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The coordination and rearrangement of some organic chalcogenides on a rhodium–rhodium bond; the reactions with dialkylsulfanes and alkanethiols [1]

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Abstract

When solutions of $[Cp_2Rh_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)]$ (**I**) in petroleum ether or chlorinated hydrocarbons were treated with the dialkylsulfanes SRR′(R = R′ = Me, Et, Pr, Bz; RR′ = MeEt), the addition products $[Cp_2Rh_2(CO)(SRR')(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**III**, **a**–**e**) were formed reversibly. The complexes (**III**) have been characterized spectroscopically in solutions containing excess ligand. Removal of excess ligand and solvent regenerated (**I**). When left in solution, a number of the dialkylsulfane complexes underwent interesting transformations. The complex (**IIIa**, R = R′ = Me) converted to $[Cp_2Rh_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-SEt})]$ (**IVa**, R = Et); this involves a β-proton transfer accompanied by a Stevens rearrangement to convert $\{S(CH_2^-)CH_3\}$ to $(SCH_2CH_3)^-$. The structure of (**IVa**) was determined by X-ray crystallography. Two rearrangement products were formed when (**IIIb**, R = R′ = Et) was left in solution. One was characterized from spectroscopic data as $[Cp_2Rh_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-SCHMeEt})]$ (**IVb**), which is formed by a Stevens rearrangement after transfer of a β-proton. The other was identified as (**IVa**, R = Et), which is formed after proton abstraction from a γ-carbon followed by elimination of ethene. A number of μ-thiolato complexes (**IVa**–**h**, R = Me, Et, Pr, CHMeEt, Pr^i, Bu, Bu^t and Ph) were formed directly by treatment of (**I**) with the appropriate alkanethiol RSH. In some instances (R = CHMeEt, Pr^i, and Bu^t), a second product of formula $[Cp_2Rh_2(\mu\text{-CO})\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}CH(CF_3)C(CF_3)SCR^1R^2R^3\}]$ (**VI**, **a**–**c**) was formed. The molecular structure of (**VIb**, R^1 = H, $R^2 = R^3$ = Me) was determined by single crystal X-ray diffraction analysis. © 1998 Elsevier Science S.A.

Keywords: Rhodium; Chalcogenides; Dialkylsulfane; Alkanethiol; Stevens rearrangement

1. Introduction

A range of group 14 and 15 ligands add coordinatively to the dirhodium complex $[Cp_2Rh_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)]$ (**I**) to give the products $[Cp_2Rh_2(CO)(L)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**II**; e.g., L = CNR, CRR′, or PR_3) [1]. In many instances, the added ligand participates in further bond making and breaking processes within the coordination sphere of the Rh–Rh bond. The addition of nitrene sources to (**I**) is an example where initial coordination of NR leads to a spontaneous intramolecular rearrangement reaction to generate a bridging acrylamide ligand $[N(R)C(O)C(CF_3)C(CF_3)]$ [2,3]. Prompted by the considerable continuing interest in the behaviour of organosulfur ligands in metal complexes [4], we have begun an investigation of reactions between group 16 ligands and the complex (**I**). We find that facile H-transfer reactions occur with thiols, but more surprisingly, some reactions with dialkylsulfanes can also lead to H-transfer. In these latter reactions, an alkyl C–H bond of the coordinated R_2S ligand is activated under extremely mild conditions. We report the results of these investigations in the present paper. Preliminary results covering part of this study have been reported

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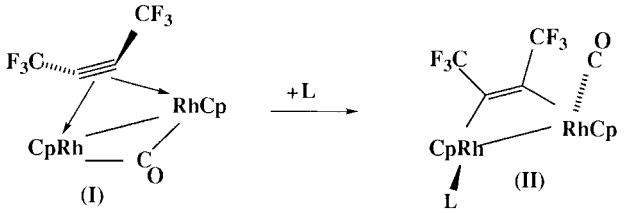
[1] Dedicated to Professor Peter Maitlis in celebration of his 65th birthday.

[5]. In a subsequent paper [6], we extend the study to some cyclic sulfanes and some organo telluranes.



2. Experimental

2.1. General procedures

All reactions were carried out under an atmosphere of purified nitrogen in oven-dried Schlenk flasks. Purification of products was generally achieved by preparative-scale thin-layer chromatography which was carried out on 20 by 20 cm glass plates with a 1:1 silica gel G-HF_{254} mixture (Type 60, Merck) as adsorbent. All separations were achieved on deactivated plates, obtained by drying at room temperature only. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Melting points were determined on an Electrothermal IAG304 instrument using analytically pure samples and are uncorrected.

2.2. Instrumentation

Solution infrared spectra (KBr windows) were obtained using a Perkin Elmer 1600 Fourier transform spectrometer. NMR spectra were measured on Bruker AC 200, AM 300, or DRX400 spectrometers. Deuterated solvents ($CDCl_3$) were used as internal locks. Chemical shifts are in parts per million from internal Me_4Si for ^1H and ^{13}C, CCl_3F for ^{19}F, and Me_2Te for ^{125}Te; in all cases, a positive chemical shift denotes a resonance downfield from the reference. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Electron impact mass spectra were obtained by using a VG TRIO-1 GCMS spectrometer operating at 70 eV and 200°C inlet temperature.

2.3. Materials

Acetone was analytical grade reagent; hydrocarbons and dichloromethane were purified by distillation under nitrogen from the appropriate drying agent [7]. All solvents were stored in the dark over activated 4A molecular sieves and were purged with nitrogen prior to use. The complex $[Cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)]$ (**I**) was prepared as described in Organometallic Syntheses [8]. Most sulfur ligands were obtained from Sigma-Aldrich and used as received; thiophenol was obtained from Merck.

2.4. Reaction of $[(Cp_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)]$ (I) with SMe_2

A large excess of dimethylsulfane (0.5 ml, 6.8 mmol) was injected into a stirred solution of (**I**) (0.084 g, 0.16 mmol) in petroleum ether (b.p. 30–40°C) (20 ml). The color of the solution changed instantly from green to dark cherry red. The complex (**I**) was regenerated when solvent and dimethylsulfane were removed under vacuum from this sample. A 4-fold excess of dimethylsulfane was added to solutions of (**I**) in chlorinated hydrocarbons, and IR and NMR spectroscopic results were recorded for the red solutions. This indicated the presence of $[Cp_2Rh_2(CO)(SMe_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**IIIa**; R = R′ = methyl). IR spectrum ($CHCl_3$): ν(CO) at 1988 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ(Cp) at 5.42 and 5.21 (the resonance for coordinated SMe_2 was obscured by that of the excess free ligand). ^{19}F NMR spectrum ($CDCl_3$): 2 × qd ($^5J_{F-F}$ = 11 Hz and $^3J_{Rh-F}$ = 3 Hz) of equal intensity at δ −52.7 and −55.1. The starting compound (**I**) (δ(Cp) at 5.45, $\delta(CF_3)$ at −52.2) was also present, with the ratio of (**I**):(**IIIa**) = 3:5. The original reaction solution in petroleum ether was stirred at room temperature for 4 h, with a slow stream of N_2 bubbling through the solution to displace CO and inhibit the formation of $[Cp_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**II**, L = CO). Monitoring of a sample by IR spectroscopy showed the total disappearance of both (**I**) and (**IIIa**). All volatiles were then removed under vacuum from the purple solution, and the residue was dissolved in a small volume of dichloromethane. TLC of this solution with dichloromethane–hexane (1:1) as eluent separated two major products from several minor impurities. A yellow band (R_f = 0.9) was extracted with dichloromethane and solvent evaporated to produce a yellow solid, which was identified spectroscopically [8] (^1H and ^{19}F NMR) as the dicarbonyl complex (**II**, L = CO) (0.015 g, 17%). Extraction of the other major band (R_f = 0.6) with dichloromethane and evaporation of solvent yielded $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-}SEt)]$ (**IVa**; R = ethyl) as a purple crystalline solid (0.056 g, 63%), mp 135°C. Anal. Found: C, 34.0; H, 3.3. $C_{16}H_{16}F_6Rh_2S$. Calc.: C, 34.3; H, 2.9%. IR spectrum ($CHCl_3$): no ν(CO) peaks observed. ^1H NMR spectrum ($CDCl_3$): δ 5.49 (s, 5H, Cp), 5.31 (s, 5H, Cp), 2.64 (m, 2H, CHH′; decoupling with the CH_3 resonance produced 2 doublets, $^2J_{H-H'}$ = 12.6 Hz), 1.44 (q, 1H, $^3J_{H-F}$ = 10.0 Hz, $C(CF_3)H$), 1.37 (t, 3H, $^3J_{H-H}$ = 7.5 Hz, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ

