Coordination and Rearrangement of Organic Chalcogenides on a Rhodium−Rhodium Bond: Reactions with Strained-Ring Cyclic Thioethers and with Selenium and Tellurium Ligands

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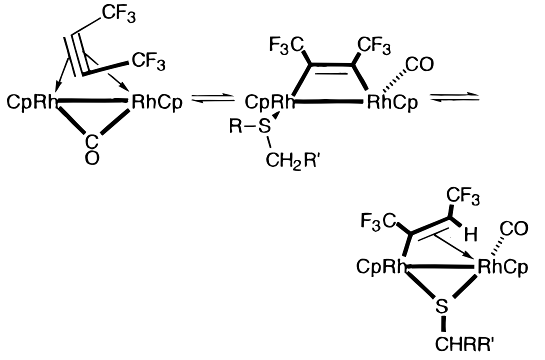
When the cyclic thioethers L = $SCH_2CH_2CH_2$, $SCH(Me)CH_2$, and $SCH_2CH_2CH_2CH_2$ were added to [(η^5-C_5H_5)$_2$$Rh_2$($\mu$-CO)($\mu$-$\eta^2$:$\eta^2$-$CF_3C_2CF_3$)] (**1**), the coordinative addition products [(η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)L] (**2a**−**c**) were formed reversibly. When it is left in solution in the presence of excess ligand, the propylene sulfide complex **2b** (L = $SCH(Me)CH_2$) transforms to the bridging sulfido complex [(η^5-C_5H_5)$_2$$Rh_2${$\mu$-$\eta^1$:$\eta^1$:$\eta^2$-C(O)C($CF_3$)C($CF_3$)}($\mu$-S)] (**3a**). A similar reaction occurred, but to a lesser extent, with the trimethylene sulfide complex **2a** (L = $SCH_2CH_2CH_2$). Comparable decompositions do not occur with the tetrahydrothiophene complex **2a** (L = $SCH_2CH_2CH_2CH_2$). The dimethylselenane complex [(η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($SeMe_2$)] (**4a**) was formed reversibly when $SeMe_2$ was added to solutions of **1**. The reactions of **1** with the organotelluranes L′ = $TeMe_2$ and $TeEt_2$ gave solid addition products [(η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)L′] (**4b**,**c**), which remained intact when dissolved in polar solvents. No rearrangement products were formed when solutions of the tellurane addition products were kept for several days. The bridging sulfido complex **3a** and the analogous complexes [(η^5-C_5H_5)$_2$$Rh_2${$\mu$-$\eta^1$:$\eta^1$:$\eta^2$-C(O)C($CF_3$)C($CF_3$)}($\mu$-E)] (**3b**, E = Se; **3c**, E = Te) were obtained from the direct reaction between E and the complex **1**. Addition of the cyclic tellurane $TeCH_2CH_2CH_2CH_2$ to **1** gave [(η^5-C_5H_5)$_2$$Rh_2$(CO)($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)($TeCH_2CH_2CH_2CH_2$)] (**6**), which underwent rapid intramolecular ligand scrambling in solution. The crystal and molecular structure of **6** was determined by X-ray crystallography.

Introduction

In a previous paper,[1] reactions between [(η^5-C_5H_5)$_2$-Rh_2(μ-CO)(μ-η^2:η^2-$CF_3C_2CF_3$)] (**1**) and several dialkylsulfanes SRR′ were described. In general, the sulfanes added coordinatively to **1** to form [(η^5-C_5H_5)$_2$$Rh_2$(CO)-($\mu$-$\eta^1$:$\eta^1$-$CF_3C_2CF_3$)(SRR′)], but all reactions were reversible. There is an indication that increasing bulkiness of the substituents R and R′ leads to decreased stability of the adduct. When the adducts formed from SMe_2 and SEt_2 were left in solution in the presence of excess ligand, interesting transformations occurred (Scheme 1). However, the rearrangement products were not formed for adducts with other dialkylsulfanes. To further explore these interesting substituent effects, additional reactions with some cyclic thioethers have been investigated, and the results are described here. We have also considered the influence of the donor atom by extending the study to some related selenium and tellurium ligands.

Scheme 1. Rearrangement of Organosulfane Addition Products



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[1] Devery, M. P.; Dickson, R. S.; Fallon, G. D.; Skelton, B. W.; White, A. M. *J. Organomet. Chem.* **1998**, *551*, 195.

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Experimental Section

The general and instrumental procedures have been described in a previous paper.[1] The complex $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}CF_3C_2CF_3)]$ **(1)** was prepared as described in the literature.[2] The cyclic thioethers and dimethylselenane were obtained from Sigma-Aldrich and were used as obtained. The dialkyltellurane ligands were prepared according to literature methods.[3,4] The ligand $TeCH_2CH_2CH_2CH_2$ was freshly prepared from $C_4H_8TeI_2$ and $NaBH_4$ in boiling methanol.[5]

