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# Dichalcogenide Cleavage and Carbonyl Insertion Reactions on a Dirhodium Bond

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**Abstract.** The reaction of the binuclear rhodium complex $[(\eta-C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2)]$ with a series of dichalcogenides, $R_2E_2$ (E = S, Se, Te; R = Me, Et, *i*-Pr, Ph, Fc; not all combinations) has provided mixtures of complexes, the majority of which have been characterized by standard spectroscopic techniques. These complexes arise as a consequence of carbonyl substitution followed by chalcogen-chalcogen bond cleavage giving $[(\eta-C_5H_5)_2Rh_2(\mu\text{-}ER)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2)]$, possibly concomitant with CO insertion into a Rh-$C_2(CF_3)_2$ bond of the product in some cases, giving $[(\eta-C_5H_5)_2Rh_2(CO)(\mu\text{-}ER)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (E = Se, Te; R = Me, Et, *i*-Pr, Ph, Fc; not all combinations). In the case of $Te_2R_2$ the dichalcogenide products have been structurally characterized for the carbonyl insertion product (for R = Et) and the simple cleavage case (for R = *i*-Pr). In both, the putative *m*-symmetry is broken by substituent dispositions and, in the R = Et adduct, torsion in the fluorocarbon skeleton.

**Keywords:** Insertion; Crystal Structure; Rhodium; Tellurium: Cleavage Reactions

## Introduction

With the oil industry potentially reaching peak production, the time for the utilisation of more marginal crude oils is approaching, those typically containing large amounts of sulfurous compounds which require removal by hydrodesulfurization over catalysts promoted by dihydrogen. This process creates large amounts of noxious $H_2S$ and a need for this to be contained for both environmentally [1, 2] and industrially important reasons, the removal of chalcogens ensuring that transition metal catalysts used in reformation reactions are not poisoned and that the environment is not polluted [3, 4].

Organometallic complexes, containing two or more adjacent metal atoms, have been proposed as models for processes occurring at associated metal sites on the surfaces of heterogeneous catalysts [5−8], and, because such complexes may display novel reactivity, notably the expectation of enhanced selectivity, utilising the impact of mutually cooperative metal atoms on substrate molecules. The role of metals in dehydrosulfurization has been explored recently [9−12] and it has been demonstrated that the interaction of chalcogenic ligands with transition metals is of major significance. The existence of several different metal atoms in an active catalyst provides many potential structural and chemical alternatives for multisite binding and catalysis of organic substrates or fragments on the metal particle [13].

The utility of molecular clusters as models for surface reactivity is based on the assumption that the reactions occurring at the metal surface mimic those taking place in simple homogeneous systems [14−17], with soluble spectroscopically accessible systems facilitating study, with the expectation that the reactivity of well-defined complexes will yield valuable information relating to interaction of the substrate and its transformation [8]. In this report we further extend our studies on the reaction of organic chalcogenides [18−20] with the dirhodium complex $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(CF_3)_2)]$, (**1**), as we seek to model the hydrodechalcogenization process.

## Experimental Section

### *General experimental conditions*

Standard techniques for handling air-sensitive materials were employed throughout this work [21]. Thin layer chromatography was performed on Kieselgel 60G: Kielselgel $60HF_{254}$ as adsorbent. Infrared spectra were recorded on a Perkin-Elmer PE 1600 FTIR spectrometer, and NMR spectra recorded on Bruker DRX400, AM300 and AC200 instruments. $^{19}F$ chemical shifts were recorded relative to internal $CFCl_3$ references, $^{31}P$ to external $H_3PO_4$ (85 %), and $^{125}Te$ to external $Me_2Te$. Electron impact mass spectra were recorded on a VG TRIO-1 GC mass spectrometer operating at 70 eV and 200 °C inlet temperature. Microanalyses were performed

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**$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(CF_3)_2)]$**, (**1**), was synthesized by the reported procedure [22].

## *Reactions of* $[(\eta-C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(CF_3)_2)]$, (1)

### (a) *With dimethyl disulfide*

Complex **1** (0.059 g, 0.112 mmol) was dissolved in diethyl ether (20 ml), and a large excess of dimethyl disulfide (0.45 g, 4.8 mmol) was added to the stirring solution. The initially green solution immediately became an orange-red colour. Stirring was continued for 75 minutes, and then all volatiles were removed under vacuum, leaving an orange solid. Four major bands were separated by TLC with hexane/dichloromethane (1:1 v/v) as eluent. Two yellow bands ($R_f$ 0.9) were extracted with dichloromethane and dried under vacuum, producing yellow solids which were identified ($^1$H NMR) as *cis*- and *trans*-$[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**2a**) (0.015 g, 24 %). A red band ($R_f$ 0.4) decomposed on work-up to give a yellow solution which was not characterized.

An orange band ($R_f$ 0.5) was extracted with dichloromethane and solvent evaporated to produce an orange solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}SMe)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$, (**3a**) (0.022 g, 34 %). Anal. Calcd. for $C_{16}H_{16}F_6Rh_2S_2$: C, 32.5; H,2.7.Found C, 32.5; H, 2.5 %.

**$^1$H NMR** ($CDCl_3$): δ 5.16 (s, 10H, $C_5H_5$); 2.51 (t, $^3J_{RhH}$ 1.3 Hz, 2.7H, $CH_3$); 1.78 (t, $^3J_{RhH}$ 1.7 HZ, 3H, $CH_3$). **$^{13}$C{$^1$H} NMR** ($CDCl_3$): δ 87.6 (d, $^1J_{Rh\text{-}C}$ 3.5 Hz, $C_5H_5$); 29.5 (s, $CH_3$); 21.9 (s, $CH_3$). **$^{19}$F NMR** ($CDCl_3$): δ −49.0 (s, $CF_3$). **MS**: *m/z* at 592 (12 %, $[M]^+$); 577 (25, $[M\text{-}Me]^+$); 562 (8, $[M\text{-}2Me]^+$); 430 (30, $[C_{12}H_{16}Rh_2S_2]^+$); 415 (80, $[C_{11}H_{13}Rh_2S]^+$); 400 (12, $[C_{10}H_{10}Rh_2S_2]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

### (b) *With diphenyl disulfide*

In a reaction similar to that described above, **1** (0.020 g, 0.038 mmol) was dissolved in dichloromethane (20 ml), and an excess of diphenyl disulfide (0.103 g, 0.472 mmol) was added to the stirring solution. A slow reaction occurred, and was not complete for 24 hours. Four major bands were isolated by TLC with hexane/dichloromethane (1:1 v/v) as eluent. Two yellow bands ($R_f$ 0.9) were extracted with dichloromethane and evaporated to dryness to give yellow solids which were identified ($^1$H NMR) as *cis*- and *trans*- **2a** (total yield 0.003 g, 14 %). An orange band ($R_f$ 0.7) was extracted with dichloromethane, and produced an orange solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}SPh)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3b**) (0.026 g, 33 %).

**$^1$H NMR** ($d_6$-acetone): δ 8.10 (d, $^3J_{HH}$ 7.8 Hz, 2H); 7.50 (m, 2H); 7.39 (m, 3H); 7.11 (m, 3H); 5.16 (s, 10H, $C_5H_5$). **$^{19}$F NMR** ($CDCl_3$): δ −49.9 (s, $CF_3$). **MS**: *m/z* 716 (12 %, $[M]^+$), 639 (1, $[M\text{-}Ph]^+$), 607 (8, $[C_{20}H_{15}F_6Rh_2S]^+$), 554 (34, $[C_{22}H_{20}Rh_2S_2]^+$), 477 (10, $[C_{16}H_{15}Rh_2S_2]^+$), 368 (12, $[C_{10}H_{10}Rh_2S]^+$), 233 (100, $[C_{10}H_{10}Rh]^+$).

