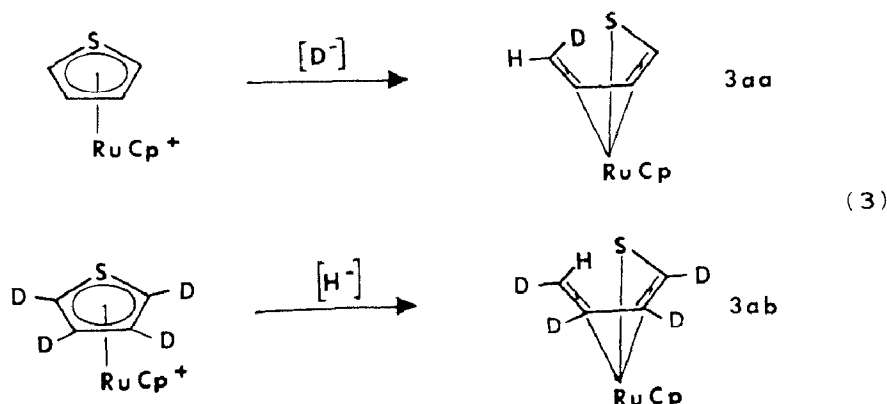
malonate is probably caused by steric rather than electronic effects of the 2,5-Me groups, because addition of malonate to the more electron rich 2,3,4-Me₃T-complex **1g** proceeds smoothly.

By comparing the addition products **2b** and **3b**, one can see that the nucleophiles not only add at different positions of the thiophene but also in stereochemically different sites. The large nucleophile $\text{CH}(\text{COOMe})_2^-$, as well as OMe^- and SEt^- [9], are found in the 2e position, whereas H^- is found specifically in the 2z position. Structural assignments were made on the basis of ^1H NMR spectroscopy (Table 2)



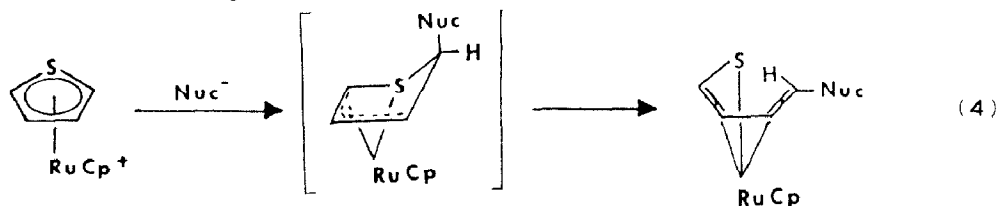
and proven by an X-ray diffraction study of complex **3d** [10]. In comparing NMR-data for complexes **3a** and **3b**, one needs to consider that substitution of H2e by a Me-group decreases the coupling of H2z to H3 from 10.3 to 8.8 Hz and shifts H2z ca. 0.9 ppm to lower field, as is observed in other olefin and butadiene systems [17,18]. H2z and H2e in complex **3a** as well as in **6a–9a** can be assigned by assuming that coupling of H2z to H3 is larger than H2e to H3; in **3a** these coupling constants are 10.3 and 8.8 Hz, respectively. No geminal coupling between H2z and H2e was observed in complex **3a**.

Deuteration experiments (eq. 3) clearly show that the H^-/D^- adds stereospecifically to the thiophene complex **1a** at the 2z position. The ^2H NMR spectrum of **3aa**

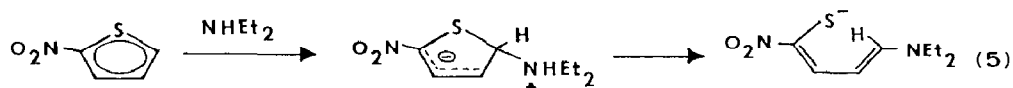


shows only one signal at 2.58 ppm for D2z and of **3ab** four signals (3.26, 4.41, 5.49, 6.26 ppm); no peaks were seen for D2e in **3aa** or for D2z in **3ab**.