Reactions of $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}CF_3C_2CF_3)]$ (1) with Cyclic Thioethers. $SCH_2CH_2CH_2$ (Trimethylene Sulfide). A large excess of trimethylene sulfide (0.22 g, 3.0 mmol) was added to a stirred solution of **1** (0.020 g, 0.038 mmol) in pentane (20 mL). A red solid precipitated out of solution and was collected by filtration and washed with pentane. The compound could not be purified by recrystallization or chromatography because it was unstable in solution, but it was identified spectroscopically as the addition product $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(SCH_2CH_2CH_2)]$ (**2a**) (0.019 g, 83%). IR (Nujol): ν(CO) at 1992 s cm^{-1}. A color change from red to green coupled with NMR data indicated that the isolated product reverted back to **1** upon dissolution. However, spectroscopic results were obtained for a solution containing excess ligand. ^{1}H NMR in $CDCl_3$: δ 5.35 (s, 5H, C_5H_5), 5.27 (s, 5H, C_5H_5) (the resonances for the coordinated ligand were obscured by those for the free ligand, which was present in excess). ^{19}F NMR in $CDCl_3$: two quartets (J(F−F) = 11.6 Hz) of equal intensity at δ −53.9 and −54.8. No further reaction was detected by NMR spectroscopy when a solution containing **2a** and excess ligand in $CDCl_3$ was left to stand for 7 days. When TLC of this solution was attempted with a 1:1 mixture of hexane and dichloromethane as eluent, a crimson band was separated from a green band containing **1** (65%). Extraction of the crimson band with dichloromethane and evaporation of solvent gave crimson crystals of $[(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C(CF_3)C(CF_3)\}(\mu\text{-}S)]$ (**3a**): 30% yield; mp 252 °C dec. Anal. Calcd for $C_{15}H_{10}F_6ORh_2S$: C, 32.2; H, 1.8; F, 20.4; S, 5.7. Found: C, 32.6; H, 2.0; F, 20.3; S, 5.5. IR (CH_2Cl_2): ν(CO) and ν(C=C) at 1707 s, 1683 s cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.65 (d, 5H, J(Rh−H) = 0.9 Hz, C_5H_5), 5.44 (s, 5H, C_5H_5). ^{19}F NMR in $CDCl_3$: two quartets (J(F−F) = 12 Hz) of equal intensity at δ −58.0 and −46.6. MS: *m/z* (relative intensity, assignment) 558 (26, [M]$^+$), 530 (64, [M − CO]$^+$), 368 (50, $[C_{10}H_{10}RhS]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

$SCH_2(CH_3)CH_2$ (Propylene Sulfide). In an NMR tube, propylene sulfide was added dropwise to a solution of **1** (0.010 g) in $CDCl_3$ until the color of the solution remained red. The NMR results indicated the presence of equal amounts of two isomers of the addition product $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(SCH_2(Me)CH_2)]$ (**2b**). ^{1}H NMR in $CDCl_3$: δ 5.15 (s, 5H, C_5H_5), 5.18 (s, 5H, C_5H_5), 5.48 (s, 5H, C_5H_5), and 5.50 (s, 5H, C_5H_5) (the resonances for the coordinated ligand were obscured by those for the free ligand, which was present in excess). ^{19}F NMR in $CDCl_3$: two quartets (J(F−F) = 11.6 Hz) of equal intensity at δ −53.4 and −54.9. The IR spectrum of a sample of **2b** in $CDCl_3$ was recorded: ν(CO) at 1981 s cm^{-1}.

TLC of a fresh solution of **2b** with a 1:1 mixture of hexane and dichloromethane as eluent separated the green complex **1** (major product) from the crimson product **3a** (trace quantity). Another solution of **2b** in dichloromethane was stirred at room temperature for 3 days. Subsequent TLC yielded predominantly the crimson product **3a**, which was identified from NMR spectroscopic data.

$SCH_2CH_2CH_2CH_2$ (Tetrahydrothiophene). In a similar manner, formation of the addition product $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(SCH_2CH_2CH_2CH_2)]$ (**2c**) was observed when **1** (0.010 g) and excess ligand were mixed in an NMR tube. ^{1}H NMR in $CDCl_3$: δ 5.19 (s, 5H, C_5H_5), 5.45 (s, 5H, C_5H_5) (the resonances for coordinated ligand were obscured by those for the free ligand, which was present in excess). ^{19}F NMR in $CDCl_3$: two quartets (J(F−F) = 11.6 Hz) of equal intensity at δ −53.0 and −54.9. Incomplete conversion was evident, with the ratio **1**:**2c** being 2:1. IR ($CDCl_3$): ν(CO) at 1978 s cm^{-1}. No further reaction was observed over a 7 day period.

Reaction of $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}CF_3C_2CF_3)]$ (1) with $SeMe_2$. In an NMR tube, an excess of dimethylselenane was added to a stirred solution of **1** in $CDCl_3$. The color of the solution changed from green to red. Spectroscopic data indicated that the addition product $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(SeMe_2)]$ (**4a**) had formed, but some unchanged **1** was still present; the ratio of **1** to **4a** was 1:4. ^{1}H NMR in $CDCl_3$: δ 5.41 (s, 5H, C_5H_5), 5.19 (s, 5H, C_5H_5) (the resonances for coordinated $SeMe_2$ were obscured by those for the 7-fold excess of free ligand). ^{19}F NMR in $CDCl_3$: δ −53.1 (qd, 3F, ^5J(F−F) = 11.7 Hz, ^3J(F−Rh) = 2.8 Hz, CF_3), −54.9 (qd, 3F, ^5J(F−F) = 11.7 Hz, ^3J(F−Rh) = 3.3 Hz, CF_3). IR ($CDCl_3$): ν(CO) at 1996 cm^{-1}.