A brown band ($R_f$ 0.2) was extracted with dichloromethane and produced a brown solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-}S_2Ph_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**2b**) (0.022 g, 27 %).

**IR** ($CH_2Cl_2$): ν(CO) 1989s; ν (C=C) at 1618m $cm^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 8.10 (d, $^3J_{HH}$ 7.8 Hz, 2H); 7.50 (m, 2H); 7.39 (m, 3H); 7.11 (m, 3H); 5.46 (s, 5H, C5H5); 5.35 (broad s, 5H, $C_5H_5$). **$^{19}$F NMR** ($CDC1_3$): δ −51.3 (q, $^5F_{FF}$ 10.3 Hz, 3F, $CF_3$); −55.3 (q, $^5F_{FF}$ 10.3 Hz, 3F, $CF_3$). **MS**: *m/z* 716 (<1, $[M\text{-}CO]^+$), 554 (1, $[C_{22}H_{20}Rh_2S_2]^+$), 477 (<1, $[C_{16}H_{15}Rh_2S_2]^+$), 368 (<1, $[C_{10}H_{10}Rh_2S]^+$), 233 (12, $[C_{10}H_{10}Rh]^+$), 186 (100, $[C_{12}H_{10}S]^+$).

This complex slowly converts to **3b** over several days.

### (c) *With diferrocenyl disulfide*

Complex **1** (0.030 g, 0.057 mmol) was dissolved in dichloromethane (20 ml), and solid diferrocenyl disulfide (0.080 g, 0.184 mmol) was added in portions with stirring. There was an immediate colour change to red. After 10 minutes, all volatiles were removed under vacuum. Tlc with hexane/dichloromethane (1:1 v/v) produced 4 bands. A yellow band ($R_f$ 0.9) was extracted with dichloromethane and evaporated to dryness to give a yellow solid which was identified ($^1$H NMR) as trace quantity of **2a**.

An orange band ($R_f$ 0.1) produced an orange solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}SFc)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3c**) (0.010 g, 19 %).

**$^1$H NMR** ($CDCl_3$): δ 5.24 (s, 10H, Rh- $C_5H_5$); 4.45 (m, 2H, $FeC_5H_4$); 4.34 (m, 2H, $FeC_5H_4$); 4.22 (s, 5H, $FeC_5H_5$); 4.16 (s, 5H, $FeC_5H_5$); 4.07 (m, 4H, $FeC_5H_4$). **$^{19}$F NMR** ($CDCl_3$): δ −49.6 (s $CF_3$). **MS**: *m/z* 932 (2 $[M]^+$); 803 (1, $[C_{28}H_{24}F_6Rh_2S]^+$); 319 (60 $[C_{10}H_8FeRhS]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

### (d) *With diphenyl diselenide*

Complex **1** (0.028 g, 0.053 mmol) was dissolved in dichloromethane (20 ml) and an excess of diphenyl diselenide (0.054 g, 0.173 mmol) was added to the stirring solution. A colour change from green to orange-red occurred within 10 minutes. After 2 hours, all volatiles were removed *in vacuo* leaving an orange-red solid. Tlc with hexane/dichloromethane (3:1 v/v) as eluent separated four main products. The two minor orange products at $R_f$ 0.3-0.4 were not further characterized. Two yellow bands ($R_f$ 0.9) were extracted with dichloromethane evaporated to dryness to give yellow solids which were identified ($^1$H NMR) as *cis*- and *trans*- **2a** (0.005 g, 17 %). A dark orange-red band ($R_f$ 0.7) produced a red solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}SePh)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3d**) (0.022 g, 51 %). Anal. Calcd. for $C_{26}H_{20}F_6Rh_2Se_2$: C, 38.6; H, 2.5. Found C, 38.5; H, 2.3 %.

**$^1$H NMR** ($CDCl_3$): δ 7.92 (dd, $^3J_{HH}$ 7.8 Hz and $^4J_{HH}$ 1.6 Hz 2H, *m*-H $C_6H_5$); 7.44 (dd, $^3J_{HH}$ 8.2 Hz and $^4J_{HH}$ 1.3 Hz, 2H, *m-H* $C_6H_5$); 7.31 (m, 3H, *o*-, *p*-H, $C_6H_5$); 7.16 (m, 3H, *o*-, *p*-H, $C_6H_5$); 5.07 (s, 10H, $C_5H_5$). **$^{19}$F NMR** (CDCl3): δ −49.9 (s, $CF_3$). **MS**: *m/z* 812 (2 % $[M]^+$); 655 (25, $[C_{20}H_{15}F_6Rh_2Se]^+$); 570 (10, $[C_{22}H_{20}Rh_2Se]^+$); 493 (12, $[C_{16}H_{15}Rh_2Se]^+$); 431 (8, $[C_5H_5Rh_2Se_2]^+$); 325 (35, $[C_{11}H_{10}RhSe]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

An orange band ($R_f$ 0.2) produced an orange solid which was characterized as as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}SePh)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4a**) (0.010 g, 23 %).

**IR** ($CH_2Cl_2$): ν(CO) 1618 $cm^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 8.10 (dd, $^3J_{HH}$ 7.6 Hz and $^4J_{HH}$ 1.6 Hz, 2H, *o*-H, $C_6H_5$); 7.72 (dd, $^3J_{HH}$ 5.7 Hz and $^4J_{HH}$ 3.2 Hz, 2H, *o*-H, $C_6H_5$); 7.52 (dd, $^3J_{HH}$ 5.7 Hz and $^4J_{HH}$ 3.2 Hz, 1H, *p*-H, $C_6H_5$); 7.35 (m, 2H, $C_6H_5$); 7.16 (m, *m*-, *p*-HI 3H, $C_6H_5$); 5.15 (s, 5H, $C_5H_5$); 5.09 (s, 5H, $C_5H_5$). **$^{19}$F NMR** ($CDCl_3$): δ −50.9 (q, $^5F_{FF}$ 15.3 Hz, 3F, $CF_3$); −55.8 (q, $^5J_{FF}$ 15.3 Hz, 3F, $CF_3$). **MS**: *m/z* 655 (10, $[C_{20}H_{15}F_6Rh_2Se]^+$); 570 (4, $[C_{22}H_{20}Rh_2Se]^+$); 493 (4, $[C_{16}H_{15}Rh_2Se]^+$); 325 (35, $[C_{11}H_{10}RhSe]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

### (e) *With diferrocenyl diselenide*

Complex **1** (0.043 g, 0.082 mmol) was dissolved in dichloromethane (20 ml). Solid diferrocenyl diselenide (0.059 g, 0.112 mmol) was added in portions with stirring. There was an immediate colour

change to red. Stirring was continued for 10 minutes, then all volatiles were removed under vacuum. TLC with hexane/dichloromethane (1:1 v/v) produced three bands. A yellow band ($R_f$ 0.9) was extracted with dichloromethane, and evaporated to dryness to give a yellow solid which was identified ($^1$H NMR) as **2a** (trace quantity).