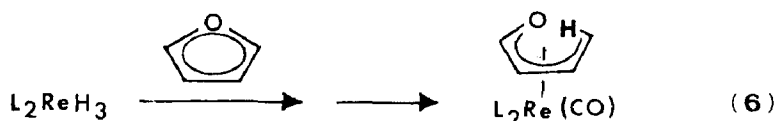
We have no conclusive mechanism to account for the different products resulting from the reactions (eq. 2) of $\text{CH}(\text{COOMe})_2^-$ (as well as OMe^- and SEt^-) and H^- donors with the coordinated thiophenes, but one reasonable possibility (eq. 4) is that certain nucleophiles add in an exo position to give an allylsulfide intermediate,



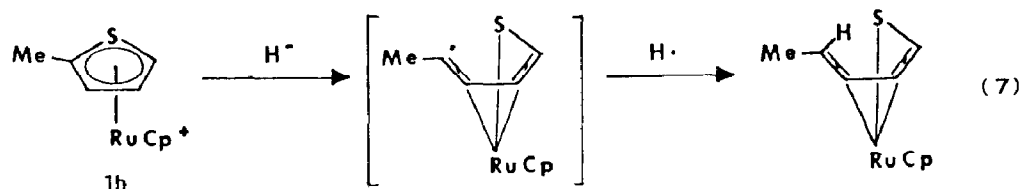
which was the observed product in reactions of a manganese thiophene complex [19]. Addition of large nucleophiles to comparable benzene systems was also only observed to occur in the *exo* position [20]. In the reaction of $\text{CH}(\text{COOMe})_2^-$ with **1b** (eq. 2) the presumed allylsulfide intermediate then can undergo C–S bond cleavage with formation of a butadiene-thiolate ligand by rotation around the C2–C3 bond to place the added nucleophile in the 2*e* position (eq. 4). Such a mechanism was also proposed for the addition of secondary amines to 2-nitrothiophene (eq. 5) [21].



While in most reactions, H^- also adds to the π -hydrocarbon in an *exo* fashion [20], there are some cases where the product contains H^- or D^- in both the *exo* and *endo* positions [22], e.g. the already-mentioned complex $(\text{CO})_3\text{Mn}(\eta^4\text{-thiophene} \cdot \text{D})$ [23], and sometimes the attacking H^-/D^- is found specifically in the *endo* position [24,25,26]. For these latter reactions an initial interaction of the H^- with the metal or a ligand, e.g. CO, is proposed. The stereospecificity of the reactions (eq. 3) leading to complexes **3aa** and **3ab** may be rationalized by a mechanism involving initial addition of H^-/D^- to the metal followed by transfer of the H^-/D^- to C2 of the thiophene to give an allylsulfide intermediate which undergoes S–C bond cleavage and rotation around C2–C3 in the same direction as in eq. 4 to give the product. This mechanism is similar to that suggested for the reaction of L_2ReH_3 ($\text{L} = \text{PPh}_3$) with furan (eq. 6) [27], where a H^- already bonded to the metal is stereospecifically transferred to the ligand with ring opening. While the *endo* H^- addition mechanism accounts for the stereochemistry of the product, it does not explain why H^- preferentially adds to the CH_3 -substituted carbon in complexes **1b**, **1d**–**1f**.



Another possible mechanism (eq. 7) is one which involves a radical intermediate resulting from the transfer of an electron from the aluminum hydride to the complex (e.g., **1b**); the radical could then add a hydrogen atom at the *endo* position. A similar radical $\text{CpFe}(\text{Me}_4\text{T})^\cdot$ has been identified in the related reaction [28] of



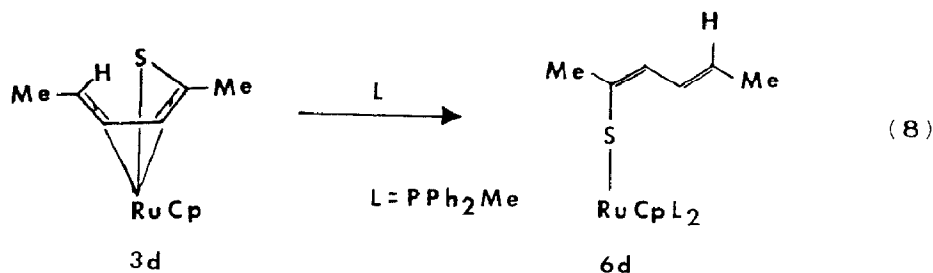
$\text{CpFe}(\text{Me}_4\text{T})^+$ with LiAlH_4 at -50°C . If the $\text{CpRu}(2\text{-MeT})^\cdot$ were to undergo C–S bond cleavage, it seems likely that a radical intermediate (eq. 7) with the electron at the CH_3 -substituted carbon rather than at the non-methylated carbon would form because of its greater stability. Reaction of this intermediate with a hydrogen atom