−50.3 (q, 3F, $^5J_{F-F}$ = 12.7 Hz, CF_3) and −53.8 (m, 3F, $^3J_{F-H}$ = 10.0 Hz and $^5J_{F-F}$ = 12.7 Hz, CF_3). ^{13}C NMR spectrum ($CDCl_3$): δ 129.0 (q, $^1J_{C-F}$ = 274 Hz, CF_3), 126.0 (q, $^1J_{C-F}$ = 275 Hz, CF_3), 91.6 (s, ***C***(CF_3)=C), 86.1 (d, $^1J_{C-Rh}$ = 5.3 Hz, Cp), 83.6 (d, $^1J_{C-Rh}$ = 5.3 Hz, Cp), 64.3 (q, C=***C***(CF_3)H), 43.2 (s, CH_2), 18.1 (s, Me). Mass spectrum, *m/z* (relative intensity, assignment): 560 (20, M), 531 (10, M–Et), 368 (30, $[C_{10}H_{10}RhS]^+$), 303 (15, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

2.5. Alternative preparation of [(η⁵-C_5H_5)$_2$$Rh_2${μ-η²:η¹-$C(CF_3)C(CF_3)H$}(μ$_2$-SEt)] (IVa) from EtSH

An excess of ethanethiol (0.2 ml, 2.7 mmol) was added dropwise from a syringe to a stirred solution of (**I**) (0.010 g, 0.019 mmol) in petroleum ether (15 ml). There was an instant color change from green to deep crimson. Stirring was continued for 4 h, and all volatiles were then removed under vacuum. TLC of a solution of the residue dissolved in dichloromethane with dichloromethane–hexane (1:1) as eluent separated two major bands from minor impurities. A yellow band (R_f = 0.9) was extracted with dichloromethane; evaporation of solvent from the extract gave the dicarbonyl complex (**II**, L = CO) (0.001 g, 10%) which was characterized spectroscopically. Extraction of a dark purple band (R_f = 0.6) with dichloromethane and removal of solvent yielded [Cp_2Rh_2{μ-η²:η¹-$C(CF_3)C(CF_3)H$}(μ$_2$-SEt)] (**IVa**, R = ethyl) (0.007 g, 65%) as a purple solid.

2.6. Reaction of [(Cp_2Rh_2(μ-CO)(μ-η²:η²-$CF_3C_2CF_3$)] (1) with diethylsulfane

The general procedure described in Section 2.4 for the reaction with SMe_2 was followed. The initial product in solution was identified as [$Cp_2Rh_2(CO)(SEt_2)$(μ-η¹:η¹-$CF_3C_2CF_3$)] (**IIIb**, R = R′ = ethyl). IR spectrum ($CHCl_3$), ν(CO) at 1990 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 5.44 (s, 5H, Cp), 5.22 (s, 5H, Cp) (the resonances for coordinated SEt_2 were obscured by those for the large excess of free ligand). ^{19}F NMR spectrum ($CDCl_3$): two quartets (J_{F-F} = 11.4 Hz) of equal intensity at δ −52.4 and −55.1. The starting compound (**I**) was also present; even with a 60-fold excess of the ligand, the ratio of (**I**):(**IIIb**) was determined to be 5:2. A solution containing complex (**I**) (0.061 g, 0.16 mmol) and SEt_2 (0.50 ml, 4.6 mmol) in petroleum ether (30 ml) was left for 18 h. TLC workup with hexane–dichloromethane (1:1) as eluent separated four bands that were each extracted with dichloromethane. The first yellow band (R_f = 0.9) gave (**II**, L = CO) (0.025 g, 37%). The second band (R_f = 0.8) was purple and this yielded [Cp_2Rh_2{μ-η²:η¹-$C(CF_3)C(CF_3)H$}(μ$_2$-SCHMeEt}] (**IVb**, R = 1-methylpropyl) (0.007 g, 10%) as a purple solid, mp 140°C. This complex was isolated in significantly higher yield from the reaction of (**I**) with 2-butanethiol which is described in Section 2.7; spectroscopic characterization of the compound is given there. Another purple band (R_f = 0.6) yielded [Cp_2Rh_2{μ-η²:η¹-$C(CF_3)C(CF_3)H$}(μ$_2$-SEt)] (**IVa**, R = ethyl) (0.020 g, 31%) which was described in Section 2.5. The final band (R_f = 0.2) was blue; it was present in trace quantities and was not further characterized.

2.7. Alternative preparation of [(Cp_2Rh_2{μ-η²:η¹-$C(CF_3)C(CF_3)H$}{μ-η¹:η¹-SCHMeEt}] (IVb) from 2-butanethiol

To a stirred solution of (**I**) (0.045 g, 0.086 mmol) in dichloromethane (15 ml) was added 2-butanethiol (0.5 ml, 4.6 mmol). There was an instant color change from green to crimson. After stirring the reaction mixture at room temperature for 4 h, all volatiles were removed under vacuum. The residue was dissolved in dichloromethane, and TLC of the solution with a mixture of hexane–dichloromethane (1:1) as eluent separated three bands. The first, a yellow band, was present in trace amounts only. It was identified from its color and R_f value (0.9) as (**II**, L = CO). A major purple band (R_f = 0.8) was extracted with dichloromethane, and evaporation of solvent left a purple solid which was identified as [Cp_2Rh_2{μ-η²:η¹-$C(CF_3)C(CF_3)H$}(μ$_2$-SCHMeEt}] (**IVb**, R = 1-methylpropyl) (0.022 g, 43%), mp 140°C. Anal. Found: C, 37.7; H, 4.3. $C_{18}H_{20}F_6Rh_2S$. Calc.: C, 36.8; H, 3.4%. IR spectrum ($CHCl_3$), no ν(CO) peaks observed. ^1H NMR spectrum ($CDCl_3$): δ 5.50 and 5.48 (2 × d of approximately equal intensity, 5H, $^2J_{H-Rh}$ = 0.5 Hz, Cp of stereoisomers), 5.33 and 5.31 (2 × d, 5H, $^2J_{H-Rh}$ = 0.5 Hz, Cp), 2.50 (m, 1H, CH), 1.9–1.6 (br m, 2H, CH_2), 1.49 (q, 1H, $^3J_{H-F}$ = 10.0 Hz, $C(CF_3)$**H**), 1.35 and 1.32 (2 × d, 3H, $^3J_{H-H}$ = 6.7 Hz, S-CH-**C**H_3), 1.00 (td, 3H, $^3J_{H-H}$ = 7.5 Hz and $^4J_{H-H}$ = 1.5 Hz, **C**H_3 of ethyl). ^{19}F NMR spectrum ($CDCl_3$): δ −49.9 (2 × q of equal intensity separated by 0.02 Hz, 3F, $^5J_{F-F}$ = 13.0 Hz, CF_3) and −53.9 (m, 3F, **C**F_3H). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$): δ 86.1 and 86.0 (2 × s, Cp), 83.7 and 83.6 (2 × s, Cp), 55.7 and 55.6 (2 × s, CH), 33.4 and 32.3 (2 × s, CH_2), 23.2 and 22.1 (2 × s, S-CH-**C**H_3), 11.4 (s, CH_3 of ethyl)-resonances for the alkenyl carbons could not be assigned with confidence. Mass spectrum, *m/z* (relative intensity, assignment): 588 (6, M), 531 (8, M–C_4H_9), 368 (15, $[C_{10}H_{10}RhS]^+$), 303 (12, $[C_5H_5Rh_2S]^+$, 233 (100, $[C_{10}H_{10}Rh]^+$), 168 (18, $[C_5H_5Rh]^+$), 57 (18, $[C_4H_9]^+$).

