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Heterocyclic organotellurium compounds as precursors for new organometallic derivatives of rhodium

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The reaction of the pentamethylcyclopentadienylrhodium(III) dichloride dimer, [{Rh(η-C_5Me_5)Cl_2}$_2$], with tellurophene in the presence of Ag(O_3SCF_3) afforded the expected [Rh(η-C_5Me_5)(η^5-C_4H_4Te)][O_3SCF_3]$_2$ **1** which on reaction with [Co(cp)$_2$] (cp = η-C_5H_5) gives a rhodacyclic material [Rh(η-C_5Me_5){η^5-C_5H_4Rh(η-C_5Me_5)}] **2**. The reaction of **2** with [$Fe_3(CO)_{12}$] gave [Rh(η-C_5Me_5){η^5-$C_4H_4Fe(CO)_3$}] **3**. The reaction of [{Rh(η-C_5Me_5)Cl_2}$_2$] with dibenzotellurophene, dbt, in the presence of Ag(O_3SCF_3) gives [Rh(η-C_5Me_5)(dbt)][O_3SCF_3]$_2$ **4**, in which the mode of coordination of dbt in $CDCl_3$ solution appears to be η^1. The reaction of **4** with [Co(cp)$_2$] and [$Fe_3(CO)_{12}$] gave a variety of products including [Rh(η-C_5Me_5)($C_{12}H_8$)(η^1-dbt)] **5**, a known dibenzoferrole, **6**, and compound **7** in which the η^1-dbt of **5** is substituted by CO. Also isolated were the known [{Fe(η-C_5Me_5)(CO)$_2$}$_2$] **8** and FeTe. The direct reaction of [{Rh(η-C_5Me_5)Cl_2}$_2$] and dbt gave [Rh(η-C_5Me_5)Cl_2(η^1-dbt)]. Two complexes of 2-telluraindane were synthesized for comparison, [Rh(η-C_5Me_5)(C_8H_8Te)][O_3SCF_3]$_2$ **10** and [Rh(η-C_5Me_5)Cl_2-(C_8H_8Te)] **11** the latter showing fluxionality about co-ordinated tellurium at room temperature. It is suggested that the magnitude of $J(^{125}Te-^{103}Rh)$ has the potential to differentiate the modes of co-ordination of heterocyclic tellurium compounds to rhodium. The crystal and molecular structures have been determined for compounds **5**, **7** and **9**.

We have recently demonstrated that the reaction of dibenzotellurophene with triiron dodecacarbonyl results in the removal of tellurium from the aromatic system and the isolation of the ferrole $C_{12}H_8Fe_2(CO)_6$.[1] This is in contrast to the lack of reactivity of dibenzothiophene in the presence of the same carbonyl. Much of the interest in this chemistry stems from the fact that desulfurisation reactions of thiophenic derivatives *via* organometallic reagents may provide useful models of the initial steps in the heterogeneously catlysed hydrodesulfurisation reactions of oils and of coal-derived liquids.[2,3] In that context, Rauchfuss and co-workers[4] have shown that the pentamethylcyclopentadienylrhodium dichloride dimer, [{Rh(η-C_5Me_5)-Cl_2}$_2$], will react with tetramethylthiophene to give a product containing an η^4-bonded tetramethylthiophene which, following reaction with [$Fe_3(CO)_{12}$], gives further products some of which contain organic fragments arising from loss of sulfur from the thiophene ring. A further paper from the same laboratory[5] provided fascinating insight into the mechanism of thermolysis of [Rh(η-C_5Me_5)(η^4-C_4Me_4S)] which involves a characterised intermediate, trimeric with respect to rhodium, containing two η^4,η^1-Me_4C_4S molecules. The η^1(S) mode of co-ordination of thiophene is known and may be promoted by the use of 16-electron metal electrophiles, *e.g.* [Re(η-C_5Me_5)(CO)$_2$-(thf)] (thf = tetrahydrofuran) will react with simple thiophenes to give [Re(η-C_5Me_5)(CO)$_2${η^1(S)-$C_4H_{4-x}Me_xS$}] as air-stable solids.[6] The η^5 co-ordination mode of thiophene in which the ligand acts as a six-electron donor analogous to $C_5H_5^-$ is commonly encountered, indeed the first example was reported as long ago as 1958.[7] A recent review[8] suggests that electron density on the sulfur heteroatom increases in the following order: dibenzothiophene (dbt) > benzothiophene (bt) > thiophene. If this is so, it is also likely to apply to the related series of tellurophenes and the implication may be drawn that η^1 co-ordination of the polycyclic derivatives may be more commonly encountered than for the monocyclic materials. It is apparent that η^4 co-ordination of simple thiophenes, in which the chalcogen atom is bent out of the C_4 plane, enhances the S-donor power of the heteroatom.[5] An observation of relevance to the work reported in this paper is that rhodium and iridium dimers, [{M(η-C_5Me_5)Cl_2}$_2$] (M = Rh or Ir) will react with dbt to give [M(η-C_5Me_5)Cl_2{η^1(S)-dbt}].[9] It should also be noted that η^6 co-ordination is possible for the condensed systems, as demonstrated for example by Fischer *et al.*[10] with their reports of η^6-bt and η^6-dbt tricarbonylchromium complexes. Clearly this background chemistry has relevance to results presented in this paper.

Experimental

Triiron dodecacarbonyl was obtained from Aldrich and used as received. Rhodium trichloride trihydrade was provided by Johnson-Matthey and used for the preparation of the pentamethylcyclopentadienylrhodium dichloride dimer.[11] Tellurophene[12] and dibenzotellurophene[13] were prepared by the indicated literature methods. Acetone was AR grade and purged with argon for an hour prior to use; hexane, chloroform and dichloromethane were distilled from CaH_2 and toluene and diethyl ether were distilled from sodium. All manipulations were carried out under an atmosphere of pure argon with the use of standard Schlenk techniques.

Physical measurements

Proton, ^{13}C and ^{125}Te NMR spectra were obtained with a Bruker AC-300 instrument for $CDCl_3$ and CD_3COCD_3 solutions using $SiMe_4$ (^1H, ^{13}C) and (*p*-$EtOC_6H_4$)$_2Te_2$, δ 456[14] *vs.* Me_2Te (^{125}Te), as standards (^{125}Te data are cited with reference to Me_2Te). Infrared spectra were recorded on a Bio-Rad FTS-40A spectrometer and electron impact (EI) and FAB mass spectra were obtained from the EPSRC service at University College, Swansea. Electron spectroscopy for chemical analysis (ESCA) was carried out using a VG Scientific ESCALAB 200-D instrument with Mg-Kα (1254 eV, *ca.* 2 × 10^{-16} J) radiation. Elemental analyses were carried out by Medac Ltd, Department of Chemistry, Brunel University.