Reactions of $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}CF_3C_2CF_3)]$ (1) with Dialkyltelluranes. $TeMe_2$. An excess of dimethyltellurane (0.5 mL, 6.8 mmol) was added to a stirred solution of **1** (0.084 g, 0.16 mmol) in dichloromethane (10 mL). The color of the solution changed immediately from green to dark red. The reaction solution was stirred for 30 min, and all volatiles were then removed, leaving an orange solid. This was redissolved in dichloromethane. TLC of the solution with a 1:1 mixture of hexane and dichloromethane as eluent separated one orange band from minor impurities. Extraction of the orange band with dichloromethane and evaporation of solvent gave an orange solid, which was identified as the addition product $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(TeMe_2)]$ (**4b**; 0.11 g, 100%). Anal. Calcd for $C_{17}H_{16}F_6ORh_2Te$: C, 29.9; H, 2.4; F, 16.7. Found: C, 30.2; H, 2.1; F, 16.8. IR ($CHCl_3$): ν(CO) at 1990 s cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.40 (s, 5H, C_5H_5), 5.21 (s, 5H, C_5H_5), 2.01 (d with ^{125}Te satellites, J(Rh−H) = 96 Hz and J(Te−H) = 22.5 Hz), 6H, 2 × CH_3). ^{19}F NMR in $CDCl_3$: δ −53.9 (qd, 3F, ^5J(F−F) = 11.6 Hz, ^3J(F−Rh) = 2.7 Hz, CF_3), −54.6 (qd, 3F, ^5J(F−F) = 11.6 Hz, ^3J(F−Rh) = 3.3 Hz, CF_3). MS: *m/z* (relative intensity, assignment) 526 (12, [M − $TeMe_2$]$^+$), 233 (100, $[C_{10}H_{10}Rh]^+$), 160 (5, $[TeMe_2]^+$).

A solution of **4b** in toluene was heated to 70 °C for 2 h; NMR monitoring indicated that no reaction occurred except for partial ligand dissociation, resulting in the formation of some **1**.

$TeEt_2$. The complex $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(TeEt_2)]$ (**4c**) was formed in a similar manner and isolated as an orange solid (100% yield). Anal. Calcd for $C_{19}H_{20}F_6ORh_2Te$: C, 32.1; H, 2.8; F, 16.0. Found: C, 32.3; H, 2.7; F, 16.0. IR ($CHCl_3$): ν(CO) at 1990 cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.42 (s, 5H, C_5H_5), 5.22 (s, 5H, C_5H_5), 2.64 (d of m, 4H, J(Rh−H) = 90 Hz, 2 × CH_2), 1.55 (d of t, 6H, ^3J(H−H) = 7.8 Hz and J(Rh−H) = 45 Hz, 2 × CH_3). ^{19}F NMR in $CDCl_3$: δ −53.6 (qd, 3F, ^5J(F−F) = 11.8 Hz, ^3J(F−Rh) = 2.8 Hz, CF_3), −54.8 (qd, 3F, ^5J(F−F) = 11.8 Hz, ^3J(F−Rh) = 3.4 Hz, CF_3). ^{125}Te NMR in $CDCl_3$: δ 594 (d, ^1J(Te−Rh) = 110 Hz). MS: *m/z* (relative intensity, assignment) 526 (10, [M − $TeEt_2$]$^+$), 233 (100, $[C_{10}H_{10}Rh]^+$), 188 (5, $[TeEt_2]^+$).

Reactions of $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}CF_3C_2CF_3)]$ (1) with Elemental Chalcogens. Sulfur. An excess of sulfur powder (0.53 g, 16.5 mmol) was added in portions to a stirred solution of **1** (0.050 g, 0.095 mmol) in dichloromethane (20 mL). The color of the solution changed over 10 min from green to

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(2) Dickson, R. S.; Johnson, S. H.; Pain, G. N. *Organomet. Synth.* **1988**, *4*, 283.

(3) Tshugaeff, L.; Choplin, W. *Chem. Ber.* **1914**, *47*, 1269.

(4) Petragnani, N. *Tellurium in Organic Synthesis*; Academic Press: London, 1994.

(5) Al-Rubaie, A. Z.; Alshirayda, H. A. Y. *J. Organomet. Chem.* **1985**, *287*, 321.

red. The reaction solution was stirred for 4 h, and all volatiles were then removed under vacuum. The residue was redissolved in dichloromethane. TLC of the solution with a 1:1 mixture of hexane and dichloromethane as eluent separated two major bands from minor impurities. Extraction of a yellow band (R_f 0.9) with dichloromethane and evaporation of solvent gave $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]$ (0.017 g, 32%), which was identified from NMR data.[2] A red band (R_f 0.3) was extracted with dichloromethane; evaporation of solvent gave a red crystalline solid which was identified as $[(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C(CF_3)C(CF_3)\}(\mu\text{-}S)]$ (**3a**; 0.029 g, 55%). The spectroscopic data for this product were identical with those reported earlier for **,** isolated following chromatography of **2a**.