Extraction of the remaining significant band (R_f = 0.3) gave a dichroic green-brown solid which was identified as [Cp_2Rh_2(μ-CO){μ-η²:η¹-$C(CF_3)HC(CF_3)SCHMeEt$}] (**VIa**, R = 1-methylpropyl)

(0.012 g, 23%). Anal. Found: C, 37.2; H, 3.2. $C_{19}H_{20}F_6ORh_2S$. Calc.: C, 37.0; H, 3.3%. IR spectrum ($CHCl_3$), ν(CO) at 1801 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 5.49 (s, 5H, Cp), 5.37 (s, 5H, Cp), 2.0–1.2 (br m, 4H, CH_2, CH and C(CF_3)**H**), 1.15 and 0.98 (2 × d of equal intensity, 3H, $^3J_{H-H} = 6.7$ and 6.9 Hz, SCH**C**$\mathbf{H}_3$ of stereoisomers), 0.90 and 0.89 (2 × t of equal intensity, 3H, $^3J_{H-H} = 7.4$ Hz, **C**$\mathbf{H}_3$ of ethyl). ^{19}F NMR spectrum ($CDCl_3$): δ −52.3 and −52.5 (2 × m of equal intensity, 3F, **C**$\mathbf{F}_3$H of stereoisomers,) and −57.7 (m, 3F, CF_3). Mass spectrum, *m/z* (relative intensity, assignment): 616 (5, M), 588 (25, M–CO), 531 (35, M-CO-C_4H_9), 368 (10, $[C_{10}H_{10}RhS]^+$), 303 (12, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

*2.8. Reactions of [(η^5-C_5H_5)$_2$Rh$_2$(μ-CO)(μ-η^2:η^2-$CF_3C_2CF_3$)] (**I**) with other dialkylsulfanes*

2.8.1. SEtMe

When excess ethylmethylsulfane (0.42 g, 5.5 mmol) was added with stirring to a solution of (**I**) (0.032 g, 0.061 mmol) in chloroform (20 ml), an instant colour change from green to red occurred, indicating the presence of [Cp_2Rh_2(CO)(SEtMe)(μ-η^1:η^1-$CF_3C_2CF_3$)] (**IIIc**, RR′ = MeEt). IR spectrum ($CHCl_3$): ν(CO) at 1990 s cm^{-1}. The reaction was repeated in an NMR tube with an 80-fold excess of ligand. ^1H NMR spectrum ($CDCl_3$): δ 5.42 (s, 5H, Cp), 5.21 (s, 5H, Cp) (the resonances for coordinated SEtMe were obscured by those for the large excess of free ligand). ^{19}F NMR spectrum ($CDCl_3$): two quartets ($J_{F-F} = 11.6$ Hz) of equal intensity at δ −52.5 and −55.1. The starting material (**I**) was still present; the ratio of (**I**):(**IIIc**) was 1:2. The addition of further portions of SEtMe did not change this ratio significantly. If these solutions were evaporated to dryness at any stage, (**I**) was recovered quantitatively. A solution containing (**I**) and a large excess of ethylmethylsulfane in $CDCl_3$ was left stirring for 6 h. Monitoring by NMR spectroscopy indicated that traces of the complex [Cp_2Rh_2\{μ-η^2:η^1-C(CF_3)C(CF_3)H\}(μ_2-SMe)] (**IVc**) had formed. This complex was identified spectroscopically by comparison with an authentic sample prepared by reaction of (**I**) with methanethiol, described separately in Section 2.9.1. Numerous attempts were made to induce a rearrangement of the coordinated sulfane. In separate experiments, solutions of the addition product (**IIc**) were stirred for prolonged periods (up to 5 weeks) at room temperature, refluxed, irradiated with a UV source, and exposed to sunlight. There was extensive decomposition upon UV irradiation, but in the other cases (**IIc**) was recovered as the major species. On all occasions, numerous trace bands were evident on TLC workup; these usually included (**IVc**) and [Cp_2Rh_2\{μ-η^2:η^1-C(CF_3)C(CF_3)CO\}(μ_2-S)] (**VII**), but there was no evidence of any other rearranged products. Characterization of the complex (**VII**) will be described in a subsequent paper [6].

2.8.2. SPr$_2^n$

The procedure described in Section 2.4 was used. A very large excess (250-fold) of this ligand was required to effect a colour change from green to red. The addition product [Cp_2Rh_2(CO)(SPr_2^n)(μ-η^1:η^1-$CF_3C_2CF_3$)] (**IIId**) was characterized spectroscopically. IR spectrum (CH_2Cl_2): ν(CO) at 1988 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 5.24 (s, 5H, Cp), 5.02 (s, 5H, Cp) (the resonances for coordinated SPr_2^n were obscured by those for the free ligand.). ^{19}F NMR spectrum ($CDCl_3$): two quartets ($J_{F-F} = 11.7$ Hz) of equal intensity at δ −52.3 and −55.0. The starting material (**I**) was present, with a 1:4 ratio of (**I**):(**IIId**). Attempts to isolate (**IIId**) resulted in the reformation of (**I**).

2.8.3. SBz$_2$

Again, a very large excess of the ligand was required to effect a colour change from green to red. The addition product [Cp_2Rh_2(CO)(SBz_2)(μ-η^1:η^1-$CF_3C_2CF_3$)] (**IIIe**) was identified spectroscopically. IR spectrum (CH_2Cl_2): ν(CO) at 1976 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 5.67 (s, 5H, Cp), 5.28 (s, 5H, Cp) (the resonances for coordinated Bz_2S were obscured by those for the free ligand). ^{19}F NMR spectrum ($CDCl_3$): two quartets ($J_{F-F} = 11$ Hz) of equal intensity at δ −52.0 and −55.1. The starting material (**I**) and (**IIIe**) were present in a ratio of 3:1.

2.8.4. SPr$_2^i$

No addition product was evident in solution at room temperature. When a mixture of (**I**) and SPr_2^i in dichloromethane was refluxed or exposed to sunlight, a red solution formed. Chromatographic workup yielded the dicarbonyl complex (**II**, L = CO) (20% yield) and the bridging sulfido complex (**VII**) (5% yield).

*2.9. Reactions of [Cp$_2$Rh$_2$(μ-CO)(μ-η^2:η^2-$CF_3C_2CF_3$)] (**I**) with other thiols*

The general procedure described above in Section 2.5 for the reaction with ethanethiol was followed.

2.9.1. MeSh

Methanethiol was generated by stirring dimethylsulfane with conc. sulfuric acid. The evolved gas was bubbled through a solution of (**I**) (0.026 g, 0.049 mmol) in dichloromethane (20 ml) until the color of the solution was deep crimson. The reaction solution was stirred for a further 3 h. All volatiles were removed under vacuum, and the residue was redissolved in dichloromethane. Workup by TLC separated three major bands from several minor impurities. Extraction of a yellow band ($R_f = 0.9$) with dichloromethane and re-

moval of solvent yielded the dicarbonyl complex (**II**, L = CO) (0.005 g, 18%). A major purple product (R_f = 0.8) was extracted with dichloromethane and isolated by evaporation of solvent as a purple solid. It was characterized spectroscopically as [$Cp_2Rh_2\{\mu$-η^2:η^1-$C(CF_3)C(CF_3)H\}(\mu_2$-SMe)] (**IVc**) (0.010 g, 37%). IR spectrum (CH_2Cl_2): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 5.48 (s, 5H, Cp), 5.31 (s, 5H, Cp), 2.41 (dd, 3H, $^3J_{H-Rh} = {}^3J_{H-Rh'} = 1.5$ Hz, SCH_3). ^{19}F NMR spectrum ($CDCl_3$): δ −50.4 (q, 3F, $J_{F-F} = 13$ Hz, CF_3), −54.0 (m, 3F, CF_3). Mass spectrum, *m/z* (relative intensity, assignment) 546 (20, M), 531 (5, M–Me), 368 (5, $[C_{10}H_{10}RhS]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$). Only one other major product was present (green, R_f = 0.3), but it decomposed before it could be characterized.

2.9.2. PrSH

A purple crystalline solid (R_f = 0.7) was isolated (yield 57%) and identified as [$Cp_2Rh_2\{\mu$-η^2:η^1-$C(CF_3)C(CF_3)H\}\{\mu_2$-SPr}] (**IVd**), mp 141°C. Anal. Found: C, 35.8; H, 3.2; F, 19.6. $C_{17}H_{18}F_6Rh_2S$. Calc.: C, 35.6; H, 3.2; F, 19.9%. IR spectrum ($CHCl_3$): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 5.47 (s, 5H, Cp), 5.31 (s, 5H, Cp), 2.58 (t, 2H, $^3J_{H-H}$ = 7.0 Hz, S–CH_2), 1.71 (m, 2H, CH_2), 1.45 (q, 1H, $^3J_{H-F} = 10.0$ Hz, $C(CF_3)H$), 1.04 (t, 3H, $^3J_{H-H} = 7.4$ Hz, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ −50.3 (q, 3F, $^5J_{F-F} = 12.7$ Hz, CF_3) and −53.8 (m, 3F, $^3J_{F-H}$ = 10.0 Hz and $^5J_{F-F} = 12.7$ Hz, CF_3). Mass spectrum, *m/z* (relative intensity, assignment) 574 (7, M), 531 (5, M–Pr), 368 (25, $[C_{10}H_{10}RhS]^+$), 303 (10, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

A minor yellow band which also developed during the TLC workup was identified (IR spectrum) as the dicarbonyl complex (**II**, L = CO).