Reactions

Tellurophene with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ and $Ag(O_3SCF_3)$. An acetone solution (20 cm^3) of $Ag(O_3SCF_3)$ (1.88 g, 7.30 mol) was added in one portion to an acetone suspension (30 cm^3) of $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (1.12 g, 1.81 mmol) and tellurophene (1.15 g, 6.42 mmol). The homogeneous red solution gradually changed to yellow with concomitant precipitation of AgCl. After 2 h of stirring the mixture was filtered through Celite in air to remove the AgCl precipitate and the yellow filtrate was concentrated under vacuum to approximately 10 cm^3. Slow addition of $CHCl_3$ to the concentrated filtrate resulted in the precipitation of yellow, flaky crystals shown to have the formula $[Rh(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_4H_4Te)][O_3SCF_3]_2$ **1**: yield 1.69 g, 86% based on $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (Found: C, 26.9; H, 2.7; S, 8.95. Calc. for $C_{16}H_{19}F_6O_6RhS_2Te$: C, 26.8; H, 2.65; S, 8.95%). NMR (CD_3COCD_3); ^{1}H, δ 8.31 (q, 2 H), 8.20 (q, 2 H) and 2.41 (s, 15 H); ^{13}C, δ 121.6 ($J_{FC} = 322$), 114.2 ($J_{RhC} = 7.6$), C_4H_4Te), 112.0 ($J_{RhC} = 4.4$, C_4H_4Te), 110.9 ($J_{RhC} = 7.6$, C_5Me$_5$) and 10.8 (C$_5$*Me*$_5$); ^{125}Te, δ 577.0 ($J_{TeRh} = 20$ Hz); 780.8 (tellurophene). FAB mass spectrum (3-nitrobenzyl alcohol matrix; all data are reported with reference to ^{130}Te): $m/z = 569$, $[Rh(C_5Me_5)(C_4H_4Te)(O_3SCF_3)]^+$; 420, $[Rh(C_5Me_5)(C_4H_4Te)]^+$.

$[Rh(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_4H_4Te)][O_3SCF_3]_2$ with $[Co(cp)_2]$. An acetone suspension (20 cm^3) of compound **1** (1.08 g, 1.62 mmol) was cooled to −78 °C and a red-brown solution of $[Co(cp)_2]$ (cp = η-C_5H_5) (0.62 g, 3.28 mmol) in acetone (15 cm^3) was added in small portions over a period of 0.5 h. The reaction mixture was warmed slowly to room temperature and then stirred for 2 h followed by concentration to approximately 10 cm^3 under vacuum. The concentrated solution was diluted with an equal volume of hexane and filtered to remove a black solid, thought to be a mixture containing elemental tellurium and $[Co(cp)_2O_3SCF_3]$, and shown by ESCA analysis certainly to contain Co, Te and some Rh. The cycle of hexane addition followed by concentration was repeated until no further solid was obtained. The resulting dark red solution was then evaporated to dryness, yielding a purple solid identified as the mixed-oxidation-state compound $[Rh(\eta\text{-}C_5Me_5)\{\eta^5\text{-}C_4H_4Rh(\eta\text{-}C_5Me_5)\}]$ **2**: yield 0.2 g, 47% based on **1** (Found: C, 53.6; H, 6.75. Calc. for $C_{24}H_{34}Rh_2$: C, 54.5; H, 6.45%). EI mass spectrum: $m/z = 528$ (M^+).

$[Rh(\eta\text{-}C_5Me_5)\{\eta^5\text{-}C_4H_4Rh(\eta\text{-}C_5Me_5)\}]$ with $[Fe_3(CO)_{12}]$. Compound **2** (0.13 g, 0.25 mmol) and $[Fe_3(CO)_{12}]$ (0.18 g, 0.36 mmol) were dissolved in toluene (35 cm^3) and heated and stirred under reflux for 3 h during which time the solution gradually changed from dark green to deep orange. After cooling the solution was filtered to remove a black residue and the deep orange filtrate was evaporated to dryness affording a dark orange solid. The solid was chromatographed on a 2.5 × 12 cm column of TLC-grade silica gel, thereby giving a small yellow band preceded by a small purple band and a larger yellow band. Elution with hexane–CH_2Cl_2 (2 : 1) and removal of solvent gave yellow crystals from the first eluate and small traces of a purple solid and a yellow solid from the second and third eluates respectively. The yellow crystals melted at 146 °C and were identified as the ferrarhodocene $[Rh(\eta\text{-}C_5Me_5)\{\eta^5\text{-}C_4H_4Fe(CO)_3\}]$ **3**: yield 50 mg, 47% based on **2** (Found; C, 47.2; H, 4.45. Calc. for $C_{17}H_{19}FeO_3Rh$: C, 47.4; H, 4.4%). Infrared (KBr, cm^{-1}): ν(CO) 2011, 1944, 1922 and 1890. FAB mass spectrum: $m/z = 430$ (M^+) and 346 ($M^+ - 3CO$), with reference to ^{56}Fe. The purple solid, as yet unidentified, gave an infrared spectrum (KBr) showing the presence of terminal carbonyl groups: ν(CO) 2014, 1984, 1943, 1923 and 1890 cm^{-1}. The yellow solid from the third eluate was not identified. The reaction sequence for tellurophene is shown in Scheme 1.

