# Facile Nucleophilic Addition of Thioethers to $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)Br_2]CF_3SO_3$. X-ray Structure of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SEt_2)Br_2]CF_3SO_3$

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*Received February 24, 1997*[⊗]

*Summary:* $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)Br_2]^+$ (**1**) *reacts with 1 equiv of* $SR_2$ *(R = Et, i-Pr) at −20 °C in* $CH_2Cl_2$ *to afford the new dibromo-containing Ru(IV)* $\eta^3$*-allyl complexes* $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SR_2)Br_2]^+$ (**2**, **3**) *in good yields. Reaction of* **1** *with the cyclic thioether* $SC_4H_8$ *gave a mixture of the respective Ru(IV)* $\eta^3$*-allyl complex and the cationic complex* $[Ru(\eta^5\text{-}C_5Me_5)(SC_4H_8)_2Br_2]^+$ (**5**) *in a ratio of about 2:1.* **2** *(as the syn isomer) has been characterized by X-ray crystallography.*



## Introduction

Cationic $\eta^4$-diene complexes are considered to be among the substrates most receptive toward nucleophilic attack, this being favored at the terminal carbon atoms.[1] We have recently reported[2] that the diene fragment in the cationic Ru(IV) complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-diene})Br_2]^+$ (diene = butadiene, isoprene) is exceptionally susceptible to even very weak nucleophiles, such as $Cl^-$, $Br^-$, and $CF_3COO^-$, generating dibromo-containing functionalized Ru(IV) $\eta^3$-allyl complexes. Here, we report on the reactivity of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)Br_2]CF_3SO_3$ toward the thioethers $SR_2$ (R = Et, *i*-Pr) and tetrahydrothiophene ($SC_4H_8$). Included is the X-ray structure of one of the products, *viz.* $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SEt_2)Br_2]CF_3SO_3$. To our knowledge, this is the first report of a direct nucleophilic addition of thioethers onto a coordinated unsaturated hydrocarbon molecule.

## Results and Discussion

Treatment of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)Br_2]^+$ (**1**) (introduced as the $CF_3SO_3^-$ salt) with 1 equiv of $SEt_2$ at −20 °C in $CH_2Cl_2$ affords, on workup, the new dibromo-containing Ru(IV) $\eta^3$-allyl complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SEt_2)Br_2]^+$ (**2a**) in 76% isolated yield (Scheme 1). Nucleophilic attack of $SEt_2$ occurred regioselectively at the terminal carbon atom, apparently on the face of the *cisoid* $\eta^4$-diene group opposite to the metal center. Under these reaction conditions, the addition is kinetically controlled, resulting exclusively in the formation of the *anti* $\eta^3$-allyl isomer as drawn in Scheme 1. However, already at room temperature, slow isomerization to the thermodynamically favored *syn* product **2b** takes place.[3,4] Thus, when a solution of **2a** in $CH_2Cl_2$ was set aside for crystallization by vapor diffusion with diethyl ether, crystals of **2b** were obtained. Complexes **2** have been characterized by elemental analysis and $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy. The $^1H$ NMR spectra of **2a** shows the expected singlet resonance for the $C_5Me_5$ ring appearing at 1.25 ppm. The resonance of the central allyl proton appears as double double doublet centered at 4.89 ppm ($^3J_{34}$ = 6.4 Hz, $^3J_{23}$ = 6.4 Hz, $^3J_{13}$ = 10.2 Hz). The coupling constant of $^3J_{34}$ = 6.4 Hz places the $CH_2SEt_2$ substituent *anti* with respect to the allyl moiety. In the $^1H$ NMR spectrum of **2b**, the central allyl proton is found as a double double doublet centered at 5.21 ppm, but the larger coupling constant of $^3J_{34}$ = 8.5 Hz suggests that the $CH_2SEt_2$ moiety takes the *syn* configuration around the $C^3$−$C^4$ bond. The $^{13}C\{^1H\}$ NMR spectra of **2** contain no surprising features, with the resonance of the $sp^3$ carbon atom bearing the $SEt_2$ substituent observed in the range of 41.3−44.9 ppm. A structural view of **2b**, as determined by X-ray crystallography, is shown in Figure 1, with important bond distances and angles reported in the caption. The allyl ligand is bonded asymmetrically to the metal center with the Ru−C bonds to the unsubstituted terminal and central allyl carbon atoms (C11) and C(12) (2.195(5) and 2.150(4) Å, respectively) being distinctly shorter than the Ru−C bond to the third allyl carbon atom C(13) (2.260(4) Å). The Ru−Br(1) and Ru−Br(2) distances are nearly identical, being 2.563(1) and 2.566(1) Å, respectively. The C(14)−S(1) bond distance is 1.816(5) Å. The asymmetric bonding of the allyl moiety to the metal center is in good agreement with observations on other substituted $\eta^3$-allyl complexes.[3−6]