Selenium. An excess of selenium powder (1.28 g, 16.2 mmol) was added in portions to a stirred solution of **1** (0.110 g, 0.209 mmol) in dichloromethane (40 mL). There was no initial change in the color of the solution. Stirring was continued for 3 days, during which time the color of the solution gradually turned red. All volatiles were then removed under vacuum. The residue was redissolved in dichloromethane. TLC of a solution of the residue in dichloromethane with dichloromethane as eluent separated three major bands from minor impurities. Extraction of a yellow band (R_f 1.0) with dichloromethane and evaporation of solvent gave $[(\eta^5\text{-}C_5H_5)_2\text{-}Rh_2(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]$ (0.024 g, 21%), which was identified from NMR data.[2] A red band (R_f 0.7) was extracted with dichloromethane; evaporation of solvent gave a red solid which was identified as $[(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C(CF_3)C(CF_3)\}\text{-}(\mu\text{-}Se)]$ (**3b**; 0.035 g, 28%) mp 157 °C. Anal. Calcd for $C_{15}H_{10}F_6ORh_2Se$: C, 29.8; H, 1.7. Found: C, 29.6; H, 1.7. IR ($CHCl_3$): ν(CO) at 1712 s, 1685 s cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.62 (s, 5H, C_5H_5), 5.43 (s, 5H, C_5H_5). ^{19}F NMR in $CDCl_3$: δ −45.3 (q, 3F, ^5J(F−F) = 14.2 Hz, CF_3), −58.1 (q, 3F, ^5J(F−F) = 13.7 Hz, CF_3). MS: *m/z* (relative intensity, assignment) 606 (1, $[M]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). A brown band (R_f 0.7) was extracted with dichloromethane; evaporation of solvent gave a brown solid which was identified as an isomer of **3b**. It was characterized spectroscopically as $[(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C(CF_3)C(CF_3)\}(\mu\text{-}Se)]$ (**5**; 0.052 g, 41%). IR ($CHCl_3$): ν(CO) at 1710 s, 1617 s cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.72 (s, 5H, C_5H_5), 5.36 (s, 5H, C_5H_5). ^{19}F NMR in $CDCl_3$: δ −49.4 (q, 3F, ^5J(F−F) = 10.3 Hz, CF_3), −58.4 (q, 3F, ^5J(F−F) = 10.3 Hz, CF_3). MS: *m/z* (relative intensity, assignment) 606 (1, $[M]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). When left in solution, **5** slowly converted to another brown species with different spectroscopic properties. IR ($CHCl_3$): ν(CO) at 1711 s cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.71 (s, 5H, C_5H_5), 5.18 (s, 5H, C_5H_5). ^{19}F NMR in $CDCl_3$: δ −53.7 (q, 3F, ^5J(F−F) = 7.7 Hz, CF_3), −60.3 (q, 3F, ^5J(F−F) = 7.7 Hz, CF_3). MS: *m/z* (relative intensity, assignment) 578 (20, $[C_{14}H_{10}F_6Rh_2Se]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). No formula can be assigned to this product.

Tellurium. An excess of freshly powdered tellurium (0.62 g, 4.86 mmol) was added in portions to a stirred solution of **1** (0.046 g, 0.087 mmol) in chloroform (20 mL). There was no initial change in the color of the solution. Stirring was continued for 7 days, during which time the color of the solution slowly changed to red. All volatiles were then removed under vacuum. The residue was extracted with dichloromethane. TLC of the solution obtained with a 1:1 mixture of hexane and dichloromethane as eluent separated three major bands from minor impurities. A green band (R_f 0.95) was extracted with dichloromethane, and evaporation of solvent produced a green solid which was identified (NMR spectra) as unchanged **1** (0.016 g, 35%). Extraction of a yellow band (R_f 0.9) with dichloromethane and evaporation of solvent gave $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]$ (0.005 g, 10%) which was identified from NMR data. A red band (R_f 0.3) was extracted with dichloromethane; evaporation of solvent gave a red solid which was identified as $[(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C(CF_3)C(CF_3)\}(\mu\text{-}Te)]$ (**3c**; 0.020 g, 35%), mp 160 °C. IR ($CHCl_3$): ν(CO) at 1726 s, 1692 s cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 5.61 (s, 5H, C_5H_5), 5.46 (s, 5H, C_5H_5). ^{19}F NMR in $CDCl_3$: δ −43.7 (q, 3F, ^5J(F−F) = 14.8 Hz, CF_3), −58.1 (q, 3F, ^5J(F−F) = 14.8 Hz, CF_3). MS: *m/z* (relative intensity, assignment) 656 (10, $[M]^+$), 466 (4, $[C_{10}H_{10}Rh_2Te]^+$), 401 (5, $[C_5H_5Rh_2Te]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

Table 1. Summary of Crystal Structure Data for the Complex $[(\eta^5\text{-}C_5H_5)_2Rh_2((CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(TeCH_2CH_2CH_2CH_2)$ (6)

mol formula	$C_{19}H_{18}F_6ORh_2Te$
mol wt	709.8
cryst dimens (mm^3)	0.62 × 0.22 × 0.20
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
lattice params	
a (Å)	8.898(4)
b (Å)	16.350(2)
c (Å)	15.859(11)
β (deg)	115.03(5)
V (Å^3)	2091(2)
Z	4
D_{calcd} (g cm^{-3})	2.25_4
F_{000}	1344
μ(Mo Kα) (cm^{-1})	30.1
$A^*_{min, max}$	1.50, 1.99
λ(Mo Kα) (Å)	$0.710\ 7_3$
N, N_o	6079, 4381
R, R_w	0.054, 0.065
T (K)	ca. 295
diffractometer	Enraf-Nonius CAD-4