A red band ($R_f$ 0.4) was similarly worked up to produce a red solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}SeFc)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3e**) (0.030 g, 36 % yield). Anal. Calcd. for $C_{34}H_{28}F_6Fe_2Rh_2Se_2$: C, 39.8; H, 2.8. Found C, 39.4; H, 2.5 %.

**$^1$H NMR** ($CDCl_3$): δ 5.21 (s, 10H, $RhC_5H_5$); 4.38 (m, 2H, $FeC_5H_4$); 4.31 (m, 2H, $FeC_5H_4$); 4.22 (s, 5H, $FeC_5H_5$); 4.15 (s, 5H, $FeC_5H_5$); 4.10 (m, 4H, $FeC_5H_4$). **$^{19}$F NMR** ($CDCl_3$): δ −49.5 (s, $CF_3$). **MS**: *m/z* 763 (24 %, $[M\text{-}SeFc]^+$); 578 (5, $[C_{14}H_{10}F_6Rh_2Se]^+$); 433 (10, $[C_{15}H_{14}FeRhSe]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

An orange band ($R_f$ 0.1) was similarly worked up to produce an orange solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}SeFc)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4b**) (0.010 g, 12 % yield).

**IR** ($CH_2Cl_2$): ν(CO) 1598 cm$^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.49 (s, 5H, $RhC_5H_5$); 5.05 (s, 5H, $RhC_5H_5$); 4.38 (m, 2H, $FeC_5H_4$); 4.31 (m, 2H, $FeC_5H_4$); 4.22 (s, 5H, $FeC_5H_5$); 4.13 (s, 5H, $FeC_5H_5$); 4.13 (m, 4H, $FeC_5H_4$). **$^{19}$F NMR** ($CDC1_3$): δ −51.0 (q, $^5J_{FF}$ 15.0 Hz, 3F, $CF_3$); −55.4 (q, $^5J_{FF}$ 15.0 Hz, 3F, $CF_3$). **Mass spectrum**: *m/z* at 763 (20, $[M\text{-}SeFc\text{-}CO]^+$); 578 (10, $[C_{14}H_{10}F_6Rh_2Se]^+$); 433 (12, $[C_{15}H_{14}FeRhSe]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

On standing, **4b** slowly converted to an alternative form, **4b′**. The conversion occurred over several weeks, and did not appear to accelerate when the complex was left in solution.

**IR** ($CH_2C1_2$): ν(CO) at 1600 cm$^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.49 (s, 5H, $RhC_5H_5$); 5.41 (s, 5H, $RhC_5H_5$); 4.38 (m, 2H, $FeC_5H_4$); 4.30 (m, 2H, $FeC_5H_4$); 4.19 (s, 5H, $FeC_5H_4$); 4.13 (s, 5H, $FeC_5H_5$); 4.10 (m, 4H, $FeC_5H_4$). **$^{19}$F NMR** ($CDC1_3$): δ −51.4 (q, $^5J_{FF}$ 15.0 Hz, 3F, $CF_3$); −55.8 (q, $^5J_{FF}$ 15.0 Hz, 3F, $CF_3$). The mass spectrum was identical to that for **4b**.

## (f) *With dimethyl ditelluride*

In a reaction similar to that described above, complex **1** (0.032 g, 0.061 mmol) was dissolved in dichloromethane (20 ml), and an excess of dimethyl ditelluride (0.07 g, 0.25 mmol) was added to the stirring solution. After stirring for 30 minutes, the volatiles were removed and three major bands were separated by TLC. An orange band ($R_f$ 0.9) was extracted with dichloromethane, and evaporation of the solvent left an orange oil which was identified ($^1$H NMR) as unreacted dimethyl ditelluride.

A red band ($R_f$ 0.7) was similarly worked up and produced a red solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}TeMe)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3f**) (0.020 g, 42 % yield).

**$^1$H NMR** ($CDCl_3$): δ 5.17 (s, 10H, $C_5H_5$); 1.77 (s, 3H, $CH_3$); 1.76 (s, 3H, $CH_3$). **$^{19}$F NMR** ($CDC1_3$): δ −49.8 (s, $CF_3$). **Mass spectrum**: *m/z* 784 (4 %, $[M]^+$); 769 (24, $[M\text{-}Me]^+$); 643 (5, $[M\text{-}TeMe]^+$); 628 (5, $[C_{14}H_{10}F_6Rh_2Te]^+$); 592 (4, $[C_{10}H_{10}F_6Rh_2Te_2]^+$; 464 (4, $[C_{10}H_{10}Rh_2Te]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

An orange band ($R_f$ 0.3) was similarly worked up and produced an orange solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}TeMe)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4c**) (0.015 g, 30 % yield).

**IR** ($CH_2Cl_2$): ν(CO) 1599 cm$^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.40 (s, 5H, $RhC_5H_5$); 5.32 (s, 5H, $RhC_5H_5$); 1.89 (s, 3H, $CH_3$); 1.70 (s, 3H, $CH_3$). **$^{19}$F NMR** ($CDCl_3$): δ −50.6 (q, $^5J_{FF}$ 15.3 Hz, 3F, $CF_3$); −55.1 (q, $^5J_{FF}$ 15.3 Hz, 3F, $CF_3$). **Mass spectrum**: *m/z* at 784 (45, $[M\text{-}CO]^+$); 769 (22, $[C_{15}H_{13}F_6Rh_2Te_2]^+$); 643 (10, $[C_{15}H_{13}F_6Rh_2Te]^+$); 628 (8, $[C_{14}H_{10}F_6Rh_2Te]^+$); 592 (8, $[C_{10}H_{10}Rh_2Te_2]^+$); 464 (4, $[C_{10}H_{10}Rh_2Te]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

## (g) *With diethyl ditelluride*

In a reaction similar to that described above, complex **1** (0.030 g, 0.057 mmol) was dissolved in dichloromethane (20 ml), and an excess of diethyl ditelluride (0.102 g, 0.326 mmol) was added to the stirring solution. An immediate colour change from green to dark orange occurred. The mixture was stirred for 2 hours. All volatiles were then removed, leaving an orange solid. TLC with hexane/dichloromethane (1:1 v/v) separated seven bands.

An orange band ($R_f$ 0.9) was extracted with dichloromethane, and evaporation of the solvent left an orange oil which was identified ($^1$H NMR) as excess diethyl ditelluride.

A yellow band ($R_f$ 0.8) was similarly worked up and produced a small quantity of a yellow solid which was identified (IR) as **2a**.

A red band ($R_f$ 0.7) was similarly worked up and produced a red solid which was identified $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}TeEt)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3g**) (0.024 g, 15 % yield).

**$^1$H NMR** ($CDCl_3$): δ 5.20 (s, 10H, $C_5H_5$); 2.42 (q, 2H, $^3J_{HH}$ 7.6 Hz, $CH_2$); 2.36 (q, 2H, $^3J_{HH}$ 6.8 Hz, $CH_2$); 1.42 (t, 3H, $^3J_{HH}$ 7.6 Hz, $CH_3$); 1.22 (q, 3H, $^3J_{HH}$ 6.8 Hz, $CH_3$). **$^{19}$F NMR** ($CDCl_3$): δ −49.4 (s, $CF_3$). **Mass spectrum**: *m/z* at 812 (<1 %, $[M]^+$); 783 (7, $[M\text{-}Et]^+$); 754 (1, $[M\text{-}2Et]^+$); 628 (6, $[C_{14}H_{10}F_6Rh_2Te]^+$); 592 (8, $[C_{10}H_{10}Rh_2Te_2]^+$); 527 (4, $[C_5H_5Rh_2Te_2]^+$); 466 (3, $[C_{10}H_{10}Rh_2Te]^+$); 424 (5, $[C_5H_5RhTe_2]^+$) ; 233 (100, $[C_{10}H_{10}Rh]^+$).