In a similar fashion to $SEt_2$, S-*i*-$Pr_2$ reacts with **1** to give the $\eta^3$-allyl complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCH\text{-}CH_2S\text{-}i\text{-}Pr_2)Br_2]^+$ (**3**) in 57% yield (Scheme 1). Under these reaction conditions, however, only the *syn* isomer **3b** could be obtained, as shown by the $^1H$ NMR spectroscopy. Indicative of this conformation is the *trans* coupling constant of $^3J_{34}$ = 8.5 Hz unequivocally placing the $CH_2S$-*i*-$Pr_2$ substituent *syn* with respect to the allyl moiety.

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⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

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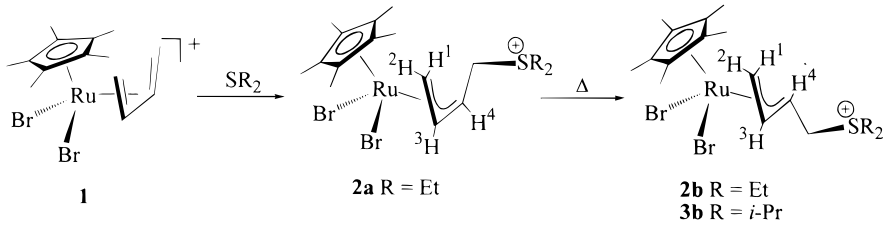
S0276-7333(97)00133-7 CCC: $14.00 

**Scheme 1**




In contrast to $SR_2$, with the cyclic thioether $SC_4H_8$, no clean reaction takes place and a mixture of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SC_4H_8)Br_2]CF_3SO_3$ as the *syn* isomer **4a** and $[Ru(\eta^5\text{-}C_5Me_5)(SC_4H_8)_2Br_2]^+$ (**5**) in a ratio of about 2:1 is obtained. The formation of **5**, i.e., attack of $SC_4H_8$ at the softer ruthenium center, may be explained by the higher $\pi$-donor strength of $SC_4H_8$ in comparison to the acyclic thioethers. Attempts to separate these complexes resulted in the complete decompostion of **4a** to several intractable materials, whereas **5** could be obtained in pure form, albeit in low yield. Thus, **4a** has been characaterized only by $^1$H NMR spectroscopy. Characterization of **5** was by elemental analysis and $^1$H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR spectra of **5** are very similar to the analogous chloro complex $[Ru(\eta^5\text{-}C_5Me_5)(SC_4H_8)_2Cl_2]^+$ reported previously,[7] and are, therefore, not further discussed.

## Experimental Section

**General Information.** All reactions were performed under an inert atmosphere of purified argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified and dried according to standard procedures and stored over 4 Å molecular sieves.[8] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CHCHCH_2)Br_2]CF_3SO_3$ (**1**) was prepared according to the literature.[2] $^1$H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalysis were done by Microanalytical Laboratories, University of Vienna.

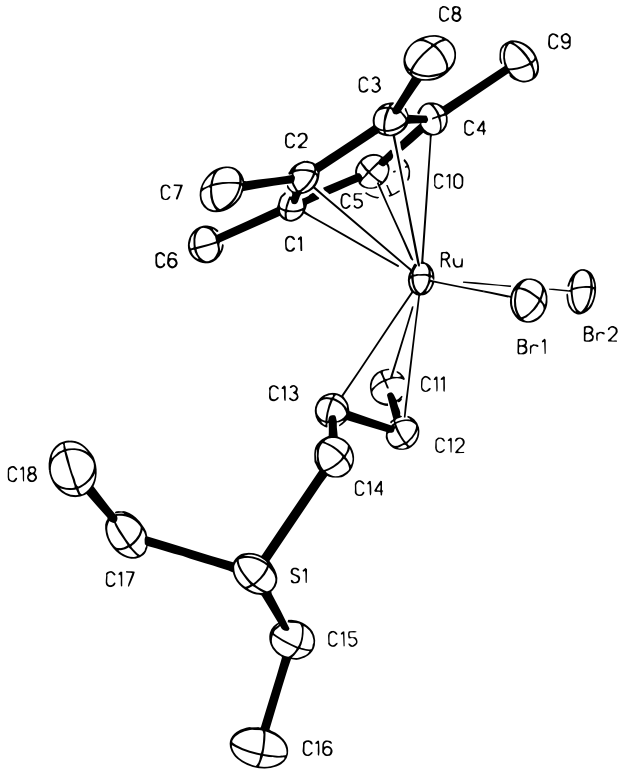



**Figure 1.** Structural view of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SEt_2)Br_2]CF_3SO_3$ (**2b**). Selected bond lengths (Å) and angles (deg): $Ru-C(1-5)_{av}$ 2.242(4), Ru−C(11) 2.195(5), Ru−C(12) 2.150(4), Ru−C(13) 2.260(4), Ru−Br(1) 2.563(1), Ru−Br(2) 2.566(1), C(11)−C(12) 1.390(7), C(12)−C(13) 1.418(6), S(1)−C(14) 1.816(5), Br(1)−Ru−Br(2) 84.1(1), C(11)−C(12)−C(13) 114.7(4).