2.9.3. Pr^{i}SH

The same reaction procedure was used. TLC workup with a 3:1 mixture of petroleum spirit and dichlomethane as eluent separated two major products. One (R_f = 0.7) was isolated as a purple crystalline solid (54%). It was identified as [$Cp_2Rh_2\{\mu$-η^2:η^1-$C(CF_3)C(CF_3)H\}\{\mu_2$-SPr^i}] (**IVe**), mp 143°C. Anal. Found: C, 36.1; H, 3.0. $C_{17}H_{18}F_6Rh_2S$. Calc.: C, 35.6; H, 3.2%. IR spectrum ($CHCl_3$): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 5.49 (s, 5H, Cp), 5.33 (s, 5H, Cp), 2.72 (septet, 1H, $^3J_{H-H} = 6.8$ Hz, CH), 1.46 (q, 1H, $^3J_{H-F}$ = 10.0 Hz, $C(CF_3)H$), 1.38 (t, 6H, $^3J_{H-H} = 6.8$ Hz, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ −49.9 (q, 3F, $^5J_{F-F}$ = 13.0 Hz, CF_3) and −53.8 (m, 3F, $^3J_{F-H} = 10.0$ Hz and $^5J_{F-F} = 13.0$ Hz, CF_3). Mass spectrum, *m/z* (relative intensity, assignment) 574 (10, M), 531 (15, M–Pr^i), 368 (5, $[C_{10}H_{10}RhS]^+$), 303 (8, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

The other product (R_f = 0.3) was obtained as a dichroic green-brown solid which was identified as [$Cp_2Rh_2(\mu$-CO)$\{\mu$-η^2:η^1-$C(CF_3)HC(CF_3)SPr^i\}$] (**VIb**) (35% yield). Anal. Found: C, 35.7; H, 2.9. $C_{18}H_{18}F_6ORh_2S$. Calc.: C, 35.9; H, 3.0%. IR spectrum ($CHCl_3$): ν(CO) at 1801 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 5.49 (s, 5H, Cp), 5.38 (s, 5H, Cp), 2.04 (septet, 1H, $^3J_{H-H} = 6.7$ Hz, CH), 1.89 (q, 1H, $^3J_{H-F}$ = 10.0 Hz, $C(CF_3)$**H**), 1.20 (d, 3H, $^3J_{H-H} = 6.6$ Hz, CH_3), 1.02 (d, 3H, $^3J_{H-H} = 6.8$ Hz, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ −52.3 (m, 3F, $C(CF_3)H$), and −57.8 (q, 3F, $^5J_{F-F} = 10.9$ Hz, CF_3). Mass spectrum, *m/z* (relative intensity, assignment) 602 (1, M), 574 (9, M–CO), 531 (10, M–Pr^i), 368 (5, $[C_{10}H_{10}Rh_2S]^+$), 303 (10, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

2.9.4. BuSH

The same procedures were used. A purple crystalline solid (54%) was identified as [$Cp_2Rh_2\{\mu$-η^2:η^1-$C(CF_3)C(CF_3)H\}\{\mu_2$-SBu)}] (**IVf**), mp 142°C. Anal. Found: C, 36.7; H, 3.2; F, 18.9. $C_{18}H_{21}F_6Rh_2S$. Calc. C, 36.8; H, 3.4; F, 19.4%. IR spectrum ($CHCl_3$): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 5.47 (s, 5H, Cp), 5.30 (s, 5H, Cp), 2.60 (m, 2H, S–CH_2), 1.66 (m, 2H, CH_2), 1.46 (q, 1H, $^3J_{H-F} = 10.0$ Hz, $C(CF_3)H$), 1.45 (m, 2H, CH_2), 0.95 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ −50.2 (q, 3F, $^5J_{F-F} = 12.8$ Hz, CF_3) and −53.8 (m, 3F, $^3J_{F-H} = 10.0$ Hz and $^5J_{F-F} = 12.8$ Hz, CF_3). Mass spectrum, *m/z* (relative intensity, assignment) 588 (25, M), 531 (18, M–Bu), 368 (25, $[C_{10}H_{10}RhS]^+$), 303 (6, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

2.9.5. Bu^{t}SH

Two major products were separated by TLC, with a 3:1 mixture of petroleum spirit and dichloromethane as eluent. Extraction of one product (R_f = 0.7) gave a

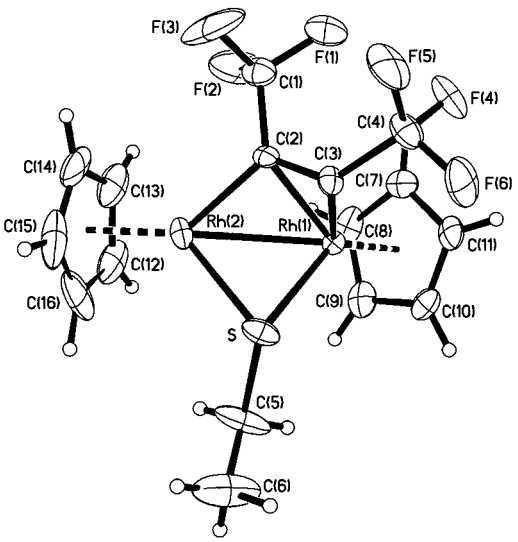


Fig. 1. Molecular projection showing the atom arrangement for **IVa**; the non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms as spheres of arbitrary radius.

purple crystalline solid (50%) which was identified as $[(\eta^5\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}\{\mu_2\text{-}SBu^t\}]$ (**IVg**), mp 160°C. Anal. Found: C, 36.9; H, 3.6. $C_{18}H_{20}F_6Rh_2S$. Calc.: C, 36.8; H, 3.4%. IR spectrum ($CHCl_3$): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 5.52 (s, 5H, Cp), 5.37 (s, 5H, Cp), 1.59 (q, 1H, $^3J_{H-F} = 9.5$ Hz, $C(CF_3)H$), 1.37 (s, 9H, CH_3). ^{19}F NMR spectrum ($CDCl_3$: δ −50.3 (q, 3F, $^5J_{F-F} = 12.9$ Hz, CF_3) and −53.4 (m, 3F, $^3J_{F-H} = 9.5$ Hz and $^5J_{F-F} = 12.9$ Hz, CF_3). Mass spectrum, m/z (relative intensity, assignment) 588 (6, M), 531 (5, M–Bu^t), 368 (40, $[C_{10}H_{10}RhS]^+$), 303 (10, $[C_5H_5Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

The second product ($R_f = 0.3$) was isolated as a dichroic green-brown solid which was identified as $[Cp_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)HC(CF_3)SBu^t\}]$ (**VIc**). Anal. Found: C, 37.5; H, 3.9. $C_{19}H_{20}F_6ORh_2S$. Calc.: C, 37.0; H, 3.3%. IR spectrum ($CHCl_3$): ν(CO) at 1802 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 5.48 (s, 5H, Cp), 5.40 (s, 5H, Cp), 2.07 (q, 1H, $^3J_{H-F} = 10.1$ Hz, $C(CF_3)$**H**), 1.12 (s, 9H, $C(CH_3)_3$). ^{19}F NMR spectrum ($CDCl_3$): δ −51.9 (m, 3F, $C(CF_3)H$), and −56.6 (q, 3F, $^5J_{F-F} = 11.0$ Hz, CF_3). Mass spectrum, m/z (relative intensity, assignment) 616 (2, M), 588 (1, M–CO), 559 (6, M–Bu^t), 531 (12, M-CO-Bu^t), 368 (15, $[C_{10}H_{10}Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

2.9.6. PhSH

The reaction and workup were similar to that described above. A purple crystalline solid (64%) was isolated by TLC ($R_f = 0.8$) and identified as $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}\{\mu_2\text{-}SPh\}]$ (**IVh**), mp 157°C. Anal. Found: C, 39.8; H, 2.6. $C_{18}H_{21}F_6Rh_2S$. Calc.: C, 39.5; H, 2.7%. IR (spectrum ($CHCl_3$): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 7.60 (m, 2H, *o*-H of C_6H_5), 7.21 (m, 3H, *m*- and *p*-H of C_6H_5), 5.41 (s, 5H, Cp), 5.20 (s, 5H, Cp), 1.44 (q, 1H, $^3J_{H-F} = 10.0$ Hz, $C(CF_3)H$). ^{19}F NMR spectrum ($CDCl_3$): δ −50.2 (q, 3F, $^5J_{F-F} = 12.7$ Hz, CF_3) and −53.7 (m, 3F, $^3J_{F-H} = 10.0$ Hz and $^5J_{F-F} = 12.7$ Hz, CF_3). Mass spectrum, m/z (relative intensity, assignment): 608 (15, M), 444 (6, $[C_{10}H_{10}RhSPh]^+$), 368 (15, $[C_{10}H_{10}RhS]^+$), 277 (45, $[C_5H_5RhSPh]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