An orange band ($R_f$ 0.3) was similarly worked up and produced an orange solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}TeEt)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4d**) (0.041 g, 58 % yield).

**IR** ($CH_2C1_2$): ν(CO) 1597 cm$^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.36 (s, 5H, $C_5H_5$); 5.32 (s, 5H, $C_5H_5$); 2.56 (q, 2H, $^3J_{HH}$ 7.7 Hz, $CH_2$); 2.11 (q, 2H, $^3J_{HH}$ 7.7 Hz, $CH_2$); 1.47 (t, 3H, $^3J_{HH}$ 7.7 Hz, $CH_3$); 1.04 (q, 3H, $^3J_{HH}$ 7.7 HZ, $CH_3$). **$^{19}$F NMR** ($CDCl_3$): δ −50.6 (q, 3F, $^5J_{FF}$ 15.3 HZ, $CF_3$); −55.1 (q, 3F, $^5J_{FF}$ 15.3 HZ, $CF_3$). **Mass spectrum**: *m/z* 812 (<1 %, $[M\text{-}CO]^+$); 783 (3, $[C_{16}H_{15}F_6Rh_2Te_2]^+$); 754 (1, $[C_{14}H_{10}F_6Rh_2Te_2]^+$); 650 (2, $[C_{14}H_{20}Rh_2Te_2]^+$); 628 (4, $[C_{14}H_{10}F_6Rh_2Te]^+$); 592 (5, $[C_{10}H_{10}Rh_2Te_2]^+$); 527 (3, $[C_5H_5Rh_2Te_2]^+$); 466 (3, $[C_{10}H_{10}Rh_2Te]^+$); 424 (5, $[C_5H_5RhTe_2]^+$) ; 233 (100, $[C_{10}H_{10}Rh]^+$). Crystals of **4d** were grown by slow evaporation of a dichloromethane solution of the complex.

## (h) *With diisopropyl ditelluride*

In a reaction similar to that described above, complex **1** (0.044 g, 0.084 mmol) was dissolved in dichloromethane (20 ml). An excess of diisopropyl ditelluride (0.10 g, 0.29 mmol) was added dropwise with stirring. There was an immediate colour change to reddish orange. Stirring was continued for 30 minutes, then all volatiles were removed under vacuum. TLC with hexane/dichloromethane (1:1 v/v) produced four bands.

An orange band ($R_f$ 0.9) was identified ($^1$H NMR) as unreacted diisopropyl ditelluride (trace quantity).

A yellow band ($R_f$ 0.8) was identified ($^1$H NMR) as **2a** (trace quantity).

A red band ($R_f$ 0.7) produced a red solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}Te(i\text{-}Pr))_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3h**) (0.24 g, 34 % yield).

**$^1$H NMR** ($CDCl_3$): δ 5.22 (s, 10H, $C_5H_5$); 3.07 (septet, $^3J_{HH}$ 7.2 Hz, 1H, CH); 2.79 (septet, $^3J_{HH}$ 7.2 Hz, 1H, CH); 1.45 (d, $^3J_{HH}$ 7.2 Hz, 6H, $CH_3$); 1.33 (d, $^3J_{HH}$ 7.2 Hz, 6H, $CH_3$). **$^{19}$F NMR** ($CDCl_3$): δ −52.1 (s, $CF_3$). **Mass spectrum**: *m/z* 797 (4 %, $[M\text{-}Pr]^+$); 754 (2, $[C_{14}H_{10}F_6Rh_2Te_2]^+$); 628 (4, $[C_{14}H_{10}F_6Rh_2Te]^+$); 592 (10, $[C_{10}H_{10}Rh_2Te]^+$); 527 (2, $[C_5H_5Rh_2Te_2]^+$); 462 (4, $[Rh_2Te_2]^+$); 424 (2, $C_5H_5RhTe_2$); 233 (100, $[C_{10}H_{10}Rh]^+$). Crystals of **3h** were grown by slow evaporation of a dichloromethane solution of the complex.

An orange band ($R_f$ 0.3) produced an orange solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}Te(i\text{-}Pr))_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4e**) (0.041 g, 56 % yield).

**IR** ($CH_2C1_2$): ν(CO) 1599m $cm^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.38 (s, 5H, $C_5H_5$); 5.36 (s, 5H, $C_5H_5$); 2.92 (septet, $^3J_{HH}$ 7.1 Hz, 1H, CH); 2.70 (septet, $^3J_{HH}$ 7.2 Hz, 1H, CH); 1.55 (d, $^3J_{HH}$ 7.1 HZ, 3H, $CH_3$); 1.46 (d, $^3J_{HH}$ 7.2 Hz, 3H, $CH_3$); 1.15 (d, $^3J_{HH}$ 7.1 Hz, 3H, $CH_3$); 1.10 (d, $^3J_{HH}$ 7.2 Hz, 3H, $CH_3$). **$^{19}$F NMR** ($CDCl_3$): δ −50.5 (q, $^5J_{FF}$ 5.4 Hz, 3F, $CF_3$); −55.2 (q, $^5J_{FF}$ 15.4 Hz, 3F, $CF_3$). **Mass spectrum**: *m/z* at 825 (2 %, $[M\text{-}CO]^+$); 797 (2 %, $[C_{17}H_{17}F_6Rh_2Te_2]^+$); 754 (2, $[C_{14}H_{10}F_6Rh_2Te_2]^+$); 628 (3, $[C_{14}H_{10}F_6Rh_2Te]^+$); 592 (8, $[C_{10}H_{10}Rh_2Te_2]^+$); 527 (4, $[C_5H_5Rh_2Te_2]^+$); 462 (6, $[Rh_2Te_2]^+$); 424 (6, $C_5H_5RhTe_2$); 233 (100, $[C_{10}H_{10}Rh]^+$).

## (i) *With diphenyl ditelluride*

A slight excess of diphenyl ditelluride (0.028 g, 0.068 mmol) was added in portions over 2 minutes to a stirred solution of complex **1** (0.031 g, 0.059 mmol) in dichloromethane (20 ml) after 2 hours all volatiles were then removed, leaving a reddish-orange solid. TLC with hexane/dichloromethane (1:1 v/v) as eluent separated seven bands. Each band was extracted with dichloromethane and solvent was removed under vacuum.

An orange band ($R_f$ 0.9) was extracted with dichloromethane, and evaporated to dryness, producing an orange solid which was identified ($^1$H NMR) as unreacted diphenyl ditelluride (trace quantity).

Two yellow bands ($R_f$ 0.8) were similarly worked up and produced yellow solids which were identified ($^1$H NMR) as *cis*- and *trans*- **2a** (total yield 0.005 g, 17 %).

A dark orange-red band ($R_f$ 0.7) produced a red solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}TePh)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3i**) (0.010 g, 19 %).