donor would give the product with the H on the methylated carbon, as observed. Attempts to identify the $\text{CpRu(T)}^\cdot$ radical by reaction of CpRu(T)^+ with LiAlH_4 in THF at -78°C showed no major color change as occurred in the analogous Fe complex reaction. Thus, there is no substantive evidence which favors either the endo H^- addition or the radical mechanism.

A ^1H NMR study shows that **3d** is also formed when **1d** is reacted with LiAlH_4 or $\text{Na}(\text{BEt}_3\text{H})$ as H^- sources instead of $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$. No reaction with NaBH_4 is observed. The reaction of complex **1d** with $[\text{HFe}(\text{CO})_4](\text{PPN})$ [29] caused the solution to turn immediately yellow, as with the other hydride sources, but after several minutes the color changed to red and no product could be isolated. No tractable products could be obtained from reactions of the 2-MeT complex **1b** with MeLi or MeMgBr .

In order to compare the reactivity of **1** with more electron-rich thiophene complexes, the compounds $\text{Cp}^*\text{Ru(Th)}^+$, with $\text{Th} = \text{T}$ or 2,5-Me₂T, were prepared. However, they only react with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ in the same way as the Cp complexes to form **5a** and **5d**. Because of the greater electron donating effect of Cp^* compared to Cp, all ^1H NMR signals (Table 2) are shifted upfield except that from H_{2z} , which will be discussed later.

Reactions of the butadiene thiolate complexes 3 with PR_3 and CO. Phosphines and CO slowly displace from the metal the butadiene part of the butadiene thiolate ligand in complexes **3a** and **3d** (eq. 8). Reactions with PPh_2Me were performed in a



sealed NMR-tube and were completed in four days. No side products or decomposition was observed. During the reaction there was no NMR evidence for an intermediate, such as $\text{CpRu}(\text{PPh}_2\text{Me})(\eta^3\text{-SC}(\text{Me})=\text{CHCH}=\text{CH}(\text{Me}))$. An X-ray study of **6d** yielded the structure shown in Fig. 1. It shows clearly that the butadiene portion of the ligand is displaced from the metal and exists in the energetically preferred transoid configuration. Bond distances and angles are given in Table 5. The four C atoms of the butadiene lie essentially in a plane, ± 0.05 Å from the least squares plane. The angle Ru-S-C5 is 111° , which shows that the S is sp^3 hybridized. The plane defined by S, P1 and P2 is within experimental error parallel to the Cp-ring, resulting in a piano stool type structure.

The products of the reaction of **3a** and **3d** with CO have comparable NMR spectra. Interestingly the mass spectra (20 eV) of **7a** and **7d** show intense peaks at $m/e = 85$ (SC_4H_5^+) and 113 ($\text{SC}_4\text{Me}_2\text{H}_3^+$), respectively, which represent the butadiene thiolate fragments. This suggests that this ligand is readily cleaved from the metal. Mass spectra of the phosphine complexes **6a** and **6d** show a large number of peaks in this region; therefore, it was impossible to assign the fragments of the butadiene thiolate.