Dibenzotellurophene with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ and $Ag(O_3SCF_3)$. An acetone solution (20 cm^3) of $Ag(O_3SCF_3)$ (1.67 g, 6.48 mmol) was added in one portion to an acetone suspension (30 cm^3) of $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (1.00 g, 1.62 mmol). The dark red solution immediately changed to yellow and the precipitated AgCl was removed by filtration through Celite. Dibenzotellurophene (1.00 g, 3.57 mmol) was then added to the yellow filtrate which gradually changed to dark orange and a red-orange precipitate formed. The reaction mixture was stirred for 3 h after which precipitation was completed by concentration of the solution under vacuum to 5 cm^3 followed by the addition of diethyl ether (20 cm^3). The red-orange precipitate was filtered off and shown to have the formula $[Rh(\eta\text{-}C_5Me_5)(C_{12}H_8Te)][O_3SCF_3]_2$ **4**: yield 1.66 g, 63% based on $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (Found: C, 35.4; H, 3.05. Calc. for $C_{24}H_{32}F_6O_6RhS_2Te$: C, 35.3; H, 2.85%). NMR (CD_3COCD_3): ^{1}H, δ 8.35 (m, 2 H), 8.13 (m, 2 H), 7.75 (m, 2 H) and 7.56 (m, 2 H); ^{13}C, δ 135.2, 131.7, 130.3, 126.7 and 8.83 (C_5Me_5); ^{125}Te, δ 622.1 ($J_{TeRh} =$ 88 Hz); 678.6 (dibenzotellurophene). FAB mass spectrum: $m/z = 669$, $[Rh(C_5Me_5)(C_{12}H_8Te)(O_3SCF_3)]^+$; 520, $[Rh(C_5Me_5)(C_{12}H_8Te)]^+$.

$[Rh(\eta\text{-}C_5Me_5)(C_{12}H_8Te)][O_3SCF_3]_2$ with $[Co(cp)_2]$ subsequent reaction with $[Fe_3(CO)_{12}]$. An acetone suspension (20 cm^3) of compound **4** (1.00 g, 1.23 mmol) was cooled to −78 °C and a solution of $[Co(cp)_2]$ (0.48 g, 2.54 g) in acetone (15 cm^3) was added dropwise over a period of 0.5 h. The reaction mixture was warmed slowly to room temperature and then stirred for 2 h followed by evaporation under vacuum to dryness, yielding a dark brown solid (1.03 g). The latter was dissolved in toluene (50 cm^3) together with $[Fe_3(CO)_{12}]$ (0.70 g, 1.39 mmol) then heated and stirred under reflux for 4 h, during which time the dark green solution gradually changed to deep purple. After cooling, the mixture was filtered to remove a black residue (0.82 g), ESCA analysis of which revealed the presence of Te, Rh and Co in small quantities. The deep purple filtrate was evaporated to dryness under vacuum, affording a dark purple solid. The solid was chromatographed on a 2.5 × 15 cm column of silica gel, thereby giving five distinct bands. Elution with hexane–CH_2Cl_2 (2 : 1) followed by removal of solvent gave yellow crystals from the first eluate, a dark brown solid from the second, purple crystals from the third, yellow crystals from the fourth and orange crystals from the fifth. A brown residue, immobile on silica, remained on the column.

The identity of the yellow crystals from the first eluate was confirmed by infrared spectroscopy as dibenzotellurophene (10 mg). The brown solid, **6**, from the second eluate was shown to be the dibenzoferrole $C_{12}H_8Fe_2(CO)_6$:[1] yield 44 mg, 17% based on compound **4**. Infrared (KBr, cm^{-1}): ν(CO) 2059, 2026, 2004, 1997, 1973, 1949, 1932 and 1883. EI mass spectrum: $m/z = 432$ (M^+) and 264 ($M^+ - 6CO$). The purple crystals from the third eluate were identified as the dimeric mixed-ligand compound $[\{Fe(\eta\text{-}C_5Me_5)(CO)_2\}_2]$[15] **8** (60 mg). Infrared (KBr, cm^{-1}): ν(CO) 1920, 1884 and 1745. The yellow crystals from the fourth eluate melted at 206 °C (decomp.) and were shown to have the formula $[Rh(\eta\text{-}C_5Me_5)(CO)(C_{12}H_8)]$ **7**: yield 55 mg, 21% based on **4**. Infrared (KBr, cm^{-1}): ν(CO) 2004, 1996 and 1953. EI mass spectrum: $m/z = 418$ (M^+) and 390 ($M^+ - CO$). The orange crystals from the fifth eluate (trace) had a melting point >234 °C and were shown to be a by-product from the reduction of **4**, having the formula $[Rh(\eta\text{-}C_5Me_5)(C_{12}H_{18})(\eta^1\text{-}C_{12}H_8Te)]$ **5**. EI mass spectrum: $m/z = 672$ (M^+). Crystals of **5** and **7** suitable for X-ray diffraction measurements were grown by slowly cooling concentrated CH_2Cl_2 solutions.

Dibenzotellurophene with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$. The compound $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.25 g, 0.41 mmol) was dissolved in $CHCl_3$ (2.5 cm^3) and dibenzotellurophene (0.28 g, 1.00 mmol) was rapidly added resulting in the gradual formation of a red precipitate. After 30 min of stirring the precipitate was filtered off and washed with ether (20 cm^3). Its identity was confirmed as $[Rh(\eta\text{-}C_5Me_5)Cl_2(\eta^1\text{-}C_{12}H_8Te)]$ **9**: yield 0.47 g, 98% based on $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (Found: C, 44.9; H, 3.85. Calc. for $C_{22}H_{23}Cl_2RhTe$: C, 44.9; H, 3.95%). NMR (CD_3COCD_3): ^{1}H, δ 8.01 (q, 2 H), 7.94 (q, 2 H), 7.56 (q, 2 H), 7.35 (q, 2 H) and 1.18 (s, 15 H); ^{13}C, δ 133.4, 128.9, 128.3, 128.0, 124.3, 96.0 (C_5Me_5, $J_{RhC} = 7.6$) and 8.14 (C_5Me_5); ^{125}Te, δ 611.6 ($J_{TeRh} =$ 142 Hz). FAB mass spectrum: $m/z = 555$, $[Rh(C_5Me_5)Cl(C_{12}H_8Te)]^+$; 520, $[Rh(C_5Me_5)(C_{12}H_8Te)]^+$. Crystals of **9** suitable for X-ray diffraction measurements were grown by slowly cooling a concentrated toluene solution. The reaction sequences for dibenzotellurophene are shown in Scheme 2.