**$^1$H NMR** ($CDCl_3$): δ 7.72 (d, $^3J_{HH}$ 7.0 Hz, 2H, *o*-H, $C_6H_5$); 7.55 (d, $^3J_{HH}$ 7.0 HZ, 2H, *o*-H, $C_6H_5'$); 7.34 (m, 1H, *p*-H, $C_6H_5$); 7.26 (m, 1H, *p*-H, $C_6H_5$); 7.21 (m, 2H, *m*-H, $C_6H_5$); 7.11 (m, 2H, *m*-H, $C_6H_5'$); 5.16 (s, 10H, $C_5H_5$). $^{19}$F NMR ($CDCl_3$): δ −50.5 (s, $CF_3$). **$^{125}$Te NMR** ($CDCl_3$): δ −7 (d, $^1J_{TeRh}$ 87 Hz, TePh); −115 (dd, $^1J_{TeRh} \approx {}^1J_{TeRh'}$ 76 Hz, TePh). **Mass spectrum**: *m/z* 908 ( <1 %, $[M]^+$); 831 (2, $[M\text{-}Ph]^+$); 705 (2, $[M\text{-}\ TePh]^+$); 628 (4, $[C_{14}H_{10}F_6Rh_2Te]^+$); 604 (2, $[C_{11}H_{10}Rh_2Te_2]^+$); 462 (4, $[Rh_2Te_2]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

An orange band at $R_f$ 0.2 produced an orange solid which was characterized as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}Te(i\text{-}Pr))_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4f**) 0.037 g, 69 %). Anal. Calcd. for $C_{27}H_{20}F_6ORh_2Te_2$: C, 34.7; H, 2.2; F, 12.2. Found C, 36.1; H, 2.1; F, 11.4 %.

**IR** ($CH_2Cl_2$): ν(CO) 1608m $cm^{-1}$. $^1$H NMR ($CDCl_3$): δ 7.86 (dd, $^3J_{HH}$ 8.0 Hz, $^4J_{HH}$ 1.2 HZ, 2H, *o*-H, $C_6H_5$); 7.39 (t, $^3J_{HH}$ 6.2 HZ, 1H, *p*-H, $C_6H_5$); 7.06 (m, 2H, *m*-H, $C_6H_5$); 7.2-7.3 (m, 5H *o*-,*m*-,*p*-H, $C_6H_5'$); 5.30 (s, 5H, $C_5H_5$); 5.15 (s, 5H, $C_5H_5$). $^1$H NMR ($d_6$-acetone): δ 8.02 (d, $^3J_{HH}$ 7.0 Hz, 2H, *o*-H, $C_6H_5$); 7.50 (t, $^3J_{HH}$ 7.2 Hz, 1H, *p*-H, $C_6H_5$); 7.3-7.4 (m, 4H *o*,*m*-H, $C_6H_5$); 7.20 (t, 1H, *p*-H $C_6H_5'$); 7.02 (m, 2H, m-H, $C_6H_5$); 5.40 (s, 5H, $C_5H_5$); 5.30 (s, 5H, $C_5H_5$). $^{19}$F NMR ($CDCl_3$): δ −50.6 (q, $^5J_{FF}$ 5.5 Hz, 3F, $CF_3$); −55.8 (q, $^5J_{FF}$ 5.5 Hz, 3F, $CF_3$). $^{125}$Te NMR ($CDCl_3$): δ −246 (dd, $^1J_{TeRh} \approx {}^1J_{TeRh'}$ 97 HZ, TePh); −8 (dd, $^1J_{TeRh} \approx {}^1J_{TeRh'}$ 75 Hz). Mass spectrum: *m/z* at 908 (<1 %, $[M\text{-}CO]^+$); 705 (5, $[C_{20}H_{15}F_6Rh_2Te_2]^+$); 628 (2, $[C_{14}H_{10}F_6Rh_2Te]^+$); 604 (2, $[C_{11}H_{10}Rh_2Te_2]^+$); 462 (3, $[Rh_2Te_2]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$).

## (j) *With diferrocenyl ditelluride*

In a reaction similar to that described above, complex **1** (0.062 g, 0.118 mmol) was dissolved in dichloromethane (20 ml). Diferrocenyl ditelluride (0.070 g, 0.112 mmol) was added in portions with stirring, after 10 minutes all volatiles were removed under vacuum. TLC with hexane/dichloromethane (1:1 v/v) produced four bands.

An orange band ($R_f$ 0.9) was extracted with dichloromethane, and evaporation of the solvent produced an orange solid which was identified ($^1$H NMR) as excess diferrocenyl ditelluride (trace quantity).

A yellow band ($R_f$ 0.8) was similarly worked up and produced a yellow solid which was identified ($^1$H NMR) as **2a** (trace quantity).

A red band ($R_f$ 0.4) was similarly worked up and produced a red solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}TeFc)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3j**) 0.040 g, 30 % yield). Anal. Calcd. for $C_{34}H_{28}F_6Fe_2Rh_2Te_2$: C, 36.4; H, 2.5; F, 10.1 %. Found C, 36.3; H, 2.6; F, 10.3 %.

**$^1$H NMR** ($CDCl_3$): δ 5.25 (s, 10H, $RhC_5H_5$); 4.28 (m, 4H, $FeC_5H_4$); 4.21 (s, 5H, $FeC_5H_5$); 4.18 (m, 4H, $FeC_5H_4$); 4.17 (s, 5H, $FeC_5H_5$). **$^{19}$F NMR** ($CDCl_3$): δ −50.1 (s, $CF_3$). **Mass spectrum**: *m/z* at 813 (9 %, $[M\text{-}TeFc]^+$); 651 (6, $[C_{20}H_{19}FeF_6Rh_2Te]^+$); 498 (15, $[C_{10}H_{10}Fe_2Te_2]^+$); 353 (55, $[C_{15}H_{14}FeRh]^+$); 233 (85, $[C_{10}H_{10}Rh]^+$); 186 (100, $[C_{10}H_{10}Fe]^+$).

A red band ($R_f$ 0.5) was similarly worked up and produced a red solid which was identified as an alternative form of $[(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}TeFc)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2)]$ (**3j′**) (0.010 g, 8 % yield).

**$^1$H NMR** ($CDCl_3$): δ 5.25 (s, 10H, $RhC_5H_5$); 4.13 (s, 10H, $FeC_5H_5$); 4.05 (m, 4H, $FeC_5H_4$); 3.84 (m, 4H, $FeC_5H_4$). **$^{19}$F NMR** ($CDCl_3$): δ −49.9 (s, $CF_3$). **Mass spectrum**: *m/z* 813 (15 %, $[M\text{-}TeFc]^+$); 651 (10, $[C_{20}H_{19}FeF_6Rh_2Te]^+$); 498 (10, $[C_{10}H_{10}Fe_2Te]^+$); 353 (65, $[C_{15}H_{14}FeRh]^+$); 233 (100, $[C_{10}H_{10}Rh]^+$); 186 (60, $[C_{10}H_{10}Fe]^+$)).

An orange band ($R_f$ 0.1) produced an orange solid which was identified as $[(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}Fc_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2(CF_3)_2C(O))]$ (**4g**) (0.015 g, 11 % yield).

**IR** ($CH_2C1_2$): ν(CO) 1604 $cm^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.53 (s, 5H, $RhC_5H_5$); 5.13 (s, 5H, $RhC_5H_5$); 4.1-4.4(m, 8H, $FeC_5H_4$); 4.20 (s, 5H, $FeC_5H_5$); 4.14 (s, 5H, $FeC_5H_5$). **$^{19}$F NMR** ($CDCl_3$): δ −50.6 (q, 3F, $^5J_{FF}$ 15.4 HZ, $CF_3$); −55.2 (q, 3F, $^5J_{FF}$ 15.4 HZ, $CF_3$). **Mass spectrum**: *m/z* 813 (10 %, $[M\text{-}TeFc]^+$); 651 (10, $[C_{20}H_{19}FeRh_2Te]^+$); 498 (20, $[C_{10}H_{10}Fe_2Te_2]^+$); 353 (40, $[C_{15}H_{14}FeRh]^+$); 233 (90, $[C_{10}H_{10}Rh]^+$); 186 (100, $[C_{10}H_{10}Fe]^+$).