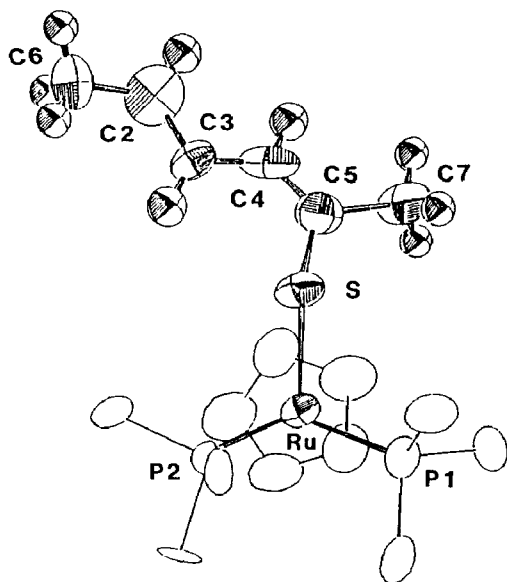
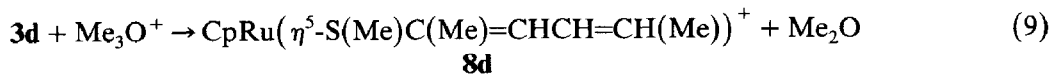


Fig. 1. An ORTEP-drawing of [CpRu(PPh₂Me)₂(η¹-SC(Me)=CHCH=CH(Me))] (6d).

Reactions of the butadiene thiolate complexes (3) with electrophiles. The coordinated S of 3a and 3d is alkylated with Me₃O⁺ to give the thioether complexes 8a and 8d (eq. 9). They were characterized by their ¹H, ¹³C NMR, and MS spectra, and elemental analysis for 8d. Peaks in the ¹H NMR spectra of 8 are shifted downfield



compared to those of the analogous complexes 3, as expected for a cationic complex. However, the H_{2z} protons were again shifted in the opposite direction, which will be discussed later. The SMe peak is not coupled to any other proton

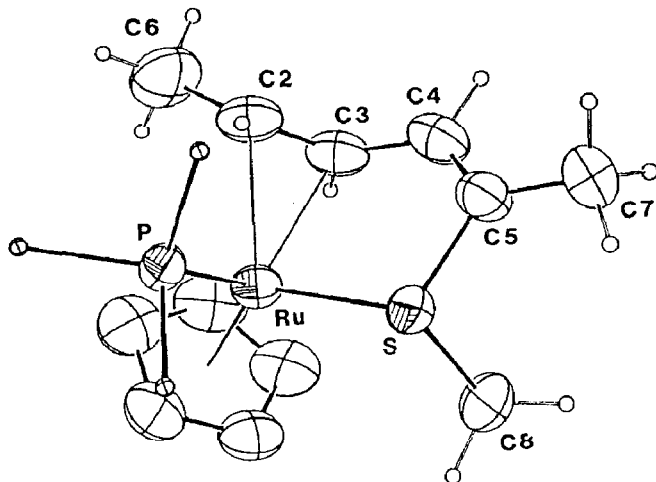


Fig. 2. An ORTEP-drawing of [CpRu(PPh₂Me)(η³-S(Me)C(Me)=CHCH=CH(Me))]BF₄ (9d).

Table 5

Relevant bond distances (Å) and angles (°) in $\text{CpRu}(\text{PPh}_2\text{Me})_2(\eta^1\text{-SC}(\text{Me})=\text{CHCH}=\text{CH}(\text{Me}))$ (**6d**) and $[\text{CpRu}(\text{PPh}_2\text{Me})(\eta^3\text{-S}(\text{Me})\text{C}(\text{Me})=\text{CHCH}=\text{CH}(\text{Me}))]\text{BF}_4$ (**9d**)