2-Telluraindane with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ in the presence of $Ag(O_3SCF_3)$. An acetone solution (10 cm^3) of $Ag(O_3SCF_3)$ (0.83 g, 3.23 mmol) was added in one portion to an acetone suspension (30 cm^3) of $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.50 g, 0.81 mmol) and 2-telluraindane[16] (0.38 g, 1.64 mmol). Silver chloride gradually precipitated from the dark orange solution. After 2 h of stirring at room temperature, the mixture was filtered through Celite in air to remove AgCl and the orange filtrate was concentrated under vacuum to half volume. Addition of an equal volume of hexane to the concentrated filtrate resulted in the precipitation of an orange solid shown to have the composition $[Rh(\eta\text{-}C_5Me_5)(C_8H_8Te)][O_3SCF_3]_2$ **10** (Found: C, 31.7; H, 3.4. Calc. for $C_{20}H_{23}F_6O_6RhS_2Te$: C, 31.3; H, 3.0%). NMR ($CDCl_3$): ^{1}H, δ 7.13 (m, 2 H), 7.03 (m, 2 H), 4.61 (q, 4 H) and 1.60 (s, 15 H); ^{13}C, δ 140.2, 128.5, 128.2, 20.9 and 9.97 (C_5Me_5); ^{125}Te, δ 74.8 [$J(^{125}Te\text{–}^{103}Rh) = 66$ Hz]. FAB mass spectrum: $m/z = 621$, $[Rh(\eta\text{-}C_5Me_5)(C_8H_8Te)(O_3SCF_3)]^+$: 472, $[Rh(\eta\text{-}C_5Me_5)(C_8H_8Te)]^+$.

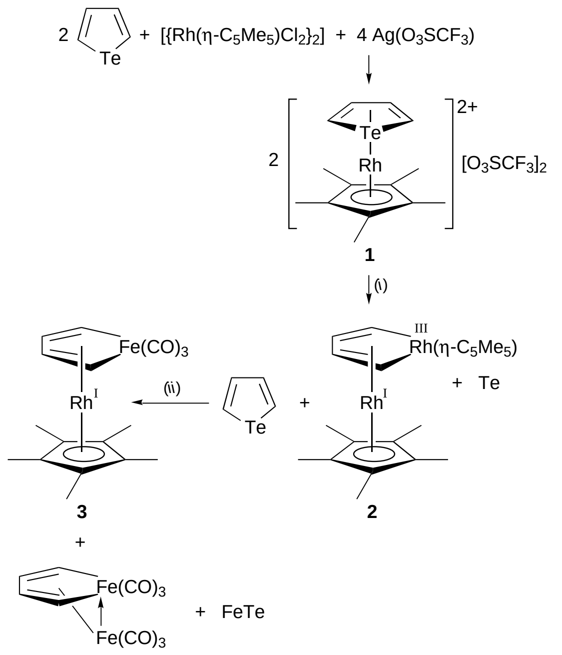
2-Telluraindane with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$. 2-Telluraindane (0.38 g, 1.64 mmol) was dissolved in toluene (40 cm^3) together with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.50 g, 0.81 mmol) and heated, with stirring, under reflux for 3 h. The reaction mixture was then filtered, affording a brown residue (0.11 g) and a deep red-brown filtrate. Removal of toluene under vacuum from the filtrate yielded a dark red solid (m.p. >234 °C), thought to be $[Rh(\eta\text{-}C_5Me_5)Cl_2(C_8H_8Te)]$ **11**; yield 0.54 g, 62% based on $[Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (Found: C, 40.2; H, 4.25. Calc. for $C_{18}H_{23}Cl_2RhTe$: C, 39.9; H, 4.25%). NMR ($CDCl_3$): ^{1}H, δ 7.13 (m, 2 H), 7.03 (m, 2 H), 4.59 [br s, 4 H (room temperature)] and 1.68 (s, 15 H): ^{13}C, δ 141.3, 127.6, 126.7, 96.2 (C_5Me_5), 21.6 and 9.47 (C_5Me_5); ^{125}Te, δ 540.9 [$J(^{125}Te-^{103}Rh) = 108$ Hz (223 K)] FAB mass spectrum: $m/z = 507$, $[Rh(\eta\text{-}C_5Me_5)Cl(C_8H_8Te)]^+$; 472, $[Rh(\eta\text{-}C_5Me_5)(C_8H_8Te)]^+$.

X-Ray crystallography

The crystal structures of compounds **5**, **7** and **9** were determined and the crystal parameters are included in Table 1. Data for all three structures were collected on a Rigaku R-axis II area-detector diffractometer at 293(2) K using graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\ 69$ Å. For **5**, **7** and **9** respectively, sixty 3°, thirty-six 5° and thirty 6° oscillation exposures were made with crystal-to-detector distances of 80, 105 and 80 mm. Absorption corrections were not applied since the crystals were nearly equidimensional (Table 1).

The structures were determined by direct methods[17] and refined[18] on F^2 by full-matrix least squares using anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters. The ORTEP[19] plots of the complexes are shown in Figs. 1–3; selected bond lengths and angles in Table 2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any requests to the CCDC for this material should quote the full literature citation and the reference number 186/430.



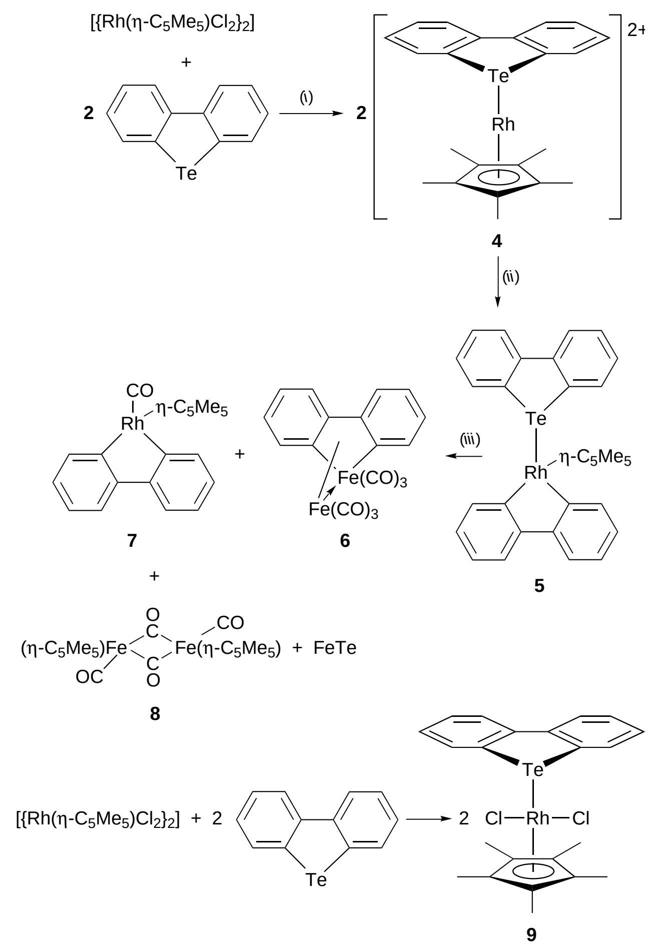
Scheme 1 Reaction of tellurophene with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$. (*i*) $[Co(cp)_2]$; (*ii*) $[Fe_3(CO)_{12}]$