Reaction of $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}CF_3C_2CF_3)]$ (1) with $TeCH_2CH_2CH_2CH_2$. A slight excess of $TeCH_2CH_2\text{-}CH_2CH_2$ was added to a green solution of **1** (0.062 g, 0.118 mmol) in dichloromethane (10 mL). There was an immediate color change to orange. The reaction solution was filtered through a 1 cm plug of silica, and solvent was removed from the filtrate by evaporation under reduced pressure. The residue was washed several times with pentane to remove excess ligand, and the remaining solid was recrystallized from dichloromethane by cooling at −4 °C. This gave orange crystals of $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(TeCH_2CH_2CH_2CH_2)]$ (**6**; 0.077 g, 100%). Anal. Calcd for $C_{19}H_{18}F_6ORh_2Te$: C, 32.2; H, 2.6; F, 16.1. Found: C, 32.2; H, 2.3; F, 15.9. IR ($CHCl_3$): ν(CO) at 1990 s cm^{-1}. ^{1}H NMR in $CDCl_3$ (−28 °C): δ 5.40 (s, 5H, C_5H_5), 5.17 (s, 5H, C_5H_5), 3.5−2.6 (m, 4H, CH_2), 2.5−1.8 (m, 4H, CH_2). ^{19}F NMR in $CDCl_3$ (245 K): δ −53.8 (qd, 3F, ^5J(F−F) = 11.2 Hz, ^3J(F−Rh) = 2.7 Hz, CF_3), −54.3 (qd, 3F, ^5J(F−F) = 11.2 Hz, ^3J(F−Rh) = 3.2 Hz, CF_3). ^{125}Te NMR in C_6D_6: δ 552 (d, ^1J(Te−Rh) = 86 Hz). MS: *m/z* (relative intensity, assignment) 526 (20, $[M - (CH_2)_4Te]^+$), 498 (5, $[M - CO - (CH_2)_4Te]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$), 186 (15, $[(CH_2)_4\text{-}Te]^+$).

Structure Determination. A unique room-temperature four-circle diffractometer data set was measured ($2\theta/\theta$ scan mode, $2\theta_{max} = 60°$; monochromatic radiation) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were also refined. Conventional R and R_w values on $|F|$ are quoted (statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$). Neutral atom complex scattering factors were employed, with computation using the XTAL 3.2 program system.[6] Pertinent results are given in Figure 2 and Tables 1 and 2.

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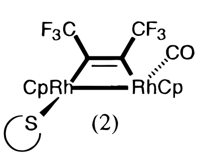
[6] Hall, S. R., Flack, H. D., Stewart, J. M., Eds. *The XTAL 3.2 User's Manual*; Universities of Western Australia, Geneva, and Maryland, 1992.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Bond Distances			
Rh(1)−Rh(2)	2.708(1)	Te−C(02)	2.155(9)
Rh(1)−Te	2.540(2)	Te−C(05)	2.14(1)
Rh(1)−C(1)	2.007(9)	C−O	1.16(1)
Rh(2)−C	1.82(1)	C(02)−C(03)	1.45(2)
Rh(2)−C(2)	2.02(1)	C(03)−C(04)	1.40(2)
		C(04)−C(05)	1.53(2)
Bond Angles			
Rh(2)−Rh(1)−Te	88.63(5)	Rh(2)−Rh(1)−C(1)	70.7(3)
Te−Rh(1)−C(1)	82.5(3)	Rh(1)−Rh(2)−C	83.0(3)
Rh(1)−Rh(2)−C(2)	69.7(2)	C−Rh(2)−C(2)	84.6(4)
Rh(1)−Te−C(02)	105.8(3)	Rh(1)−Te−C(05)	110.0(2)
C(02)−Te−C(05)	84.0(5)	Rh(2)−C−O	175.0(8)
Te−C(02)−C(03)	106.4(8)	C(02)−C(03)−C(04)	119(1)
C(03)−C(04)−C(05)	115(1)	Te−C(05)−C(04)	107(1)
Rh(1)−C(1)-C(11)	123.7(6)	Rh(1)−C(1)−C(2)	109.1(7)
C(11)−C(1)−C(2)	127.2(9)	Rh(2)−C(2)−C(1)	110.5(6)

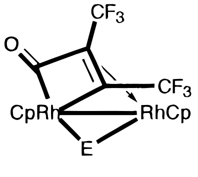
Results and Discussion

To further explore the substituent effects revealed in our study[1] of the reactions of **1** with dialkylsulfanes SRR′, we have extended the study to three cyclic thioethers. Reaction with the thietane trimethylene sulfide, $\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2$, in pentane resulted in the immediate precipitation of a red solid which was characterized as the addition product $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2)]$ (**2a**). The solid-state IR spectrum (Nujol mull) showed a terminal carbonyl stretching frequency at 1992 cm^{-1}. The complex reverted to **1** and free trimethylene sulfide when dissolved in chloroform, but NMR data were obtained for a solution containing excess ligand. Under these conditions, no unchanged **1** was evident. Further NMR experiments established that the solution remained unchanged when kept for 7 days at room temperature.



(2)

However, chromatographic workup of the solution produced **1** and the bridging sulfido complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-C(O)C(CF}_3\text{)C(CF}_3\text{)}\}(\mu\text{-S})]$ (**3a**) in 30% yield. The complex **3a** was also formed in 55% yield in the direct reaction between **1** and elemental sulfur. The attachment of enone groups to metal−metal bonds has been discussed previously,[7] and several bonding modes have been structurally characterized.[7−9] Spectroscopic data for **3a** are consistent with the structure shown (**3**, E = S). The IR spectrum shows strong enone absorptions at 1683 and 1707 cm^{-1} which are similar to those reported for $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\{\mu\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-C(O)C(CF}_3\text{)C(CF}_3\text{)}\}(\text{CO})]$.[7] In this complex and in **3a**, the observation of two absorptions in the "ketonic carbonyl" region is attributed to the effects of conjugation of the ketone with the neighboring C═C. The bridging sulfido group presumably has structural characteristics similar to those established for the complexes $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-E})]$ (E = S, Se).[10] The formation of **3a** from **2a** formally involves two C−S bond scissions and is apparently enhanced by the absorption of the complex on chromatographic supports. This observation may be of significance in hydrodesulfurization studies[11−18] and deserves further consideration.