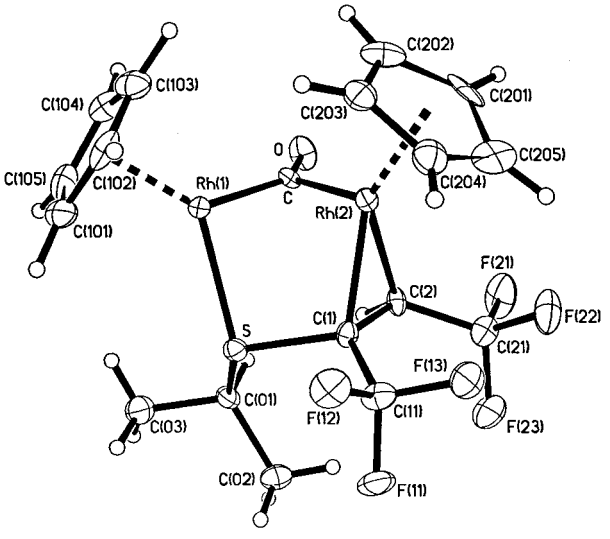


Fig. 2. Molecular projection showing the atom arrangement in **VIb**; the non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms as spheres of arbitrary radius.

Table 1
Summary of crystal structure data for the complexes (**IVa**) and (**VIb**)[a]

	(**IVa**)	(**VIb**)
	$C_{16}H_{16}F_6SRh_2$	$C_{18}H_{18}F_6ORh_2S$
M_r	560.2	602.2
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca* (No. 61)	$P\,2_12_12_1$ (No. 19)
a (Å)	16.061(2)	16.679(5)
b (Å)	18.165(2)	15.609(3)
c (Å)	12.344(3)	7.484(5)
V (Å^3)	3601	1948
D_c g cm^{-3}	2.07	2.05
F(000)	2176	1176
μ_{Mo} cm^{-1}	20.0	18.6
Specimen mm	0.40×0.12×0.12 (dark red, acicular)	0.17×0.08×0.60 (green-brown)
$\bar{T}_{min,\,max}$	0.76, 0.86	0.78, 0.89
N	5248	3211
N_0	2082	2194
R	0.048	0.059
R_0	0.048	0.058
Z	8	4
Programs	Texsan [19]	XTAL92 [20]

[a]Abnormal features/variations in procedure: (**IVa**): a ω-scan data collection mode was employed; reflection weights were $\omega^{-1} = \sigma^2(F)$; 'numerical' absorption correction (face indexed); (**VIb**): a Gaussian absorption correction was applied; residuals quoted apply to both chiralities.

2.9.7. Spectroscopic monitoring of the early stages of the reaction with PhSH

In an NMR tube, 1 drop of benzenethiol was added to a solution of (**I**) in $CDCl_3$. Within 5 min, ^{1}H and ^{19}F NMR spectra were recorded. One major product was evident, making up 70% of all trifluoromethyl resonances. It could not be identified from the spectroscopic results. ^{1}H NMR spectrum ($CDCl_3$): δ 5.82 (q, 1H, $^3J_{H-F} = 10.1$ Hz, $C(CF_3)H$), 5.4–5.0 (br s, 10H, 2× Cp). ^{19}F NMR spectrum ($CDCl_3$): δ −49.8 (q, 3F, $^5J_{F-F} = 12.4$ Hz, CF_3) and −57.5 (m, 3F, CF_3). An IR spectrum of the solution showed ν(CO) at 1989 cm^{-1}. After 20 min, the resonances for this intermediate had totally disappeared, and the spectra indicated that the major species present were the dicarbonyl complex (**II**, L = CO) and the μ-thiolato complex (**IVh**) in approximately equal amounts. After 18 h, a new product was evident; this is described in Section 2.9.8.

*2.9.8. Reaction of (**IVh**) with thiophenol*

An excess of thiophenol (0.5 ml, 4.9 mmol) was added to a solution of (**IVh**) (0.028 g, 0.046 mmol) in dichloromethane (10 ml) and the solution was stirred for several hours. During this time, the color of the solution changed from purple to orange. All volatiles were removed from the reaction mixture under vacuum. The residue was dissolved in dichloromethane. TLC of the solution with a 1:1 mixture of dichloromethane and hexane as eluent separated one major band from several minor species. The major orange band ($R_f = 0.5$) was extracted with dichloromethane, and evaporation of solvent left an orange solid, which was identified spectroscopically as [$Cp_2Rh_2(\mu$-SPh)(HSPh){μ-η^2:η^1-C(CF_3)C(CF_3)H}] (**VIII**) (0.015 g, 45%). IR spectrum ($CHCl_3$): no ν(CO) peaks observed. ^{1}H NMR spectrum ($CDCl_3$): δ 8.1–7.0 (br m, 10H, Ph), 5.06 (br s, 5H, Cp), 4.92 (br s, 5H, Cp), 3.73 (m, 1H, SH), 2.25 (m, 1H, C(CF_3)H). ^{19}F NMR spectrum ($CDCl_3$): δ −54.4 (br m, 3F, CF_3) and −55.8 (br m, 3F, C(CF_3)H). Mass spectrum, m/z (relative intensity, assignment): 718 (1, M), 554 (65, [$C_{10}H_{10}Rh_2SPh_2]^+$), 477 (20, [$C_{10}H_{10}Rh_2S(SPh)]^+$), 368 (25, [$C_{10}H_{10}Rh_2S_2]^+$), 233 (100, [$C_{10}H_{10}Rh]^+$).

Table 2
Selected bond lengths and angles for complex (**IVa**)

Atoms	*d* (Å)	Atoms	*d* (Å)
(*a*) *Bond lengths*			
Rh(1)–Rh(2)	2.630(1)	C(1)–F(1)	1.32(1)
Rh(1)–S	2.306(3)	C(1)–F(2)	1.28(1)
Rh(1)–C(2)	2.10(1)	C(1)–F(3)	1.25(1)
Rh(1)–C(3)	2.14(1)	C(2)–C(3)	1.43(1)
Rh(1)–C(7)	2.19(1)	C(3)–C(4)	1.50(1)
Rh(1)–C(8)	2.19(1)	C(4)–F(4)	1.33(1)
Rh(1)–C(9)	2.18(1)	C(4)–F(5)	1.34(1)
Rh(1)–C(10)	2.21(1)	C(4)–F(6)	1.34(1)
Rh(1)–C(11)	2.21(1)	C(7)–C(8)	1.41(2)
Rh(2)–S	2.299(3)	C(7)–C(11)	1.41(2)
Rh(2)–C(2)	2.02(1)	C(8)–C(9)	1.39(2)
Rh(2)–C(12)	2.23(1)	C(9)–C(10)	1.39(2)
Rh(2)–C(13)	2.19(2)	C(10)–C(11)	1.36(1)
Rh(2)–C(14)	2.16(2)	C(12)–C(13)	1.38(2)
Rh(2)–C(15)	2.15(2)	C(12)–C(16)	1.35(2)
Rh(2)–C(16)	2.20(1)	C(13)–C(14)	1.44(3)
S–C(5)	1.83(1)	C(14)–C(15)	1.38(3)
C(5)–C(6)	1.34(2)	C(15)–C(16)	1.34(3)
C(1)–C(2)	1.51(21)		
(*b*) *Bond angles*			
Rh(2)–Rh(1)–S	55.06(8)	S–C(5)–C(6)	117.0(1)
Rh(2)–Rh(1)–C(2)	49.1(2)	C(1)–C(2)–C(3)	121.3(9)
Rh(2)–Rh(1)–C(3)	78.0(2)	C(1)–C(2)–Rh(1)	124.3(7)
S–Rh(1)–C(2)	83.2(2)	C(1)–C(2)–Rh(2)	117.4(8)
S–Rh(1)–C(3)	78.0(3)	Rh(1)–C(2)–Rh(2)	79.2(3)
C(2)–Rh(1)–C(3)	39.5(3)	Rh(1)–C(2)–C(3)	71.8(5)
Rh(1)–Rh(2)–S	55.31(7)	Rh(2)–C(2)–C(3)	121.2(6)
Rh(1)–Rh(2)–C(2)	51.7(2)	C(2)–C(3)–C(4)	128.3(10)
S–Rh(2)–C(2)	85.0(3)	C(2)–C(3)–Rh(1)	68.7(5)
Rh(1)–S–Rh(2)	69.63(8)	Rh(1)–C(3)–C(4)	119.2(7)
Rh(1)–S–C(5)	111.3(5)		
Rh(2)–S–C(5)	108.2(6)		

Estimated standard deviations in parentheses.