Discussion

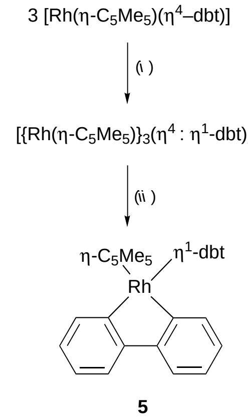
The reaction of the pentamethylcyclopentadienylrhodium dimer $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$, with tellurophene in the presence of silver triflate $Ag(O_3SCF_3)$ gives in good yield, and not unexpectedly, the η^5 complex **1** in Scheme 1. This formulation is strongly supported by the NMR data. Thus the observed $^{13}C\text{–}^{103}Rh$ coupling constants are in close agreement with those reported for the tetramethylthiophene (tmt) complex, $[Rh(\eta\text{-}C_5Me_5)(\eta^5\text{-tmt})][O_3SCF_3]_2$, reported by Rauchfuss and co-workers.[4] Also the observed $^{125}Te\text{–}^{103}Rh$ coupling of 20 Hz is less than would be expected for η^1 co-ordination (see below). Thus the precedent established by related thiophene species is followed, *e.g.* tetramethylthiophene with rhodium(III)[4] and 2,5-dimethylthiophene with iridium(III).[2] Reduction of **1** with $[Co(cp)_2]$ affords a new complex, **2** in Scheme 1. Although no crystals suitable for X-ray crystallography were obtained the spectroscopic (IR, NMR and mass) data are consistent with the formulation given. The greater reactivity of the tellurium heterocyclic compound is thus illustrated; since in the thiophene case the $[Rh(Ir)(\eta\text{-}C_5Me_5)(\eta^4\text{-}C_4R_4S)]$ would be isolable,[2] the formation of **2** *via* a similar tellurium-containing intermediate can be postulated here. Although speculative, precedents for the intermediates are known from the work of the groups of both Angelici[20] and of Rauchfuss.[5] The direct reaction of **2** with $[Fe_3(CO)_{12}]$ affords the known[4] complex **3** depicted in Scheme 1.

The reaction of dibenzotellurophene with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ provides a greater spectrum of new compounds. Dibenzothiophene is less reactive under similar conditions, hence the observations with the more reactive tellurium compound enable us to at least examine the mechanistic *feasibility* of dechalcogenation reactions with the more conjugated heterocycles *via* the rhodium chemistry. The essential findings are summarised in Scheme 2.

Initial reaction of dibenzotellurophene (dbt) with the rhodium dimer in the presence of silver triflate affords $[\{Rh(\eta\text{-}C_5Me_5)(dbt)][O_3SCF_3]_2$, a formulation with which NMR and FAB mass spectral data are in good accord. The mode of attachment of the dbt to rhodium is a matter of some interest.



Scheme 2 Reactions of dibenzotellurophene with [{Rh(η-C_5-Me_5)Cl_2}$_2$]. (*i*) Ag(O_3SCF_3); (*ii*) −60 °C, [Co(cp)$_2$]; (*iii*) [$Fe_3(CO)_{12}$], toluene



Scheme 3 (*i*) −dbt; (*ii*) −2 Rh(η-C_5Me_5), −Te

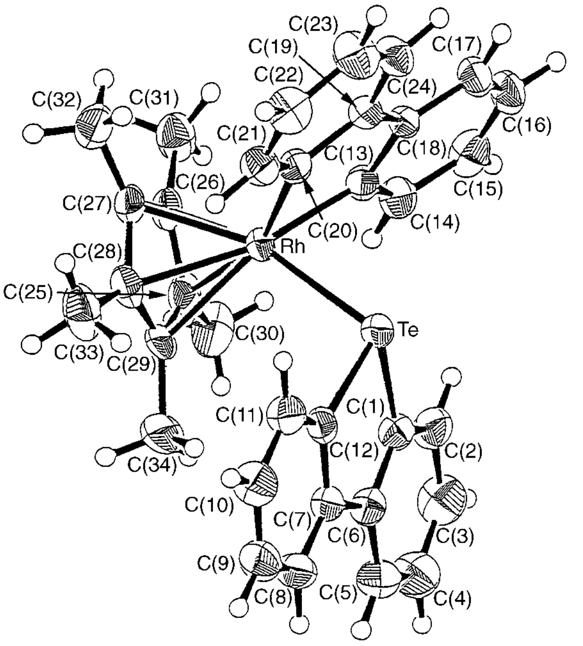


Fig. 1 View of complex **5**. Thermal ellipsoids are at the 30% probability level

Precedent from the tellurophene and thiophene cases suggests that η^5 co-ordination should be expected (the NMR data clearly indicate the presence of a plane of symmetry thereby eliminating the need to consider η^6 co-ordination); for the tellurophene complex $J(^{125}Te–^{103}Rh)$ was 20 Hz whereas the corresponding coupling constant for **4** is 88 Hz indicative of a stronger Rh–Te interaction. This could reflect a lesser degree of conjugation of tellurium lone-pair electron density in the dbt case than in the tellurophene case,[8] and a consequently stronger Rh–Te interaction in η^5 co-ordination (in a sense, $\eta^4 + \eta^1$); alternatively, η^1 co-ordination alone may need to be considered. It is interesting that the ^{125}Te nucleus in **4** is shielded with respect to free dbt ($\Delta\delta = -56.5$ ppm); this may reflect a balance between the deshielding effect of lone-pair donation to rhodium and the shielding effect of reduced delocalisation of the electron pair as a consequence of the greater localisation needed for donation to occur (a similar co-ordination shift is seen for **9**). However (see below) a crystallographically characterised case of η^1-dbt co-ordination, **9**, is associated with a value of $J(^{125}Te–^{103}Rh)$ of 142 Hz. In simple η^4 co-ordination the tellurium atom is expected to be bent out of the plane of the ring away from the rhodium atom thus producing no interaction; thus the measurement of tellurium–rhodium coupling constants should be useful for determination of the mode of attachment of tellurophene moieties to rhodium. The tellurium nucleus for **4** is more deshielded than that for the η^5-tellurophene complex discussed above (δ 622.1 for the complex *vs.* δ 577 for the tellurophene complex, *i.e.* $\Delta\delta$ for $\eta^1 < \Delta\delta$ for η^5). There are usually strong parallel trends in ^{125}Te and ^{77}Se NMR, thus the fact that Angelici and co-workers[21] find that η^5-selenophenes give selenium resonances more shielded than those from η^1 examples supports a strong Te–Rh interaction in complex **4**. In addition the co-ordination shift in **4** at −56.5 is very similar to that observed for **9** at −67; given that the dbt ligand in **9** is proven to be η^1 co-ordinated, this suggests that **4** should be similarly formulated, despite the implication of co-ordination unsaturation about rhodium, although the measurements are from solutions in which solvation may be important; also the steric demand of the η^1-dbt ligand may be considerable.