	6d	9d
Ru–S	2.44(6)	2.327(1)
Ru–P1	2.28(5)	2.331(1)
Ru–P2	2.28(5)	
Ru–C2		2.235(4)
Ru–C3		2.204(5)
Ru–C4		3.11
Ru–C5		3.27
Ru–C(Cp)	2.19–2.26(2)	2.208–2.228(6)
S–C5	1.80(2)	1.784(5)
S–C(8)		1.810(6)
C5–C4	1.27(3)	1.314(8)
C4–C3	1.51(3)	1.467(7)
C3–C2	1.31(3)	1.405(8)
C2–C6	1.45(4)	1.494(8)
C5–C7	1.46(3)	1.504(7)
P1–C20 (Ph)	1.85(2)	1.842(4)
P1–C26 (Ph)	1.87(2)	1.826(3)
P1–C32 (Me)	1.85(2)	1.819(5)
P2–C40 (Ph)	1.83(2)	
P2–C46 (Ph)	1.85(2)	
P2–C52 (Me)	1.86(2)	
within Cp	1.33–1.42(4)	1.382–1.431(10)
S–Ru–P1	92.6(2)	87.4(1)
S–Ru–P2	87.4(2)	
P1–Ru–P2	93.1(2)	
P1–Ru–C2		98.9(1)
Ru–S–C5	111.4(8)	104.5(2)
Ru–S–C8		129.5(2)
C5–S–C8		99.2(3)
S–C5–C4	122 (2)	114.7(4)
S–C5–C7	114 (2)	117.1(4)
C4–C5–C7	122 (2)	128.1(5)
C3–C4–C5	122 (2)	125.3(5)
C2–C3–C4	120 (2)	121.3(4)
C3–C2–C6	121 (2)	122.2(5)
Torsion angles		
C6–C2–C3–C4	176	142
C2–C3–C4–C5	170	81
C3–C4–C5–C7	180	170
C3–C4–C5–S	10	7

which indicates that it added to the S rather than to the butadiene portion of the ligand. Although **3d** reacts with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, the orange product was not fully characterized.

As with complexes **3**, we reacted **8a** and **8d** with PPh_2Me in order to displace the ligand. NMR spectra of the reaction mixtures showed that one phosphine adds

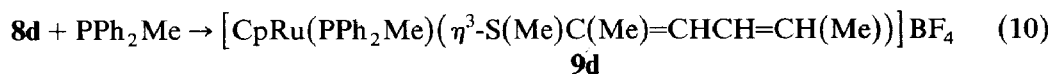
Table 6

Atom coordinates [$\times 10^4$] and average temperature factor [$\text{\AA}^2 \times 10^3$] for $\text{CpRu}(\text{PPh}_2\text{Me})_2(\eta^1\text{-S-C(Me)=CHCH=CH(Me)})$ (**6d**)

Atom ^a	x	y	z	U_{ave} ^b
Ru(1)	0.0(0)	810.0(8)	604.(1)	43.
S(1)	-693.(4)	-235.(3)	-194.(6)	59.
P(1)	-1269.(3)	1391.(3)	743.(6)	43.
P(2)	-135.(4)	341.(3)	2520.(6)	41.
C(2)	649.(16)	-2111.(14)	-1627.(25)	72.
C(3)	384.(13)	-1515.(10)	-1191.(20)	70.
C(4)	16.(24)	-972.(10)	-2047.(20)	74.
C(5)	-366.(16)	-412.(13)	-1749.(22)	70.
C(6)	955.(18)	-2660.(13)	-823.(24)	93.
C(7)	-690.(23)	74.(12)	-2669.(23)	124.
C(10)	1452.(12)	819.(13)	606.(24)	66.
C(11)	1170.(12)	687.(12)	-553.(25)	79.
C(12)	689.(14)	1261.(12)	-966.(23)	79.
C(13)	697.(13)	1737.(11)	-30.(24)	68.
C(14)	1179.(14)	1446.(12)	956.(23)	76.
C(20)	-1445.(12)	2055.(11)	-461.(19)	44.
C(26)	-1463.(13)	1937.(10)	2143.(19)	50.
C(32)	-2283.(11)	896.(11)	605.(22)	44.
C(40)	-1190.(14)	125.(11)	3156.(18)	49.
C(46)	478.(14)	-462.(10)	2821.(20)	31.
C(52)	365.(14)	882.(11)	3743.(17)	58.

^a Atom labels as shown in Fig. 1; C(10)–C(14) are Cp; C(20), C(26), C(40), C(46), C's of Ph bonded to P; C(32), C(52) PMe. ^b $U(\text{ave})$ is average of U_{11} , U_{22} , and U_{33} .