On standing **4g** slowly converted to an alternative form **4g′**. The conversion occurred in the solid state over several weeks and did not appear to accelerate in solution.

**IR** ($CH_2C1_2$): ν(CO) 1604 $cm^{-1}$. **$^1$H NMR** ($CDCl_3$): δ 5.53 (s, 5H, $RhC_5H_5$); 5.28 (s, 5H, $RhC_5H_5$); 4.1-4.5 (m, 8H, $FeC_5H_4$); 4.20 (s, 5H, $FeC_5H_5$); 4.15 (s, 5H, $FeC_5H_5$). **$^{19}$F NMR** ($CDCl_3$): δ −43.9 (q, 3F, $^5J_{FF}$ 13.4 HZ, $CF_3$); −54.6 (q, 3F, $^5J_{FF}$ 13.4 HZ, $CF_3$). **Mass spectrum**: *m/z* 813 (5 %, $[M\text{-}TeFc]^+$); 651 (4, $[C_{20}H_{19}FeRh_2Te]^+$); 498 (20, $[C_{10}H_{10}Fe_2Te_2]^+$); 353 (33, $[C_{15}H_{14}FeRh]^+$); 233 (85, $[C_{10}H_{10}Rh]^+$); 186 (100, $[C_{10}H_{10}Fe]^+$).

## *Structure determination of 4d*

A full sphere of CCD area-detector diffractometer data was measured (ω-scans, $2\theta_{max} = 70°$; monochromatic Mo Kα radiation, λ = 0.71073 Å; *T ca.* 100 K), yielding 44424 reflections, these merging to 9495 unique ($R_{int} = 0.027$) after 'empirical'/multiscan absorption correction (proprietary software; $\mu_{Mo} = 4.2$ $mm^{-1}$; specimen: 0.37 x 0.31 x 0.19 mm; '$T$'$_{min/max} = 0.63$), 8895 with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement, refining anisotropic displacement parameters for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ being included, following a riding model. Conventional residuals on $F^2$ at convergence are $R1 = 0.028$, $wR2 = 0.067$ (weights: $(\sigma^2(F^2) + (0.0202P)^2 + 9.5945P)^{-1}$) ($P = (F_o^2 + 2F_c^2)/3$, $x_{abs}$ refining to 0.04(2). Neutral atom complex scattering factors were employed within the SHELXL-97 program

[23]. Pertinent results are given below and in Table 1 and Fig. 1. A full *.cif* deposition resides with the Cambridge Crystallographic Data Centre, CCDC 615216. Copies may be obtained free of charge on application to The Director CCDC, 12 Union Road, Cambridge CB2 1EX, UK (Fax: int. code + (1223) 336-033; email for inquiry: fileserv@ccdc.cam.ac.uk; email for deposition: deposit@ccdc.cam.ac.uk).

**Table 1** Selected geometries, **4d**

| Atoms | Parameter | Atoms | Parameter |
|---|---|---|---|
| Distances/Å | | | |
| Rh(1)-Te(1) | 2.5873(5) | Rh(2)-Te(1) | 2.5755(4) |
| Rh(1)-Te(2) | 2.5756(5) | Rh(2)-Te(2) | 2.5774(5) |
| Rh(1)-C(2) | 2.095(4) | Rh(2)-C(5) | 1.991(4) |
| Rh(1)-C(cp) | 2.220(5) −2.253(4) | Rh(2)-C(cp) | 2.241(4) −2.287(5) |
| Rh(1)-C(100) | $1.87_6$ | Rh(2)-C(200) | $1.90_7$ |
| Te(1)-C(11) | 2.169(4) | Te(2)-C(21) | 2.170(4) |
| C(3)-C(2) | 1.362(6) | C(3)-C(5) | 1.512(6) |
| C(1)-C(2) | 1.512(6) | C(3)-C(4) | 1.530(5) |
| | | C(5)-O(5) | 1.227(6) |
| Angle/degrees | | | |
| C(100)-Rh(1)-Te(1) | $127._0$ | C(200)-Rh(2)-Te(1) | $128._1$ |
| C(100)-Rh(1)-Te(2) | $124._3$ | C(200)-Rh(2)-Te(2) | $131._8$ |
| C(100)-Rh(1)-C(2) | $131._9$ | C(200)-Rh(2)-C(5) | $126._1$ |
| C(2)-Rh(1)-Te(1) | 82.8(1) | C(5)-Rh(2)-Te(1) | 89.7(1) |
| C(2)-Rh(1)-Te(2) | 93.0(1) | C(5)-Rh(2)-Te(2) | 83.2(1) |
| Te(1)-Rh(1)-Te(2) | 82.27(2) | Te(1)-Rh(2)-Te(2) | 82.54(2) |
| Rh(1)-Te(1)-Rh(2) | 93.54(2) | Rh(1)-Te(2)-Rh(2) | 93.68(2) |
| C(11)-Te(1)-Rh(1) | 103.9(1) | C(11)-Te(1)-Rh(2) | 98.1(1) |
| C(21)-Te(2)-Rh(1) | 104.8(1) | C(21)-Te(2)-Rh(2) | 107.4(1) |
| Rh(1)-C(2)-C(3) | 128.9(3) | Rh(2)-C(5)-C(3) | 127.6(3) |
| Rh(1)-C(2)-C(1) | 114.1(3) | Rh(2)-C(5)-O(5) | 118.5(3) |
| C(1)-C(2)-C(3) | 116.7(4) | C(3)-C(5)-O(5) | 113.8(4) |
| C(4)-C(3)-C(2) | 126.3(4) | C(4)-C(3)-C(5) | 109.0(4) |
| C(2)-C(3)-C(5) | 124.6(4) | | |

***Crystal Data***: $C_{19}H_{20}F_6ORh_2Te_2$, $M$ = 839.4. Orthorhombic, space group $Pna2_1$ ($C^9_{2v}$, No. 33), $a$ = 21.1656(7), $b$ = 9.3360(10), $c$ = 11.082(2) Å, $V$ = 2197 Å$^3$ $D_c$ ($Z$ = 4) = $2.53_8$ g cm$^{-3}$.

## Results and Discussion

Reaction of [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)(μ-η$^2$:η$^2$-$C_2(CF_3)_2$)], (**1**), with dichalcogens gave small amounts of the dicarbonyl complex [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)$_2$(μ-η$^1$:η$^1$-$C_2(CF_3)_2$)], **2a**, the formation of which could be suppressed by the passage of dinitrogen gas through the solution, and the products of dichalcogen cleavage, [(η-$C_5H_5$)$_2$Rh$_2$(μ-ER)$_2$(μ-η$^1$:η$^1$-$C_2(CF_3)_2$)], (**3**). Also isolated from these reactions is the product of dichalogen cleavage and CO insertion, [(η-$C_5H_5$)$_2$Rh$_2$(CO)(μ-Te(*i*-Pr))$_2$(μ-η$^1$:η$^1$-$C_2(CF_3)_2$C(O))], (**4**) and in only one case, in the reaction of $Ph_2S_2$, was the coordination adduct found, *viz.* [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)($S_2Ph_2$)(μ-η$^1$:η$^1$-$C_2(CF_3)_2$)], (**2b**). The isolation of this latter complex gives some insight into the nascent reaction mechanism where coordination of the dichalcogen is required, followed by subsequent cleavage and insertion reactions, Scheme 1.