Two complexes of (η-C_5Me_5)Rh and 2-telluraindane, **10** and **11**, were prepared, in the hope that they would provide useful data for comparison with the dibenzotellurophene complexes **4** and **9**. Stoichiometrically they were very similar: [Rh(η-C_5Me_5)(C_8H_8Te)][O_3SCF_3]$_2$ and [Rh(η-C_5Me_5)Cl_2(C_8H_8Te)]. The proton and ^{13}C NMR spectra provide no evidence for anything other than η^1 co-ordination. Complex **10** gives a tellurium-125 co-ordination shift of +260 ppm and a $^{125}Te–^{103}Rh$ coupling constant of 65.9 Hz, comparable in magnitude to that given by the related dbt complex, **4**, thus implying that η^1-co-ordinated dbt is the correct formulation for **4** in $CDCl_3$ solution. The observation of an AB quartet for the 2-telluraindane methylene protons of **10** ($J_{AB} = 16$ Hz, $\Delta\nu = 49.8$ Hz) is as expected for co-ordinated 2-telluraindane, however compound **11** shows a broad singlet for these 2-methylene protons in $CDCl_3$ solution at room temperature. This singlet sharpens on heating to 323 K and resolves into the expected AB quartet ($J_{AB} = 13.5$ Hz, $\Delta\nu = 311.1$ Hz) on cooling

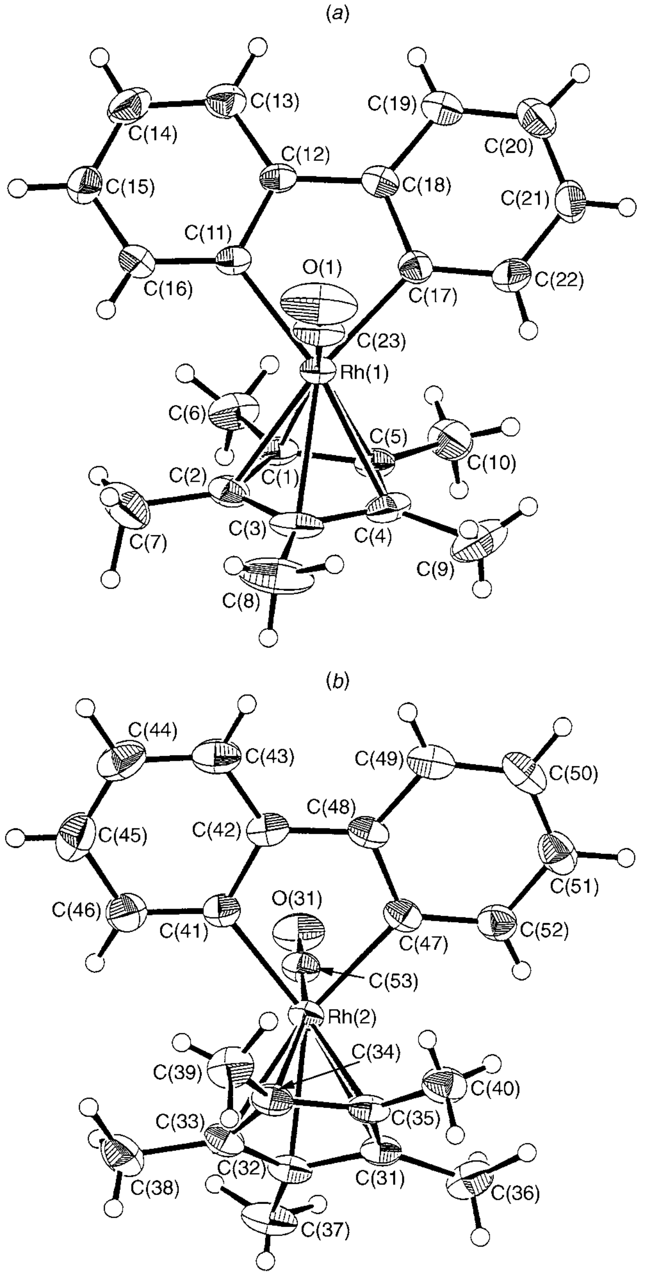


Fig. 2 Views of the two independent molecules of structure **7**. Thermal ellipsoids as in Fig. 1

to 223 K thus implying inversion about co-ordinated tellurium in this complex. The value of the ^{125}Te–^{103}Rh coupling constant of 108 Hz is again comparable with that observed for the corresponding dbt complex, shown by X-ray crystallography to be η^1 co-ordinated. Thus, greater values of coupling constants are observed for the dichloro-complexes than for the triflate materials.

When the reaction of compound **4** with [Co(cp)$_2$] was carried out in the presence of triiron dodecacarbonyl a complex sequence of reactions was observed. The products isolated and characterised are given in Scheme 2 (**5**–**8**); in addition some free dbt was recovered. Compounds **6** and **8** are known; **6** is the dibenzoferrole recently reported[1] and [{Fe(η-C$_5$Me$_5$)(CO)$_2$}$_2$], where the C$_5$Me$_5$ groups must have originated from rhodium, was first reported by Teller and Williams.[15] The black residue from the reaction was shown by ESCA analysis to contain traces of Rh, Co and Te.