rapidly; however, further substitution proceeds much more slowly. Complex **9a** was not isolated but was characterized by its ^1H NMR spectrum (Table 2). Complex **9d**



was isolated as yellow crystals. A crystal structure analysis of **9d** (Fig. 2, Table 5) shows that the double bond C4–C5 is not coordinated to the metal. The phosphine is bonded to the metal on the open side of the butadiene thioether. The coordinated thioether atoms, C2, C3, and S, as well as the P atom, lie in one plane (± 0.17 Å), which is essentially parallel ($3.1 \pm 2^\circ$) to the plane of the Cp ring. The non-bonding distances from C4 and C5 to Ru are 3.11 and 3.27 Å, respectively. The butadienethiolate system which is essentially planar in **3d** and **6d** is grossly non-planar in **9d**. Thus the planes defined by C2,C3,C4 and C4,C5,S are nearly perpendicular (85°) to each other; this non-planarity may also be seen in the 81° C2–C3–C4–C5 torsion angle. In comparison to reaction 8 which yields directly the η^1 -coordinated complex **6d**, the formation of **9d** is surprising. The electron density in the C4–C5 double bond is probably reduced by the partly positively charged S such that it is less strongly coordinated to the Ru than the C2–C3 olefin. Olefins seem to be in general weaker donors than thioethers [30].

The distortion of the butadiene system in **9a** and **9d** is also evident from the ^1H NMR spectrum which shows no coupling between H3 and H4. Two sets of ^1H NMR signals are observed for H2z, the methyl group on the S and also for H5 in

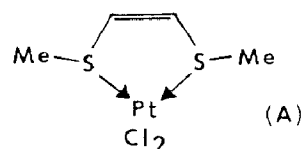
Table 7

Atom coordinates and isotropic thermal parameters ($\text{\AA}^2$) of $[\text{CpRu}(\text{PPh}_2\text{Me})(\eta^3\text{-S}(\text{Me})\text{C}(\text{Me})=\text{CH}-\text{CH}=\text{CH}(\text{Me}))\text{BF}_4$ (**9d**)

Atom ^a	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ^b
Ru(1)	0.24419(3)	0.75711(2)	0.31941(3)	3.186(9)
S(1)	0.3904(1)	0.62702(8)	0.2793(1)	3.47(2)
P(1)	0.2750(1)	0.78748(8)	0.1024(1)	3.02(2)
C(2)	0.0673(5)	0.6635(4)	0.1630(5)	4.5(1)
C(3)	0.1131(4)	0.6170(4)	0.2750(5)	4.3(1)
C(4)	0.1746(5)	0.5164(4)	0.2412(6)	4.8(1)
C(5)	0.2952(5)	0.5056(4)	0.2299(5)	4.3(1)
C(6)	-0.0545(5)	0.7191(6)	0.1568(8)	6.5(2)
C(7)	0.3593(6)	0.4049(4)	0.1743(8)	6.1(2)
C(8)	0.4866(6)	0.6270(5)	0.4584(6)	5.7(2)
C(10)	0.3656(5)	0.8659(4)	0.5318(5)	5.1(1)
C(11)	0.2683(6)	0.8119(5)	0.5657(5)	5.7(2)
C(12)	0.1486(6)	0.8425(5)	0.5015(6)	5.9(2)
C(13)	0.1714(6)	0.9117(5)	0.4227(6)	5.8(2)
C(14)	0.3084(5)	0.9262(4)	0.4449(6)	5.0(1)
C(20)	0.4411(4)	0.8280(3)	0.1042(4)	3.30(9)
C(26)	0.2363(4)	0.6791(3)	-0.0750(4)	3.33(9)
C(32)	0.1839(5)	0.8941(4)	0.0609(6)	4.7(1)

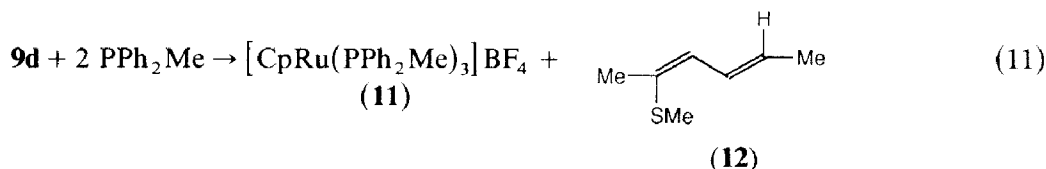
^a Atom labels in Fig. 2 and footnote *a* in Table 6. ^b *B* is defined as $(4/3)^{\star} [a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$.