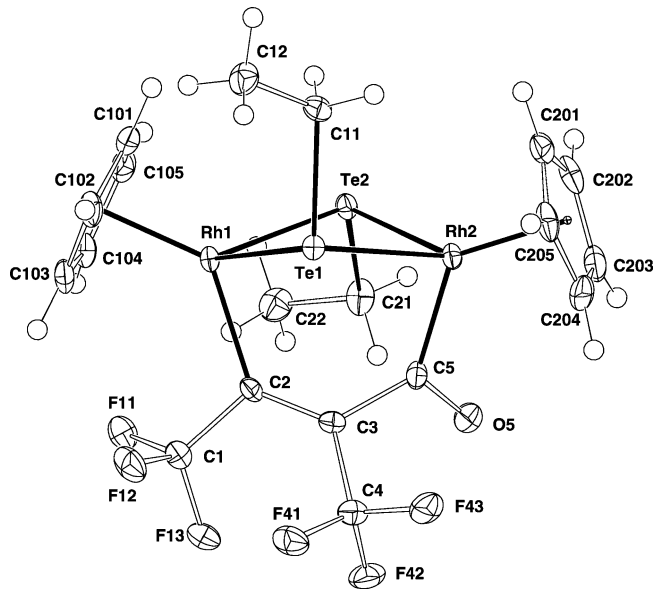
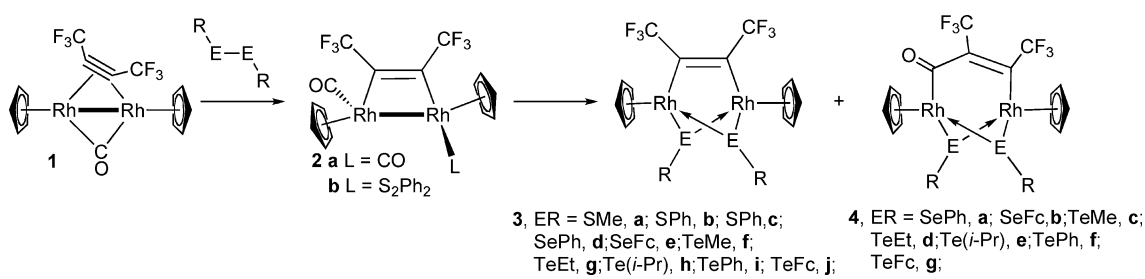


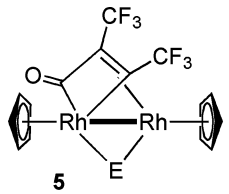

**Fig. 1** Projection of a single molecule of **4d**, showing atom labelling and 50 % probability amplitude displacement ellipsoids for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

It is of interest that the reaction of the disulfides did not result in the isolation of complexes analogous to **4** while the diselenides and ditellurides all gave moderate to low yields of the insertion product. Previously, we have shown that the reaction of dialkyl sulfides, SRR′ to [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)(μ-η$^2$:η$^2$-$C_2(CF_3)_2$)] (**1**) proceeded by coordination of the sulfide [19, 20] and giving [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)(μ-η$^1$:η$^1$-$C_2(CF_3)_2$)(SRR′)], a reaction which was reversible. On prolonged contact with $SR_2$ (R = Me, Et) interesting transformations occurred, giving [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)(μ-η$^1$:η$^2$-C(CF$_3$)=C(CF$_3$)H)(μ$_2$-SEt)] (for R = Me) and [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)(μ-η$^1$:η$^1$-C(CF$_3$)=C(CF$_3$)H)(μ$_2$-SCHMeEt)] (for R = Et), both consequent on a Stevens rearrangement. However, the analogous reactions with dialkyltellurides and dialkylselenides gave compositions corresponding to complexes **2**.



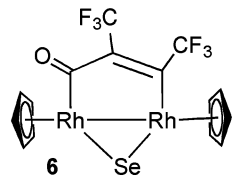

**Scheme 1**




**5**

(E = S, Se, Te)




**6**

Similarly reaction of **1** with a strained cyclic thio-, seleno- and telluro- ether compounds gave the addition products (analogous to **2**) reversibly in the first instance [18], but work-up of solutions containing excess cyclochalcoether gave complexes **5**. These complexes can also be prepared by the reaction of the elements [18] with **1**; in the case of elemental Se another isomer **6** was isolated, the structure sharing a similarity with complexes **4**.

### *Spectroscopic characterization of complexes* 3 *and* 4

In general the $^1$H-NMR spectra obtained for the complexes **3** were unremarkable with most complexes giving single resonances for their cyclopentadienyl ligands attached to Rh. The thiolates **3a,b** give spectra that are consistent with putative *m*-symmetry, although both complexes have inequivalent thiolate groups. In **3a** the Me group is coupled to the two equivalent Rh nuclei with a value that is consistent with that measured for $[Rh(CO)_2(\mu\text{-}SMe)_2]$ [24]. The $^{13}$C-NMR spectrum also reflects the inequivalence of the methyl groups while the $^1$H-NMR spectrum of **3b** clearly shows that the phenylthiolato substituents are also inequivalent. This observation is consistent with one of the groups being directed at the alkyne and the other directed away, supported, in part, by the X-ray crystal determination of **3h**[1)]. The trifluoromethyl groups were found to be equivalent with chemical shift consistent with other examples of $\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2$ complexes [18−20, 25].

In contrast to the thiolates, the reaction of the diselenides and ditellurides gave complexes **3** and **4**. Complexes **3d, f−i** are all simple alkyl substituted chalcogenides and display similar spectra while the complexes **3c, e, j** are complicated by additional resonances associated with the ferrocene moiety.

The $^1$H-NMR spectra of **3d, f−i** are consistent with those observed for the thiolates. Thus, the two alkyl groups are stereochemically distinct and the various couplings observed reflect this phenomenon. Further support for this conjecture was found in the $^{125}$Te NMR spectrum of **3i** where two resonances were observed, firstly a doublet at −7.1 ppm showing a coupling to Rh of 87 Hz and an overlapping doublet of doublets at −115 ppm, with apparent couplings to the two Rh atoms of 76 Hz. These RhTe couplings are consistent with those found for $[RhX_3(TeMe_2)_3]$(X = halide) in the range 66-94; it is of note that the range of $^{125}$Te chemical shifts spans over 4000 ppm [26]. The diferrocenyl substituted products **3c, e, j** have additional resonances in their $^1$H-NMR spectra associated with the ferrocenyl moiety. Thus singlets are seen for both the unsubstituted $Fe(\eta\text{-}C_5H_5)$ groups, reflecting the asymmetry, while the $E\text{-}(\eta\text{-}C_5H_4)Fe$ fragments give more complicated resonances consistent with expectations. In the case of **3j** an alternative isomer, **3j′**, was isolated which gave mass spectra identical to **3j** but differed in the resonances attributed to the ferrocenyl moiety, perhaps indicative of variations in orientation of the ferrocenyl substituent.