There are clearly a number of reactions which have progressed in parallel, thus the dibenzoferrole **6** reasonably arises from the direct reaction of [Fe$_3$(CO)$_{12}$] and released dbt. It is probable that compound **4** reacts, following the sequence iden-

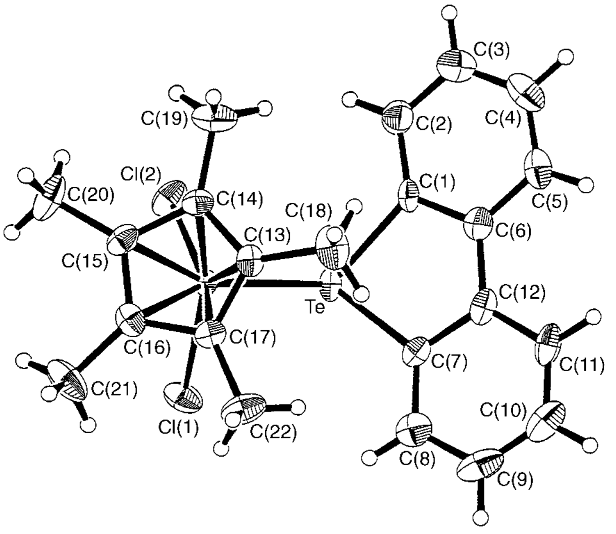


Fig. 3 View of complex **9**. Thermal ellipsoids as in Fig. 1

tified by Rauchfuss and co-workers[4,5] using tetramethylthiophene, *via* reaction intermediates [Rh(η-C$_5$Me$_5$)(η^4-dbt)$_2$] and [{Rh(η-C$_5$Me$_5$)}$_3$(η^4:η^1-dbt)$_2$] to give **5** (Scheme 3). In turn **5** could react further with [Fe$_3$(CO)$_{12}$] to give more of the dibenzoferrole and **7** together with **8**. Further speculation is not justified; however what has been established is that the greater reactivity of the tellurophene systems provides pathways to novel organometallic compounds. Altough **5** was available only in trace quantities (insufficient for ^{125}Te NMR spectroscopy), fortunately crystals suitable for X-ray crystallography were obtained, as was the case for **7**.

It was desirable to obtain a complex in which the mode of co-ordination of the dbt to rhodium was unambiguously η^1; thus a direct reaction between dbt and [{Rh(η-C$_5$Me$_5$)Cl$_2$}$_2$] to give **9** (Scheme 2) was carried out (a similar complex is known with dibenzothiophene[6]). Crystals suitable for X-ray analysis were obtained resulting in the unambiguous identification of η^1 co-ordination. The spectroscopic data are in accord with expectation and the measured value of J(^{125}Te–^{103}Rh) was 142 Hz (see earlier discussion) and the ^{125}Te chemical shift is very similar at δ 611.6 to that observed for compound **4**. Although the database is as yet limited, it is clear that ^{125}Te NMR spectroscopy will prove a valuable analytical tool with which to probe the nature of bonding of the tellurophenes to metal centres.

X-Ray crystallography

Each of the structures contains a π-bonded pentamethylcyclopentadienylrhodium residue. The Rh–C distances are 2.207–2.269, 2.232–2.270, 2.223–2.280 and 2.148–2.166 Å, in structures **5**, **7** (two independent molecules) and **9**, respectively. The mean distances are 2.238(12), 2.255(7), 2.260(10) and 2.158(4) Å, respectively. A search of the Cambridge Structural Database (CSD)[22] seems to indicate that the significantly shorter distances in **9** may be due to the presence of two sterically undemanding electronegative chlorine atoms bonded to the rhodium in this structure. The mean Rh–C distance in 515 cyclopentadienyl structures is 2.23 Å in agreement with the values found in **5** and **7**. However, for 25 RhCl$_2$ cyclopentadienyl structures the mean Rh–C distance is shorter, at 2.145 Å, comparable to the values found in structure **9**. On the other hand, the rhodium–tellurium distance is longer in **9** than in **5**, 2.603(1) against 2.525(1) Å. Both are somewhat shorter than the mean of 2.622(2) Å found in five comparable structures.[23–25]

The bonds between rhodium and the aromatic carbon atoms of the biphenyl residues in compounds **5** and **7** are all in the range 2.046–2.062 Å, with mean values 2.054$_5$, 2.058$_5$ and 2.054 Å in **5** and in the two independent molecules of **7**, res-

Table 1 Crystallographic data for compounds **5**, **7** and **9**

	5	**7**	**9**
Formula	$C_{34}H_{31}RhTe$	$C_{23}H_{23}ORh$	$C_{22}H_{23}Cl_2RhTe$
M	670.1	418.3	588.8
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/n$
a/Å	14.891(6)	16.437(2)	10.296(2)
b/Å	20.451(9)	14.741(2)	15.660(5)
c/Å	9.488(4)	31.450(4)	13.755(4)
β/°	108.57(1)	—	102.20(2)
U/Å^3	2739(2)	7620(2)	2167.7(10)
Z	4	16	4
D_c/g cm^{-3}	1.625	1.459	1.804
μ(Mo-Kα)/mm^{-1}	1.688	0.903	2.357
Crystal size/mm	0.25 × 0.2 × 0.2	0.5 × 0.3 × 0.25	0.2 × 0.15 × 0.15
hkl Ranges	−16 to 17, −24 to 24, −11 to 11	−16 to 16, −14 to 14, −27 to 31	−12 to 12, −18 to 18, −16 to 16
θ Range/°	2–25	2–21	2–25
Unique reflections [$I > \sigma(I)$]	4744	3768	3842
Variables	325	451	235
Δ/σ_{max}	0.001	0.004	0.009
Δρ/e Å^{-3}	0.49, −0.66	0.31, −0.32	0.52, −0.63
R, R'[a]	0.0487, 0.0908	0.0285, 0.0783	0.0554, 0.0671
Observed reflections [$I > 2\sigma(I)$]	4482	3657	2818
R, R' [$I > 2\sigma(I)$]	0.0441, 0.0880	0.0257, 0.0770	0.0313, 0.0582
a, b in weighting scheme[b]	0.024, 8.35	0.041, 4.92	0.018, 0.25