(3)

We are aware of one previous report[19] of the desulfurization of $\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2$ enhanced by coordination to a metal. Treatment of the cationic dimolybdenum complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\mu\text{-SMe}_2)(\mu\text{-SMe})(\mu\text{-S}_2\text{CH}_2)]^+$ with $\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2$ leads to the formation of the sulfido complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\mu\text{-S})(\mu\text{-SMe})(\mu\text{-S}_2\text{CH}_2)]^+$ with dimethylsulfane and cyclopropane as coproducts. Cyclopropane is also formed when a molybdenum or other metal surface is exposed to $\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2$.[20,21]

Since the complex **2a** reverted to **1** in solution, we investigated similar reactions between **1** and excess propylene sulfide, $\overline{\text{SCH(Me)C}}\text{H}_2$, or tetrahydrothiophene, $\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{C}}\text{H}_2$, in NMR tubes to determine the extent of reaction. With the latter sulfide, there was incomplete formation of the red addition product **2c** (L = $\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{C}}\text{H}_2$) and no transformation of the product occurred when the solution was left to stand. With the smaller strained-ring sulfide, two diastereomers of the addition product **2b** were detected by NMR spectroscopy. These arise because the ring sulfur can be attached to rhodium either from the lone pair *exo* to the methyl substituent or from that which is *endo* to the substituent (see Figure 1). Equal amounts of the two isomers were present. This complex converted quantitatively to the bridging sulfido complex **3a** when left in solution for several days. It is known that thiiranes undergo facile elimination of sulfur to yield alkenes[22−24] and that these reactions are promoted by

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(7) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *Aust. J. Chem.* **1985**, *38*, 273.

(8) Dickson, R. S.; Gatehouse, B. M.; Nesbit, M. C.; Pain, G. N. *J. Organomet. Chem.* **1981**, *215*, 97.

(9) Dyke, A. F.; Knox, S. A.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

(10) Brunner, H.; Janietz, N.; Meier, W.; Wachter, J.; Herdtweck, E.; Herrmann, W. A.; Serhadli, O.; Ziegler, M. L. *J. Organomet. Chem.* **1988**, *347*, 237.

(11) Bianchini, C.; Jiminez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 4858.

(12) Hao, L.; Xiao, J.; Vittal, J. J.; Puddephatt, J. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2183.

(13) Polam, J. R.; Porter, L. C. *Organometallics* **1993**, *12*, 3504 and references cited therein.

(14) Curtis, M. D. *J. Cluster Sci.* **1996**, *7*, 247.

(15) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Choi, D. S.; Lee, S. S.; Chung, Y. K. *Organometallics* **1997**, *16*, 5688.

(16) Bianchini, C.; Jimenez, M. V.; Meli, A.; Moneti, V. P.; Vizza, F. *Organometallics* **1997**, *16*, 5696.

(17) Sargent, A. L.; Titus, E. P. *Organometallics* **1998**, *17*, 65.

(18) Jones, W. D.; Chin, R. M.; Hoaglin, C. L. *Organometallics* **1999**, *18*, 1786.

(19) Gabay, J.; Dietz, S.; Bernatis, P.; Dubois, R. *Organometallics* **1993**, *12*, 3630.

(20) Friend, C. M.; Roberts, J. T. *Chem. Rev.* **1992**, *92*, 491 and references cited therein.

(21) Lawrence, A. H.; Liao, C. C.; DeMayo, P.; Ramamurphy, V. *J. Am. Chem. Soc.* **1976**, *98*, 2219.

(22) Zoller, U. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1985; Part 1, Vol. 42, p 333.

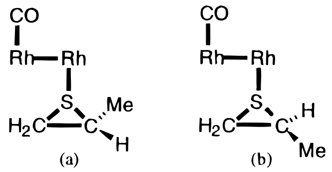
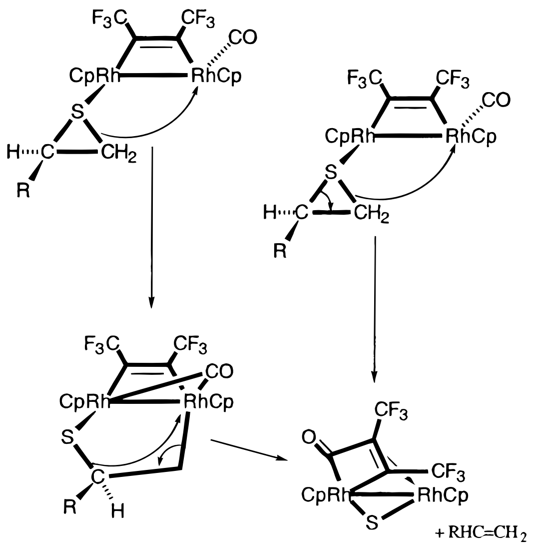


Figure 1. Geometries of the cyclic coordinated thioether in the complex **2b** (cyclopentadienyl and hexafluorobut-2-yne groups omitted for clarity).

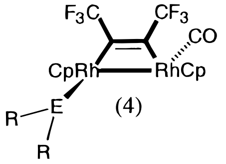
Scheme 2. Possible Pathways for the Conversion of 2b to 3a



metals.[25–27] It is thus likely that the conversion of **2b** to **3a** involves the elimination of propylene. However, attempts to detect this in NMR experiments using sealed tubes were inconclusive due to the scale of the experiment.