9a. The relative intensities of these sets of peaks suggests the presence of 2 isomers in approximately equal concentration. These isomers probably result from the two possible positions (up or down in Fig. 2) of the Me group and the non-bonding lone pair of electrons on the coordinated sulfur; these isomers could in principle be interconverted by inversion at the sulfur. The SMe group also appears as two signals in the ^{13}C NMR spectrum of **9d**. The crystal used for the diffraction studies obviously contained only the isomer where the Me-group is directed downward. In most thioether complexes, the coalescence temperature (T_c) for inversion of coordinated SMe groups is below room temperature [31], but perhaps because of the constraint in the butadiene thiolate ligand, T_c is higher and therefore the two isomers are observed in the room temperature NMR spectrum. In complex **A** which



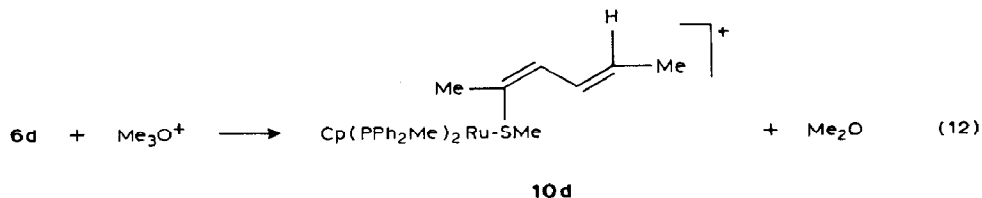
has similar bonding features to **9d**, T_c is 314 K and the signals are well separated at room temperature [32].

9a and **9d** react slowly with an excess of phosphine to give total displacement of the butadiene thioether to yield the complex $[\text{CpRu}(\text{PPh}_2\text{Me})_3]\text{BF}_4$ (**11**). No inter-



mediate with two coordinated phosphines could be observed when following the reaction by NMR. The thioether **12** was identified by its ^1H NMR spectrum in the reaction mixture, and it was distilled from complex **11** and observed separately by NMR. The coordination sphere around Ru in complex **11** is undoubtedly crowded because of the three bulky *cis*-PPh₂Me ligands. The complex $\text{CpRu}(\text{PPh}_3)_3^+$ could not be isolated, probably for steric reasons [33]. Comparable to **11** is the complex $\text{CpRu}[(\text{PPh}_2\text{CH}_2)_2\text{CR}]^+$ (R = Me, Et) with a tridentate ligand [34].

Reaction of the η^1 -butadienethiolate complex **6d** with $[\text{Me}_3\text{O}]\text{BF}_4$ yields the



η^1 -butadiene-methyl thioether complex **10d**. Compared to the chemical shifts in the ^1H NMR spectrum of the free ligand **12**, those for the S-coordinated butadiene thioether in **10d** are about 0.2 ppm downfield, as expected for a cationic complex.

Reaction of the butadienethiolate complex 3d with H₂. In order to determine if the butadiene thiolate ligand can be converted to hydrocarbon products as may occur in the HDS reaction, we treated **3d** with H₂ under pressure. Hardly any reaction occurred at 80°C; however, at 110°C and 34 atm H₂, **3d** reacted completely within 5 h. A GC-mass spectrum of the reaction solution showed that it contained n-hexane, which was formed from the dimethylbutadiene thiolate ligand. Integration of the mass spectrum showed that the n-hexane was formed quantitatively within experimental error ($\sim \pm 10\%$). The metal-containing product was soluble in all common organic solvents, even hexanes. The ^1H NMR spectrum of it showed several peaks in the region: 4.3–5.0 ppm. Mass spectra showed fragments for CpRu_2S_2 , $\text{Cp}_2\text{Ru}_2\text{S}_2$, $\text{Cp}_2\text{Ru}_3\text{S}_2$, $\text{Cp}_2\text{Ru}_3\text{S}_3$, $\text{Cp}_3\text{Ru}_3\text{S}_2$; all of these fragments



exhibited the theoretical isotope patterns expected for the Ru₂ and Ru₃ units. The spectra also showed an intense peak at $m/e = 591$; this peak could be assigned to $\text{Cp}_4\text{Ru}_2\text{S}_4$ but the isotope pattern appears to be more like that of a Ru₃-containing ion. $\text{Cp}_3\text{Ru}_3\text{S}_3$, which would complete the series of the Ru₃ fragments, has a mass of 596, but such a peak was not observed.