**Synthesis. $[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SEt_2)Br_2]CF_3SO_3$. *anti*-Isomer 2a.** A solution of **1** (86 mg, 0.143 mmol) in $CH_2Cl_2$ (3 mL) was treated with $SEt_2$ (15 mL, 0.143 mmol) at −20 °C for 1 h. Then, the volume of the solvent was reduced to about 1 mL. On addition of diethyl ether, a red precipitate was obtained, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 75 mg (76%). Anal. Calcd for $C_{19}H_{31}Br_2F_3O_3RuS_2$: C, 33.10; H, 4.53. Found: C, 33.12; H, 4.56. $^1$H NMR ($\delta$, $CDCl_3$, 20 °C): 4.89 (ddd, 1H, $J$ = 10.2 Hz, $J$ = 6.4 Hz, $J$ = 6.4 Hz), 4.72−4.56 (m, 1H), 3.69 (d, 1H, $J$ = 6.1 Hz), 3.24 (dd, 1H, $J$ = 12.2 Hz, $J$ = 2.4 Hz), 3.06 (q, 4H, $J$ = 7.3 Hz), 2.62 (t, 2H, $J$ = 11.6 Hz), 1.25 (s, 15H), 0.96 (t, 6H, $J$ = 7.3 Hz). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 107.2 ($C_5Me_5$), 96.3, 64.6, 60.2, 41.3 ($CH_2SEt_2$), 34.4 ($SCH_2CH_3$), 33.6 ($SCH_2CH_3$), 11.0 ($C_5Me_5$), 9.9 ($SCH_2CH_3$).

***syn*-Isomer 2b.** A solution of **2a** in $CH_2Cl_2$ was set aside for crystallization by vapor diffusion with diethyl ether. After 1 day, dark-red crystals of **2b** were obtained. $^1$H NMR ($\delta$, $CDCl_3$, 20 °C): 5.29−5.18 (ddd, 1H, $J$ = 8.5 Hz, $J$ = 9.7 Hz, $J$ = 6.1 Hz), 4.43 (dd, 1H, $J$ = 10.4 Hz, $J$ = 14.0 Hz), 4.26 (d, $J$ = 6.1 Hz), 3.82−3.57 (m, 5H), 2.84 (dt, 1H, $J$ = 10.4 Hz, $J$ = 3.7 Hz), 2.45 (d, 1H, $J$ = 9.7 Hz), 1.76 (m, 15H), 1.57 (t, 6H, $J$ = 7.3 Hz). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 106.5 ($C_5Me_5$), 97.9, 66.0, 63.8, 44.9 ($CH_2SEt_2$), 34.8 ($SCH_2CH_3$), 34.1 ($SCH_2CH_3$), 10.5 ($C_5Me_5$), 9.7 ($SCH_2CH_3$).

**$[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2S\text{-}i\text{-}Pr_2)Br_2]CF_3SO_3$. *syn*-Isomer 3b.** This complex has been prepared analogously to **2**, with **1** and S-*i*-$Pr_2$ as the starting materials. Yield: 57%. Anal. Calcd for $C_{21}H_{35}Br_2F_3O_3RuS_2$: C, 35.15; H, 4.92. Found: C, 35.21; H, 4.88. $^1$H NMR ($\delta$, acetone-$d_6$, 20 °C): 5.29 (ddd, 1H, $J$ = 8.5 Hz, $J$ = 8.5 Hz, $J$ = 6.5 Hz), 4.59 (dd, 1H, $J$ = 14.6 Hz, $J$ = 8.5 Hz), 4.25 (m, 2H), 3.85 (dd, 1H, $J$ = 14.6 Hz, $J$ = 3.6 Hz), 3.00 (m, 2 H), 2.47 (d, 1H, $J$ = 8.5 Hz), 1.79 (s, 15H), 1.20 (d, 12H, $J$ = 6.1 Hz). $^{13}C\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 107.6 ($C_5Me_5$), 95.6, 65.7, 60.3, 46.1 ($CH_2S$), 34.0 ($SCH$), 11.5 ($SCHMe_2$), 11.4 ($C_5Me_5$).