Table 3
Selected bond lengths and angles for complex (**VIb**)

Atoms	*d* (Å)	Atoms	*d* (Å)
(*a*) *Bond lengths*			
Rh(1)–Rh(2)	2.662(2)	C(01)–C(02)	1.53(2)
Rh(1)–C	1.94(1)	C(01)–C(03)	1.49(2)
Rh(1)–S	2.272(4)	C(1)–C(11)	1.49(2)
Rh(1)–C(101)	2.23(2)	C(1)–C(2)	1.45(2)
Rh(1)–C(102)	2.29(2)	C(11)–F(11)	1.32(2)
Rh(1)–C(103)	2.21(1)	C(11)–F(12)	1.33(2)
Rh(1)–C(104)	2.22(2)	C(11)–F(13)	1.35(2)
Rh(1)–C(105)	2.22(2)	C(2)–C(21)	1.52(2)
Rh(2)–C	2.10(1)	C(21)–F(21)	1.34(2)
Rh(2)–C(1)	2.07(1)	C(21)–F(22)	1.31(2)
Rh(2)–C(2)	2.07(1)	C(21)–F(23)	1.32(2)
Rh(2)–C(201)	2.22(2)	C(101)–C(102)	1.39(3)
Rh(2)–C(202)	2.20(2)	C(101)–C(105)	1.43(3)
Rh(2)–C(203)	2.25(2)	C(102)–C(103)	1.37(3)
Rh(2)–C(204)	2.28(2)	C(103)–C(104)	1.41(3)
Rh(2)–C(205)	2.22(2)	C(104)–C(105)	1.37(3)
C–O	1.16(2)	C(201)–C(202)	1.43(3)
S–C(01)	1.83(1)	C(202)–C(203)	1.39(3)
S–C(1)	1.80(1)	C(202)–C(203)	1.35(2)
		C(203)–C(204)	1.35(2)
		C(204)–C(205)	1.39(3)
(*b*) *Bond angles*			
Rh(2)–Rh(1)–C	51.4(4)	Rh(1)–S–C(01)	114.2(5)
Rh(2)–Rh(1)–S	77.7(1)	Rh(1)–S–C(1)	96.3(4)
C–Rh(1)–S	94.5(4)	C(01)–S–C(1)	108.0(6)
Rh(1)–Rh(2)–C	46.1(4)	Rh(2)–C(1)–S	106.7(6)
Rh(1)–Rh(2)–C(1)	79.3(4)	Rh(2)–C(1)–C(11)	119.0(9)
Rh(1)–Rh(2)–C(2)	96.5(4)	Rh(2)–C(1)–C(2)	69.4(7)
C–Rh(2)–C(1)	93.5(5)	S–C(1)–C(11)	109(1)
C–Rh(2)–C(2)	79.1(5)	S–C(1)–C(2)	117.5(9)
C(1)–Rh(2)–C(2)	41.2(5)	C(11)–C(1)–C(2)	128(1)
Rh(1)–C–Rh(2)	82.5(5)	Rh(2)–C(2)–C(1)	69.4(7)
Rh(1)–C–O	143(1)	Rh(2)–C(2)–C(21)	125(1)
Rh(2)–C–O	113(1)	C(1)–C(2)–3C(21)	123(1)

Estimated standard deviations in parentheses.

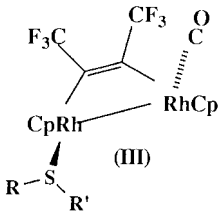
*2.10. Crystallography for complexes (**IVa**, R = Et) and (**VIb**, $R^1 = H$, $R^2 = R^3 = Me$)*

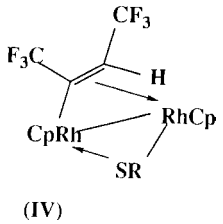
Unique room temperature diffractometer data sets were measured ($2\theta/\theta$ scan mode, $2\theta_{max}$ 60°; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; $T \sim$ 295 K), yielding N independent reflections, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least squares refinement after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Neutral atom complex scattering factors were employed. Pertinent results are given in Figs. 1 and 2 and Tables 1–3; material deposited comprises hydrogen and thermal parameters,

full non-hydrogen geometries and structure factor amplitudes.

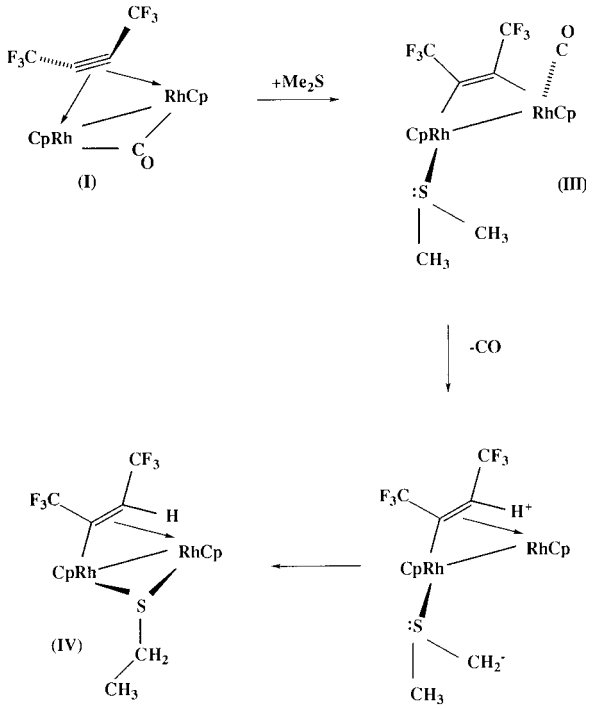
3. Results and discussion

The reaction of the complex $[Cp_2Rh_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CF_3C_2CF_3)]$ (**I**) with a large excess of dimethylsulfane, SMe_2, was carried out in petroleum ether at room temperature. There was a rapid change of color from green to cherry red indicating the formation of a new complex. When solvent and dimethylsulfane were removed from the red solution under reduced pressure, the starting complex (**I**) was the only species recovered, indicating that a reversible addition of the dimethylsulfane had occurred. It was possible to characterize the addition product in solution by recording spectroscopic data while excess dimethylsulfane was still present. The IR and multinuclear NMR results (see Section 2) were consistent with the formation of a complex $[Cp_2Rh_2(CO)(SMe_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**IIIa**) with the structure shown. The terminal carbonyl absorption at 1988 cm^{-1} in the IR spectrum, and the two cyclopentadienyl and two trifluoromethyl resonances in the NMR spectra, are similar to those in related addition products of the type $[Cp_2Rh_2(CO)L(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ [1]. The ease with which (**IIIa**) converts back to (**I**) is unexpected given the relatively high thermal stability of some other polynuclear dimethylsulfane complexes. NMR studies of some dinuclear cyclopentadienyl–molybdenum complexes, for example, indicate that dimethylsulfane does dissociate reversibly, but elevated temperatures (70°C) are required [9]. Some rhodium complexes, including $[Rh_6(CO)_{15}(SMe_2)]$ and $[Rh_6(CO)_{14}(SMe_2)_2]$, are also stable in solution and the solid state at ambient temperatures [10].





When (**IIIa**) and excess dimethylsulfane were left in solution at room temperature for several hours, there



Scheme 1. Proposed pathway based on the Stevens rearrangement for the conversion of a coordinated dimethylsulfane to a bridging ethanethiolato group.

was a further color change to purple. After removal of solvent and TLC of the residue, two products were isolated. The minor product was the dicarbonyl complex $[(Cp_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**II**, L = CO). The major product was characterized from microanalysis and spectroscopic results as $[Cp_2Rh_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-SEt})]$ (**IVa**, R = ethyl). Key features in the identification of the product were the absence of a carbonyl absorption in the IR spectrum, and the characteristic [11,12] quartet for the $C(CF_3)H$ proton plus the $AA'B_3$ spin system for the ethanethiolato group in the NMR spectrum. The apparent transformation of two methyl groups to a single ethyl group and a proton was so unexpected that the nature of the product was confirmed by an X-ray crystal structure determination. A previous communication [5] includes a diagram of the molecular structure; the structure has been further refined and an alternative view of the molecule is presented here.