When the reaction of **3d** with H₂ was carried out at 200°C, n-hexane was again produced, but in addition a black semi-crystalline residue was formed, which was not soluble in any common organic solvent. An X-ray powder pattern of this residue showed weak lines, which did not correspond to either Ru or RuS₂. Addition of acid to it liberated H₂S. There was no odor of sulfur-containing compounds when the reaction vessel was opened, which indicates that the S remains bonded to the Ru.

^1H NMR spectra of the butadienethiolate complexes. As mentioned, the H2z protons of complexes **3**, **5** and **8** show surprising ^1H NMR shifts as compared with H2e, H3 and H4. These chemical shift data are given in Table 8 together with those for some other butadiene complexes. In **5a**, **3a**, and **8a**, the H2e, H3, and H4 protons shift to lower field with decreasing electron density in the complex; in contrast, H2z

Table 8

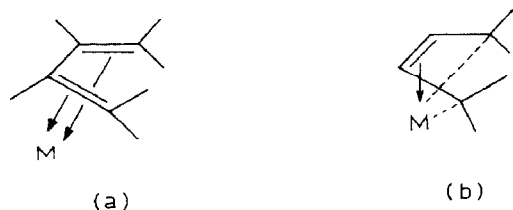
¹H NMR data for butadiene ^a complexes

	H2z	H2e	H3	H4	ref
5a	2.84	2.77	4.04	5.02	
3a	2.62	3.29	4.42	5.50	
8a	0.86	4.23	5.58	6.70	
Cp ⁺ Co(btd)	-0.10	1.33	4.40		35
CpCo(btd)	-0.23	1.82	5.01		36
btd	5.15	5.05	6.26		37

^a btd = butadiene.

moves upfield. The same trends are observed in a comparison of the analogous protons in Cp⁺Co(btd) and CpCo(btd), btd = butadiene.

For coordinated butadienes two formal bonding representations have been proposed [38]:



(a) with two more or less independent monoolefin-metal interactions; (b) with σ -bonds between the outer carbon atoms and the metal and an olefin-metal interaction with the inner C's. MO calculations suggest that electron-rich metal fragments favor formulation (b) [39]. Such a rehybridization of C2 could help to explain the chemical shifts of H2z. In the least electron-rich complex **8a**, C2 is more planar and H2z would be more in the plane of the butadiene and therefore closer to the metal which would cause an upfield shift. With increasing e^- -density in complexes **3a** and **5a**, C2 becomes more sp^3 hybridized; therefore H2z moves out of the plane and becomes less shielded by the metal. In the crystal structure of a (substituted-butadiene)Fe(CO)₃ complex, the C-H2z bond is at an angle of 30° above the btd-plane away from the metal [40].

Implications for the mechanism of thiophene hydrosulfurization. In earlier studies [9,10] we suggested that π -coordination of thiophene to an HDS catalyst surface would activate the thiophene to C-S bond cleavage upon reaction with a surface hydride. In model studies of CpRu(Th)⁺, butadienethiolate complexes resulted from reactions with hydride sources. The present studies suggest that the hydride addition (eq. 3) may occur in an *endo* fashion via a metal-hydride intermediate as may occur on a catalyst surface. These studies also suggest the butadienethiolate may be coordinated to a metal site (or sites) on the surface in an η^1 -, η^3 -, or η^5 -mode (as in compounds **3**, **6** and **9**). In addition, we have shown (eq. 13) that the butadienethiolate ligand is converted to n-hexane upon reaction with H₂ at 110 °C. Although the mechanism of this latter reaction is not clear, the formation of n-hexane indicates that the butadienethiolate ligand is capable of reacting with H₂ under conditions which are much milder than those used in HDS to form HDS products.

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Supplementary Material Available

Tables containing all atomic positions, displacement parameters and structure factors (7 pages for **6d**, 17 pages for **9d**) are available from R.J.A.

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