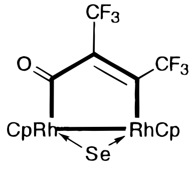
With these cyclic ligands, it is evident that the size of the ring affects the extent of formation of the addition products **2**, with the smaller rings binding more strongly. This is consistent with the behavior of the dialkylsulfanes, where the strongest binding occurred when the alkyl groups were small. There is also a correlation between ring size and the tendency to transform to the μ-sulfido complexes **3a**. Although the pathway for this transformation has not been established, it presumably involves elimination of an alkene which occurs most readily for the strained small-ring systems. Two possible pathways for this conversion are shown in Scheme 2. One involves the simultaneous breaking of two C−S bonds to yield the alkene and **3a** directly. In the other, a ring-opening transformation leads to a dimetallacyclic intermediate which then eliminates the alkene. Similar transformations to relieve ring strain in thietanes occur on triosmium cluster complexes,[28,29] but with these systems there is no alkene elimination.

The rearrangement reactions that occur with **2a** and **2b** differ substantially from the Stevens rearrangements observed[1] for the two dialkylsulfane complexes [(η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(SRR′)] (R = R′ = Me, Et). To determine if similar rearrangements occur with related ligands containing other group 16 donors, the reactions of **1** with SeMe$_2$, TeMe$_2$, and TeEt$_2$ were investigated. In each case, the addition product [(η^5-C_5H_5)$_2$Rh$_2$(CO)(μ-η^1:η^1-$CF_3C_2CF_3$)(ER$_2$)] (**4a**, E = Se, R = Me; **4b**, E = Te, R = Me; **4c**, E = Te, R = Et) was formed. Formation of the selenium complex **4a** was incomplete in solution, even with a large excess of ligand present in the solution. The two tellurium-containing complexes (**4b**,**c**) could be isolated and fully characterized from elemental analysis and spectroscopic data. When solutions of these complexes in chlorinated solvents were left for several weeks, there was evidence of decomposition but no rearrangement products analogous to [(η^5-C_5H_5)$_2$Rh$_2${μ-η^1:η^2-C(CF$_3$)C(CF$_3$)H}(μ-SR)] or **3a** were detected.



(4)

Given the ease of formation of the bridging sulfido complex **3a**, it is surprising that the corresponding complexes [(η^5-C_5H_5)$_2$Rh$_2${μ-η^1:η^1:η^2-C(O)C(CF$_3$)C(CF$_3$)}(μ-E)], where E = Se, Te, were not present in the decomposition material. To check whether such complexes can indeed be obtained, solutions of **1** were treated with elemental selenium and tellurium. The expected products were formed, but relatively slowly. A solution of **1** and selenium turned red over 3 days; in contrast, the same reaction with sulfur required less than 4 h. The product [(η^5-C_5H_5)$_2$Rh$_2${μ-η^1:η^1:η^2-C(O)C(CF$_3$)C(CF$_3$)}(μ-Se)] (**3b**, E = Se) was isolated as a red solid in 28% yield and was characterized from elemental analyses and spectroscopic results. Other major products formed in this reaction were the dicarbonyl complex [(η^5-C_5H_5)$_2$Rh$_2$(CO)$_2${μ-η^1:η^1-$CF_3C_2CF_3$}] (21% yield), which is a common product in prolonged reactions involving **1**, and a brown isomer of **3b**, which was identified as [(η^5-C_5H_5)$_2$Rh$_2${μ-η^1:η^1:η^2-C(O)C(CF$_3$)C(CF$_3$)}(μ_2−Se)] (**5**; 41% yield). The latter was characterized spectroscopically but was not obtained analytically pure because it transformed in solution to another species which was not completely characterized.



(5)

The reaction between **1** and tellurium was even slower. Workup of the reaction solution after 7 days gave unchanged **1** (35%), [(η^5-C_5H_5)$_2$Rh$_2$(CO)$_2${μ-η^1:η^1-$CF_3C_2CF_3$}] (10%), and [(η^5-C_5H_5)$_2$Rh$_2${μ-η^1:η^1:η^2-C(O)C(CF$_3$)C(CF$_3$)}(μ-Te)] (**3c**, E = Te; 35%). The last compound was characterized from spectroscopic data.

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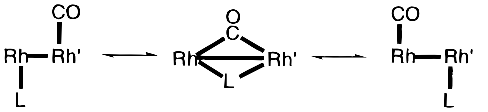
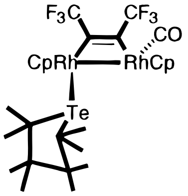
(23) Sander, M. *Chem. Rev.* **1966**, *66*, 297.
(24) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 7899.
(25) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745.
(26) Calet, S.; Alper, H. *Tetrahedron Lett.* **1986**, *27*, 3573.
(27) Lorenz, I. P.; Messelauser, J.; Hiller, W.; Conrad, M. *J. Organomet. Chem.* **1986**, *316*, 121.
(28) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992**, *11*, 2016.
(29) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992**, *11*, 2281.

Scheme 3. Fluxional Process for the Complex 6[a]



[a] The cyclopentadienyl and hexafluorobut-2-yne ligands are omitted for clarity. L = $\overline{TeCH_2CH_2CH_2CH_2}$.