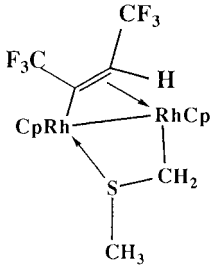
The molecular structure confirms the presence of a bridging ethanethiolato group which is symmetrically attached to the rhodium–rhodium bond. The bridging alkylidene is attached to Rh(2) by a σ-bond from C(2) and to Rh(1) by a π-bond from C(2) = C(3); the Rh(2)–C(2) σ-distance is 2.024(9) Å, and the Rh(1)–C(2) and Rh(1)–C(3) π-distances are 2.100(8) and 2.141(9) Å, respectively. The C(2)–C(3) distance for the coordinated alkene is 1.43(1)Å. The hydrogen atom attached

to C(3) was not located. There were no unusual geometric features within the trifluoromethyl or cyclopentadienyl groups.

We regard the conversion of (**IIIa**) to (**IVa**) as a metal-mediated Stevens rearrangement. In the classical Stevens rearrangement of sulfonium salts (Eq. (1)), a strong base is needed to deprotonate the alkyl group [13].

$$R-\underset{\underset{R}{|}}{S^{+}}-CH_2R' \xrightarrow{-H^{+}} R-S^{+}-\underset{\underset{R}{|}}{C}HR' \qquad (1)$$

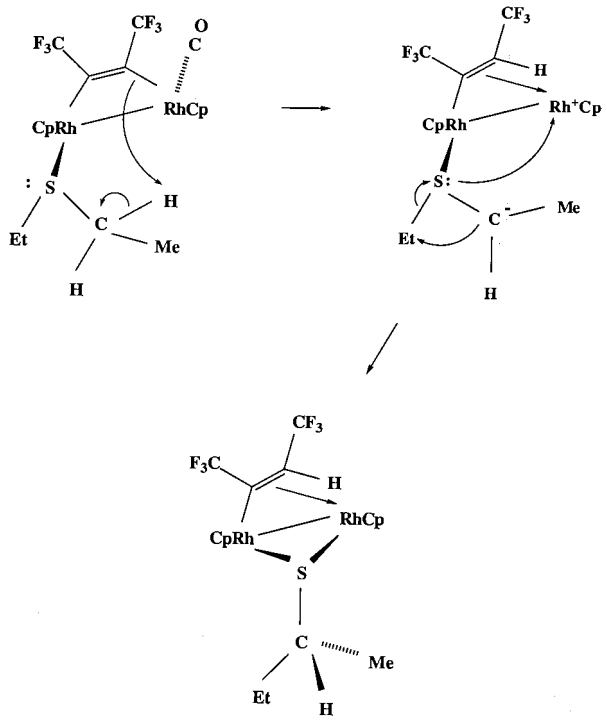
In the present system, we propose that the transfer of electron density from S to Rh in (**IIIa**) creates a pseudo-sulfonium ion, and that the alkyne with its strongly electron withdrawing substituents serves as the proton acceptor. Scheme 1 shows a possible pathway for the rearrangement. Although the zwitter ion shown in the scheme seems the most likely intermediate in the conversion of (**IIIa**) to (**IVa**), an alternative metallacyclic intermediate (**V**) cannot be discounted. However, we believe that (**V**) would be less likely than the zwitter ion to rearrange in the required manner. A closely related 2,3-sigmatropic rearrangement of allyl and propargyl sulfur ylides has been achieved on a monomeric rhenium centre [14]. Other base-promoted rearrangements of coordinated sulfur ligands have been discussed in a recent review [15].



(V)

In a previous investigation [16], we established that the reaction between (**I**) and diphenylphosphine gave the proton transfer product $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-}PPh_2)]$. It seemed reasonable to expect similar behaviour in the reactions between (**I**) and thiols. When ethanethiol was added to a solution of (**I**) in petroleum ether, there was an immediate color change from green to crimson. Work up of the reaction mixture gave some of the dicarbonyl complex (**II**, L = CO) and the complex (**IVa,** R = ethyl) in 65% yield. We did not detect the intermediate addition product $[Cp_2Rh_2(CO)(EtSH)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$, but we explored the possible formation of such intermediates in the reaction of (**I**) with the less volatile thiol PhSH. The results of this investigation are described below.

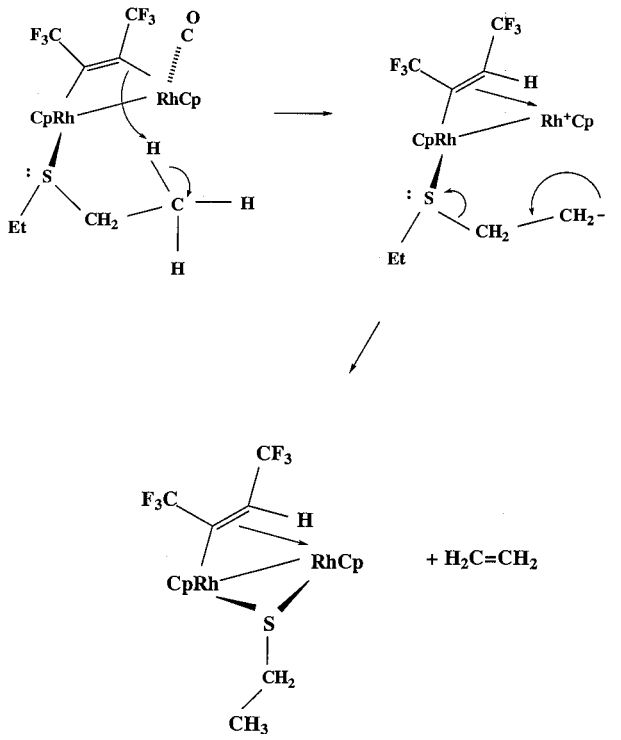
To test the generality of the metal-mediated Stevens rearrangement, the reactions between (**I**) and other dialkylsulfanes were investigated. With diethylsulfane, the initial addition was again reversible. Indeed, about 30% of (**I**) remained unchanged in solution even with an eightyfold excess of the ligand present. The addition product $[Cp_2Rh_2(CO)(SEt_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**IIIb**, R = R′ = ethyl) was characterized in solution in the presence of excess diethylsulfane from IR and NMR results. Over a period of several hours, this complex transformed into several different species. Separation of the products by TLC gave the dicarbonyl complex (**II**, L = CO) in 37% yield, a substantial amount (31% yield) of $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-}SEt)]$ (**IVa**), and a smaller amount (10% yield) of the new compound $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-}SCHMeEt)]$ (**IVb**).



Scheme 2. Proposed pathway for the conversion of (**IIIb**) to (**IVb**).

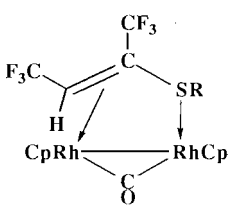
In the formation of the complexes (**IVa**) and (**IVb**) from (**IIIb**), there is loss of CO. The formation of [**II**, L = CO] in this system can be attributed to the facile displacement of coordinated diethylsulfane from (**IIb**) by this free carbon monoxide. It is possible to account for the formation of (**IVb**) in terms of another Stevens rearrangement as shown in Scheme 2. In this reaction, a proton is transferred from a methylene carbon. We propose that the formation of (**IVa**) from (**IIIb**) involves transfer of a methyl proton accompanied by ethene elimination as shown in Scheme 3.

The complex (**IVb**) was also prepared in good yield (43%) from the reaction between (**I**) and 2-butanethiol. The carbon attached to sulfur in (**IVb**) is chiral. Since the ^1H and ^{13}C resonances are duplicated in the NMR

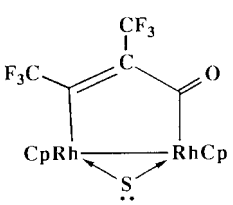


Scheme 3. Proposed pathway for the conversion of (**IIIb**) to (**IVa**).

spectra of this product (see Section 2), it is evident that both enantiomers are formed. The intensities of the appropriate peaks indicate that there are equal amounts of the two enantiomers. Clearly, there is no enantioselectivity in the formation of (**IVb**) although the initial attachment of the thiol is to a chiral rhodium centre. A second product was isolated in 28% yield from this reaction, and this green-brown solid was identified as $[Cp_2Rh_2(\mu\text{-CO})\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)HC(CF_3)SCHMeEt\}]$ (**VIa**). There is further comment on the nature of this and some related complexes below.