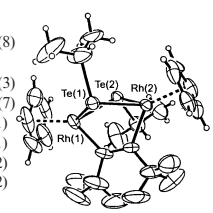
All the complexes **4** exhibit characteristic ν(CO) stretching frequencies assigned to the $\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2C(O)$ ligand. Complexes **4** lack the symmetry seen in **3** and, in consequence, two $Rh(\eta\text{-}C_5H_5)$ resonances are observed in their $^1$H-NMR spectra between 5.0 and 5.5 ppm. This inequivalence is also seen in the resonances attributable to the alkyl groups in **4a, c−f**. This is illustrated in the $^1$H-NMR spectrum of **4e** where two septets were observed for the methine proton of the *i*-Pr group at 2.70 and 2.92 ppm, respectively. Additionally, the four doublets between 1.1 and 1.6 ppm can be attributed to the *i*-Pr methyl substituents. The $^{125}$Te NMR spectrum of **4f** contains two sets of overlapping doublets of doublets at −246 and −8 ppm, respectively, each showing couplings to Rh of 97 and 75 Hz, respectively.

The $^{19}$F NMR spectra of all complexes **4** all contained two quartets at *ca.* −50 and −55 ppm, respectively, and exhibiting long range $^5J_{FF}$ couplings of *ca.* 15 Hz.

[1)] M. P. Devery, Ph.D. thesis 'The Coordination and Subsequent Rearrangement of Group 16 Donor Ligands to a Dinuclear Rhodium Complex', Monash University, 1997, reports the determination of the structure of **3h**, recording limited crystallographic and geometrical detail: $C_{20}H_{24}F_6Rh_2Te_2$, $M$ = 839.4. Monoclinic, space group $P2_1/n$, $a$ = 17.731(4), $b$ = 16.193(3), $c$ = 18.250(3) Å, β not recorded, $V$ = 4872 Å$^3$. $D_c$ = 2.30 g cm$^{-3}$ ($Z$ = 8). $N$ = 14297, $N_o$ = 6100; $R$ = 0.047, $R_w$ = 0.079; *T ca.* 295 K. The two molecules of the asymmetric unit comprise a pair of distinct rotamers 'A' and 'B', differing substantively only in respect of the orientations of the pendant $^i$Pr and $CF_3$ groups. As in **4d**, one of the Te pendants (that attached to Te(1)) lies on the side of the $Te_2Rh_2$ ring directed away from the alkene bridge, while the other lies toward; the available core geometries are summarized below.

Selected bond lengths and angles for **3h**

| Atoms | Mol. 1, p arts n = 1,2 | Mol. 2, parts n = 1,2 | < > |
|---|---|---|---|
| | Distances/Å | | |
| Rh − Te(1) | 2.575(1), 2.562(2) | 2.561(1), 2.579(2) | 2.564(8) |
| Rh − Te(2) | 2.556(1), 2.561(2) | 2.561(2), 2.557(2) | |
| Te···Te | 3.443 | 3.439 | 3.441(3) |
| Rh···Rh | 3.584 | 3.574 | 3.579(7) |
| Te(n)-C | 2.18(1), 2.19(1) | 2.18(2), 2.19(2) | 2.19(1) |
| Rh-C | 2.08(1), 2.09(1) | 2.08(1), 2.09(2) | 2.09(1) |
| C-C | 1.37(2) | 1.35(2) | 1.36(2) |
| Rh − C(cp) | 2.18(3) 2.17(3) −2.22(2) −2.23(2) | 2.22(2) 2.19(2) −2.23(2) −2.25(4) | 2.22(2) |
| < > | 2.21(2) 2.21(3) | 2.22(1) 2.23(2) | |
| | Angles (degrees) | | |
| Rh-Te-Rh | 88.5(1), 88.9(1) | 88.1(1), 88.6(1) | 88.5(3) |
| Te-Rh-Te | 84.3(1), 84.5(1) | 84.3(1), 82.6(1) | 83.9(9) |
| Rh-Te(1)-C | 108.7(4), 107.9(5) | 105.7(6), 106.3(10) | 107.2(13) |
| Rh-Te(2)-C | 105.6(5), 104.6(6) | 104.8(5), 108.2(5) | 106(2) |
| Rh-C-C | 121.1(9), 122.8(11) | 122.0(10), 122.2(8) | 122.2(8) |




A view of molecule 1 of **3h**

The diferrocenyl substituted products **4b, g** have additional resonances in their $^1$H-NMR spectra associated with the ferrocenyl moiety. However, in the case of **4g**, another isomeric form was isolated but this appears to be different to the positional isomerism associated with **3j,** being characterized by now different Rh(η-$C_5H_5$) environments and different trifluoromethyl environments. The nature of this isomerism has yet to be determined.

### *Structure of* [(η-$C_5H_5$)$_2$Rh$_2$(CO)(μ-TeEt)$_2$(μ-η$^1$:η$^1$-$C_2(CF_3)_2C(O)$)], (4d)

The result of the room-temperature single crystal X-ray structure determination is consistent with the formulation of **4d**, the connectivity of the original ligands no longer being retained in consequence, unusually, of CO insertion into the fluorocarbon, as indicated by the formulation above and depicted in Fig. 1, with pertinent structural parameteres presented in Table 1. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, overall a racemate, albeit crystallizing in a non-centrosymmetric space group. The Rh···Rh distance of 3.7618(8) Å is much longer than in related adducts defined hitherto in which Rh-Rh bonds are ascribed.

At first sight the molecule has putative *m* symmetry, only trivially broken by, primarily, the ethyl pendants of the bridging tellurium atoms. The skeleton of the bridging hydrocarbon ligand might at first sight also appear planar, but, in fact, is quite distorted, C(3)-C(5) being essentially a single bond and C(5)-O(5) multiple in character, with C(1-4) essentially planar ($\chi^2$ 676); non-defining atom deviations are: Rh(1,2); Te(1,2); C,O(5) −0.670(8), −0.35(1); −2.250(9), 0.85(1); 0.511(8), 1.488(8) Å, the C(2,3,5,)O(5) torsion angle being −126.2(5)°. The contact O(5)···F(43) may be instrumental in effecting ligand non-planarity, being 2.752(5) Å. The $Rh_2Te_2$ array is folded, the $RhTe_2/Te_2Rh$ interplanar dihedral angle being 28.62(5)°. The differences in hydrocarbon substituent type at the two rhodium atoms, despite the asymmetry, appears to have little impact: Rh-Te distances are similar (range overall: 2.5774(5)-2.5873(5)), Rh(1)-C(2) 2.095(4), *cf.* Rh(2)-C(5), 1.991(4) Å, and C-Rh-Te 82.8(1), 93.0(1)° for Rh(1) and 89.7(1), 83.2(1)° for Rh(2), there being a noticeable skewing of the array, reflected in the C-Te-Rh angles at each tellurium atom.

## Conclusions

We have shown that the dirhodium complex [(η-$C_5H_5$)$_2$Rh$_2$(μ-CO)(μ-η$^2$:η$^2$-$C_2(CF_3)_2$)] readily adds dialkyl dichalcogens by coordination, undergoing subsequent cleavage of the dichalcogen bond; in the cases of the Se and Te derivatives we have been able to isolate products that involve the insertion of CO into the Rh-fluoroalkyne bond to give enone ligands. We have also shown that the chalcogens are able to support the Rh···Rh vector while reactions occur at the Rh atoms, thus shedding some light on the interactions of dehydrochalcogenization catalysts with their substrates.

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