The addition complex $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(\overline{TeCH_2CH_2CH_2CH_2})]$ (**6**) was formed from **1** and the cyclic tellurane $\overline{TeCH_2CH_2CH_2CH_2}$ and was isolated as an orange solid. The expected structure is



(6)

shown. This complex was stable in solution, and full spectroscopic characterization was achieved. Spectra consistent with the proposed structure were observed for solutions cooled to −28 °C. However, at room temperature, the spectra showed single broad peaks for the cyclopentadienyl protons and the trifluoromethyl fluorines. These coalesced to single sharp peaks when the solution was warmed to 60 °C. These results indicate rapid exchange of the tellurane and CO ligands from one rhodium atom to the other at the higher temperatures (see Scheme 3). To confirm this, variable-temperature ^{125}Te NMR spectra were also run. At low temperatures, the ^{125}Te signal was observed at δ 552 as a doublet with Rh−Te coupling of 86 Hz; this signal became a triplet with Rh−Te coupling of 50 Hz when the temperature was raised. The chemical shift and coupling constant are similar to those reported[30] for the isomers of $RhCl_3[Te(CH_2)_4]_3$.

The sensitivity of the Stevens rearrangement reaction to the donor atom and the alkyl groups in the ligand ER_2 aroused our interest in the detail of the molecular structures of these compounds. It was not possible to grow X-ray-quality crystals of any of the sulfur complexes described above, but well-formed crystals of **6** were obtained. The molecular structure is shown in Figure 2, and bond parameters are given in Table 2. There are no unusual features in the structure. The expected trans arrangement of the tellurium ligand and the terminal CO is confirmed, as is the parallel orientation of the alkyne to the Rh−Rh bond. In general, the bond distances and angles are very similar to the corresponding parameters for the complexes $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(CO)_2]$[31] and $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(CO)(CNBu^t)]$.[32] We can find no reports of other crystal structures with organotellurium ligands linked to rhodium. In **6**, the Rh−Te distance is 2.540(2) Å and the average of the two Te−C distances is 2.15(1) Å. Our database search has revealed only one other crystal structure for a transition-metal complex of this cyclic organotellurane. In the molecular structure of $[trans\text{-}PdCl_2(\overline{TeCH_2CH_2CH_2CH_2})_2]$, the M−Te and Te−C distances are similar to those we find for **6**.[30]

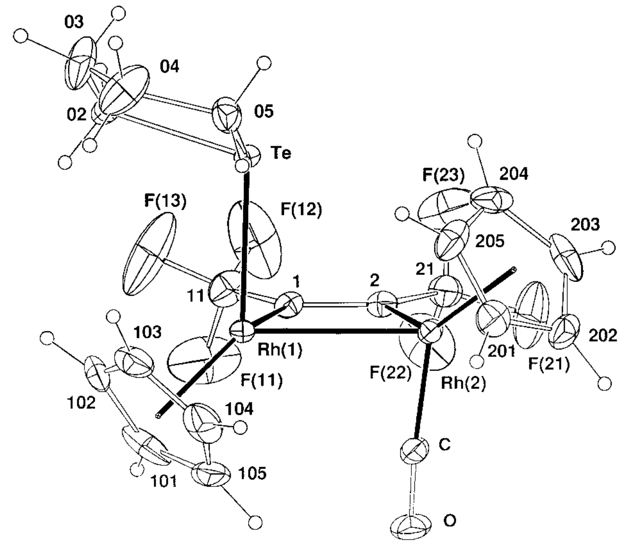


Figure 2. Molecular projection of **6** showing 20% probability amplitude thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

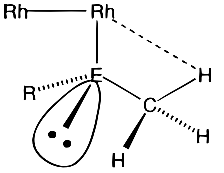


Figure 3. Ligand orientation prior to first step in the Stevens rearrangement.

We have tried to use the tellurium ligand geometry in **6** to develop a better understanding of the C−H bond activation process which is integral to the Stevens rearrangement reaction that occurs for the sulfane complexes $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)(SRR')]$. A representation of the relevant part of the structures of these complexes is given in Figure 3. From the structural data, we have estimated that the nonbonding Rh···H distance in **6** is 3.6 Å. This is well outside the Rh···H van der Waals contact distance of 2.8 Å. However, if Te was replaced by S in the representation, the Rh−E and E−C distances would each be shortened by about 0.3 Å. Changing the C−E−C angle from the 84° observed for **6** toward the tetrahedral angle expected for a dialkyl chalcogenide would bring the hydrogen even closer to rhodium. Thus, there is a reasonable expectation that the geometry allows a β-hydride transfer when E = S but not when E is a larger chalcogen. There is little likelihood of a direct transfer of H to an alkyne carbon, since the shortest nonbonding C(alkyne)···H distance is about 4.2 Å. This information supports the idea that the initial steps in our Stevens rearrangements are β-hydride transfer to rhodium followed by a 1,2-shift to the alkyne carbon.

Acknowledgment. We thank the Australian Research Council for financial support and Monash Uni-

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(30) Kemmitt, T.; Levason, W.; Oldroyd, R. D.; Webster, M. *Polyhedron* **1992**, *11*, 2165.

(31) Dickson, R. S.; Johnson, S. H.; Kirsch, H. P.; Lloyd, D. J. *Acta Crystallogr.* **1977**, *B33*, 2057.

(32) Bixler, J. W.; Bond, A. M.; Dickson, R. S.; Fallon, G. D.; Nesbit, R. J.; Pateras, H. *Organometallics* **1987**, *6*, 2508.

versity for a Post Graduate Scholarship (M.P.D.). Tania MacFarlane assisted with some of the experimental work.

Supporting Information Available: Tables of atomic positional coordinates, anisotropic thermal parameters, bond lengths, and bond angles, as well as a crystal-packing diagram for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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