(VI)



(VII)

Since the above results indicate that hydrogens on both the α and β carbons of a coordinated dialkylsulfane can be activated, it was of interest to investigate the reaction of (**I**) with ethylmethylsulfane. Although the addition product $[Cp_2Rh_2(CO)(SEtMe)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**IIIc**, R = ethyl, R′ = methyl) was formed, there was always a significant amount of (**I**) in the reaction solution even with an 80-fold excess of the ligand present. Whereas the complexes (**IIIa,** R = R′ = Me) and (**IIIb**, R = R′ = Et) transformed readily to the μ-thiolato complexes (**IV**) when left in solution for several hours, (**IIIc**, R = Et, R′ = Me) was reluctant to undergo a corresponding rearrangement even after 6 h in solution with excess ligand present. Attempts to force the conversion by thermal and photochemical means were also unsuccessful. Two products were isolated in very low yields from these experiments, and they were identified as $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-}SMe)]$ (**IVc**) and $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)CO\}(\mu_2\text{-}S)]$ (**VII**). The complex (**IVc**) is presumably formed by ethene elimination from the ethyl group of the coordinated ethylmethylsulfane accompanied by proton transfer. There was no evidence of the formation of the complex $[Cp_2Rh_2\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-}SPr)]$ which would be the product of a Stevens rearrangement resulting from H^+ abstraction from the methyl group of (**IIIc**). Formation of the complex (**VII**) involves total abstraction of the sulfur from the sulfane ligand. We have identified (**VII**) in other reactions of (**1**) with sulfur containing ligands including S_8, CS_2 and isothiocyanates. The characterization of (**VII**) will be presented in a subsequent paper [6].

To further explore the influence of the alkyl substituents on these reactions, (**I**) was treated with di-*n*-propylsulfane, dibenzylsulfane, and di-*iso*-propylsulfane. In solutions containing excess of the ligands di-*n*-propylsulfane and dibenzylsulfane, the ratio of the addition product $[Cp_2Rh_2(CO)(SRR')(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]$ (**IIId**, R = R′ = Pr^n; **IIIe**, R = R′ = Bz) to unchanged (**I**) was 4:1 (for **IIId**) and 1:3 (for **IIIe**). With di-*iso*-propylsulfane, there was no evidence that any addition product was formed. These observations expose a correlation between the extent of reaction and the steric bulk of the dialkylsulfane ligand. There was no indication that the complexes (**IIId**) and (**IIIe**) convert to the corresponding μ-thiolato complexes (**IV**) when left in solution.

The difference in behaviour of (**III**, RR′ = MeEt; R = R′ = Pr^n or Bz) compared to (**III**, R = R′ = Me or Et) is difficult to understand. To determine if steric factors could have an influence on the ability to form the μ-thiolato complexes (**IV**), we investigated some additional reactions of (**I**) with thiols. Five thiols RSH were chosen with R groups of different bulkiness. In all cases, the complexes (**IVd-g**, R = Pr^n, Bu^n, Pr^i, Bu^t, and Ph) were formed readily and isolated in yields between 50 and 75%. We conclude that the Stevens

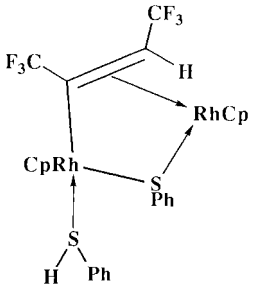
rearrangement products expected from (**III**, RR′ = MeEt; R = R′ = Pr^n or Bz) are capable of being formed, but that the weakness of the dialkylsulfane to rhodium interaction in these complexes does not support the required C–H bond activation.

As indicated above in the description of the reaction with 2-butanethiol, a second product (**VI**) can be formed in these reactions. Complexes of this type were also obtained in the reactions with Pr^iSH and Bu^tSH. Although the proposed structure is supported by the NMR results (see Section 2), and the observation of a bridging carbonyl absorption at 1801 cm^{-1} in the IR spectrum, the data could also be fitted to other possible structures. Consequently, we determined the crystal and molecular structure of complex (**VIb**; R^1 = H, R^2 = R^2 = Me) from X-ray diffraction data.

The crystal structure established that individual crystals of the compound are optically pure enantiomers; presumably, the bulk compound is a racemate. The molecular structure shows that the Rh–Rh bond (2.662(2)) is bridged by a carbonyl and an unsaturated sulfane, $Pr^iSC(CF_3)=C(CF_3)H$. The latter group is presumably formed by a 1,2-addition of Pr^iSH to the coordinated alkyne in (**I**). It is attached by a donor bond from sulfur to Rh(1) and an η^2-alkene link to Rh(2). The individual bond lengths within the dimetallacyclic unit are within the normal ranges for complexes containing the Rh–Rh–C = C–*X* (e.g. *X* = CO or CR) [17,18] and RhSRR′ [13] units. There is some asymmetry in the attachment of the carbonyl–Rh bond, with the Rh(1)–C distance being about 0.15 Å shorter than that for Rh(2)–C. This is presumably due to the different *trans*-influences of S and the alkene–C.

It is reasonable to expect that the reaction of (**I**) with thiols proceeds through an intermediate addition product (**II**, L = RSH). We attempted to substantiate this by spectroscopic monitoring of the early stages of the reaction between (**I**) and benzenethiol. Although an intermediate with a terminal carbonyl was detected by IR spectroscopy, the NMR results are not consistent with the structure (**II**). In particular, there is a quartet at δ 5.82 in the ^{1}H NMR spectrum which indicates that proton transfer to a $C(CF_3)$ carbon has already occurred. The resonances for this intermediate had totally disappeared within 20 min, and conversion to the dicarbonyl complex (**II**, L = CO) and the thiolato complex (**IV**, R = Ph) was evident. After 18 h, the NMR results showed that a new complex had been formed. We investigated this conversion further.

The reaction between (**I**) and excess benzene thiol was allowed to proceed for several hours before workup. TLC of the resultant orange solution separated a new complex that was characterized from spectroscopic data as $[Cp_2Rh_2(\mu\text{-SPh})(HSPh)(\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)C(CF_3)H]$ (**VIII**).



(VIII)

A weak molecular ion was detected in the mass spectrum, and the ^{1}H and ^{19}F NMR results (see Section 2) were consistent with the proposed formulation. Formation of (**VIII**) results from the coordinative addition of HSPh to the μ-thiolato complex (**IVh**); this results in loss of the rhodium–rhodium bonding interaction. The complex was isolated in 45% yield but was not sufficiently stable for further characterization.

4. Summary

Although the coordinative addition products (**III**) formed from (**I**) and dialkylsulfanes are unstable in solution, they can be investigated when excess ligand is present. Some of the complexes (**III**) undergo interesting Stevens rearrangements when left in solution to form thiolato complexes (**IV**). These rearrangements occur only for the two most stable addition products (**III**), indicating that the metal is intimately involved in the C–H bond activation that leads to rearrangement. Corresponding additions of the thiols RSH to (**I**) lead to rapid S–H bond activation and the formation of thiolato complexes (**IV**). These reactions occur readily with a wide range of thiols establishing that the unsuccessful Stevens rearrangements are not blocked by instability of the likely products. [2]

[2] Supplementary material. Tables of fractional atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles and observed and calculated structure factors are available as supplementary material. JOMC Supplementary Material: $[Cp_2Rh_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}(\mu_2\text{-SEt})$ (IVa, R = Et) $C_{16}H_{16}F_6Rh_2S$; Table S-IV-1 Atomic parameters; Table S-IV-2 Anisotropic thermal parameters; Table S-IV-3 Hydrogen atom positional coordinates; Table S-IV-4. Bond lengths; Table S-IV-5 Bond angles; Table S-IV-6 Structure factors. Molecular projections; JCS Chem Comm (1994) 1721. JOMC Supplementary Material: $[Cp_2Rh_2\{\mu\text{-CO}\}\{\mu\text{-}\eta^2{:}\eta^1\text{-}CH(CF_3)C(CF_3)SCHMe_2\}$ (VIb); $C_{18}H_{18}F_6ORh_2S$; Table S-VI-1 Atomic parameters; Table S-VI-2 Anisotropic thermal parameters; Table S-VI-3 Hydrogen atom positional coordinates; Table S-VI-4 Bond lengthsTable S-VI-5. Bond angles: Table S-VI-6 Structure factors; Crystal structure projection; Crystal morphology.

Acknowledgements

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