**$[Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHCH_2SC_4H_8)Br_2]CF_3SO_3$ (4a) and $[Ru(\eta^5\text{-}C_5Me_5)(SC_4H_8)_2Br_2]CF_3SO_3$ (5).** Following the protocol above, treatment of **1** (86 mg, 0.143 mmol) and tetrahydrothiopene (12.6 mL, 0.143 mmol) led to a mixture of **4a** and **5** in a ratio of about 2:1. Overall yield: 64 mg. Attempts to separate these complexes by recrystallization from $CH_2Cl_2$ resulted in the complete decomposition of **4**. **5** was obtained in analytically pure form as a dark-red solid in 20% yield. Anal. Calcd for $C_{19}H_{31}Br_2F_3O_3RuS_3$: C, 31.63; H, 4.33. Found: C, 31.65; H, 4.31. **4a**: $^1$H NMR ($\delta$, $CDCl_3$, 20 °C) 5.47

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**Table 1. Crystallographic Data for [Ru($\eta^5$-$C_5Me_5$)($\eta^3$-$CH_2CHCHCH_2SEt_2$)$Br_2$]$CF_3SO_3$ (2b)[a]**

| | | | |
|---|---|---|---|
| formula | $C_{19}H_{31}F_3O_3Br_2RuS_2$ | $\theta_{max}$, deg | 25 |
| fw | 698.45 | index ranges | $-18 \le h \le 18$ |
| cryst size, mm | 0.36 × 0.36 × 0.16 | | $0 \le k \le 11$ |
| space group | $P2_1/n$ | | $0 \le l \le 32$ |
| $a$, Å | 13.147(2) | no. of rflns measd | 18350 |
| $b$, Å | 8.462(1) | no. of unique rflns | 4528 |
| $c$, Å | 23.401(4) | no. of rflns $F > 4\sigma(F)$ | 4025 |
| $\beta$, deg | 91.57(2) | no. of params | 281 |
| $V$, Å$^3$ | 2602.4(7) | $R(F)$ ($F > 4\sigma(F)$) | 0.035 |
| $F$(000) | 1368 | $R(F)$ (all data) | 0.042 |
| $Z$ | 4 | $wR(F^2)$ (all data) | 0.084 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.760 | diff Fourier peaks min/max, eÅ$^{-3}$ | −0.41/0.47 |
| $T$, K | 297 | | |
| $\mu$, mm$^{-1}$ (Mo K$\alpha$) | 3.872 | | |
| abs corr | empirical | | |

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

(ddd, 1H, $J$ = 9.6 Hz, $J$ = 6.1 Hz, $J$ = 6.1 Hz), 5.07 (m, 2H), 4.36 (d, 1H, $J$ = 6.1 Hz), 4.31 (m, 1H), 3.65 (m, 5H), 3.09 (d, 1H, $J$ = 9.6 Hz), 1.82 (s, 15H), 1.76 (m, 4H). **5**: $^1$H NMR ($\delta$, $CDCl_3$, 20 °C) 3.10 (t, 8H, $J$ = 6.1 Hz), 2.15 (t, 8H, $J$ = 6.1 Hz), 1.65 (s, 15H). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 112.0 ($C_5Me_5$), 41.5, 30.6, 10.7 ($C_5Me_5$).

**X-ray Structure Determination for [Ru($\eta^5$-$C_5Me_5$)($\eta^3$-$CH_2CHCHCH_2SEt_2$)$Br_2$]$CF_3SO_3$ (2b).** Crystal data and experimental details are given in Table 1. X-ray data have been collected with a Siemens Smart CCD area detector diffractometer using graphite-monochromated Mo K$\alpha$ radiation, a nominal crystal-to-detector distance of 3.88 cm, and 0.3° $\omega$-scan frames. Corrections for Lorentz and polarization effects, crystal decay, and absorption were applied. The structure was solved with direct methods.[9] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[10] The structure was refined against $F^2$.

**Acknowledgment.** J.-Y.S. thanks the Fonds zur Förderung der wissenschaftlichen Forschung for a Lise-Meitner Postdoctoral Research Fellowship (Project No. M00311-CHE).

**Supporting Information Available:** Tables of hydrogen atomic coordinates, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complex **2b** (7 pages). Ordering information is given on any current masthead page.

OM9701332

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# *Additions and Corrections*

1997, Volume 16

**David A. Brown,* John C. Burns, Cordula Mock-Knoblauch, and William K. Glass:** Cyclodimerization of the Tropylium Ring by Reduction of [($\eta^7$-$C_7H_7$)Mo(CO)$_3$]$^+$ To Give [{Mo(CO)$_3$}$_2$($\mu$-$\eta^5$:$\eta^5$-$C_7H_7$-$C_7H_7$)][PPN]$_2$.

Page 139. Reference 16 in the above paper was cited incorrectly and should be replaced by *Chem. Eur. J.* **1996**, *2*, 98. The authors in this reference remain the same.

OM970295Y