[a] $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **5**, **7** and **9**

Compound **5**			
Te–C(1)	2.103(6)	Rh–C(25)	2.255(5)
Te–C(12)	2.105(5)	Rh–C(26)	2.207(5)
Te–Rh	2.525(1)	Rh–C(27)	2.212(5)
Rh–C(13)	2.053(5)	Rh–C(28)	2.246(5)
Rh–C(20)	2.056(5)	Rh–C(29)	2.269(5)
C(1)–Te–C(12)	80.8(2)	C(13)–Rh–C(20)	79.4(2)
C(1)–Te–Rh	107.9(1)	C(13)–Rh–Te	80.4(1)
C(12)–Te–Rh	108.4(1)	C(20)–Rh–Te	81.1(1)
Compound **7**			
Rh(1)–C(1)	2.232(3)	Rh(2)–C(31)	2.274(3)
Rh(1)–C(2)	2.270(3)	Rh(2)–C(32)	2.280(3)
Rh(1)–C(3)	2.269(4)	Rh(2)–C(33)	2.268(4)
Rh(1)–C(4)	2.257(3)	Rh(2)–C(34)	2.223(4)
Rh(1)–C(5)	2.249(4)	Rh(2)–C(35)	2.257(3)
Rh(1)–C(11)	2.058(3)	Rh(2)–C(41)	2.062(3)
Rh(1)–C(17)	2.059(3)	Rh(2)–C(47)	2.046(3)
Rh(1)–C(23)	1.838(5)	Rh(2)–C(53)	1.853(4)
O(1)–C(23)	1.131(5)	O(31)–C(53)	1.131(4)
C(23)–Rh(1)–C(11)	87.4(2)	C(53)–Rh(2)–C(41)	86.1(1)
C(23)–Rh(1)–C(17)	86.3(2)	C(53)–Rh(2)–C(47)	85.9(1)
C(11)–Rh(1)–C(17)	78.8(1)	C(41)–Rh(2)–C(47)	79.4(1)
Compound **9**			
Te–C(1)	2.101(4)	Rh–C(15)	2.166(5)
Te–C(7)	2.101(4)	Rh–C(16)	2.165(5)
Te–Rh	2.603(1)	Rh–C(17)	2.148(4)
Rh–C(13)	2.165(4)	Rh–Cl(1)	2.426(1)
Rh–C(14)	2.148(4)	Rh–Cl(2)	2.425(1)
C(1)–Te–C(7)	81.6(2)	Cl(2)–Rh–Cl(1)	92.7(1)
C(1)–Te–Rh	112.1(1)	Cl(2)–Rh–Te	79.8(1)
C(7)–Te–Rh	111.0(1)	Cl(1)–Rh–Te	79.1(1)

pectively. For comparison, in the analogous complex, [Rh(η-C_5Me_5)(PMe_3)($C_{12}H_{10}$)] ($C_{12}H_{10}$ = 2,2′-biphenyl)[26] the Rh–C bond length is 2.029(9) Å and the mean Rh–C (cyclopentadienyl) distance is 2.254(12) Å. The lengths of the Rh–Cl bonds in structure **9**, 2.425(1) and 2.426(1) Å, fall well within the range found for this bond, 2.225–2.615 Å,[22] but the mean, 2.381(2) Å, is somewhat shorter. The Te–C (biphenyl) bond lengths in structures **5** and **9** are closely similar, range, 2.101–2.105 Å, in good agreement with those found in dibenzotellurophene,[27] 2.084 and 2.089 Å, and with the value given by Allen *et al.*[28] for Te–C (aromatic), 2.116 Å.

The cyclopentadienyl rings are essentially planar, maximum atomic deviation ±0.017 Å in structure **9**. In all three structures the methyl substituents are displaced by distances of up to 0.175 Å from the ring plane on the side remote from the metal atom.

Acknowledgements

K. B. thanks the EPSRC and H. L. C. the University of Birmingham for research studentships. The EPSRC and the University of Birmingham are thanked for funds with which to purchase the X-ray diffractometer. We thank Johnson Matthey plc for a generous loan of rhodium salts, and are grateful to the EPSRC for access to the Mass Spectroscopy Service at University College Swansea.

References

1 K. Singh, W. R. McWhinnie, H. L. Chen, M. Sun and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1996, 1545.
2 T. B. Rauchfuss, *Prog. Inorg. Chem.*, 1991, **39**, 259.
3 R. J. Angelici, *Acc. Chem. Res.*, 1988, **21**, 387, *J. Coord. Chem. Rev.*, 1990, **105**, 61.
4 S. Luo, A. E. Ogilvy, T. B. Rauchfuss, A. L. Rheingold and S. R. Wilson, *Organometallics*, 1991, **10**, 1002.
5 S. Luo, A. E. Skaugset, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1992, **114**, 1732.
6 M. G. Choi and R. J. Angelici, *J. Am. Chem. Soc.*, 1989, **111**, 8753.
7 E. O. Fischer and K. Öfele, *Chem. Ber.*, 1958, **91**, 2395.
8 X. Ma, K. Sakanishi, T. Isoda and I. Mochida, *Energy Fuels*, 1995, **9**, 33.
9 K. M. Rao, C. L. Day, R. A. Jocobsen and R. J. Angelici, *Inorg. Chem.*, 1991, **30**, 5046.
10 E. O. Fischer, H. A. Goodwind, C. G. Kreiter, H. D. Simmons, K. Sonogashira and S. B. Wild, *J. Organomet. Chem.*, 1980, **180**, 265.
11 J. Wang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5046.

12 W. Lohner and K. Praefcke, *Chem. Ber.*, 1978, **111**, 3745.

13 J. D. McCullough, *Inorg. Chem.*, 1975, **14**, 2285.

14 P. Granger, S. Chepelle, W. R. McWhinnie and A. Z. Al-Rubaie, *J. Organomet. Chem.*, 1981, **220**, 149.

15 R. G. Teller and J. Williams, *Inorg. Chem.*, 1980, **19**, 2770.

16 A. Z. Al-Rubaie, W. R. McWhinnie, P. Granger and S. Chapelle, *J. Organomet. Chem.*, 1982, **234**, 287.

17 TEXSAN, Single Crystal Structure Analysis Software, version 1.6, Molecular Structure Corporation, Houston, TX, 1993.

18 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

19 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

20 J. Chen, L. M. Daniels and R. J. Angelici, *J. Am. Chem. Soc.*, 1990, **112**, 199.

21 C. J. White, T. Wang, R. A. Jacobsen and R. J. Angelici, *Organometallics*, 1994, **13**, 4474.

22 Cambridge Structural Database System, release. Cambridge Crystallographic Data Centre, April 1996.

23 S. Schulz, M. Andruh, T. Pape, T. Heinze, H. W. Roesky, L. Haming, A.Kuhn and R. Herbst-Irmer, *Organometallics*, 1994, **13**, 4004.

24 M. Di Vaira, M. Peruzzini and P. Stoppioni, *Inorg. Chem.*, 1989, **28**, 4614.

25 M. Di Vaira, M. Peruzzini and P. Stoppioni, *Inorg. Chem.*, 1991, **30**, 1001.

26 C. Perthuisot and W. D. Jones, *J. Am. Chem. Soc.*, 1994, **116**, 3647.

27 J. D. McCullough, *Inorg. Chem.*, 1975, **14**, 2639.

28 F. H. Allen, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.

Received 6*th December* 1996; *Paper* 6/08237H