

# The synthesis and NMR spectroscopic examination of coordination complexes of 2-telluraindane with rhodium

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## Abstract

Rhodium complexes of 2-telluraindane were synthesised and the nature of metal-ligand interactions in solution were studied using NMR spectroscopy. Two complexes were prepared;  $[(Cp^*Rh)(C_8H_8Te)](O_3SCF_3)_2$  (**1**) was prepared by the reaction of  $[Cp^*RhCl_2]_2$  with 2-telluraindane in the presence of silver triflate while  $[(Cp^*RhCl_2)(C_8H_8Te)]$  (**2**) was synthesised by a direct reaction between the rhodium dimer and the ligand. Complex **1** gives a  $^{125}Te$  coordination shift of +260 ppm and a  $^{125}Te-^{103}Rh$  coupling constant of 65.9 Hz implying that the metal is directly bonded to the tellurium in the ligand and not to the aryl ring (i.e.  $\eta^1$  not  $\eta^6$  coordination is envisaged). The observation of an AB quartet for the methylene protons ( $J_{AB} = 16$  Hz) is as expected for 2-telluraindane coordinated in this manner. In contrast, complex **2** shows a broad singlet for these methylene protons at room temperature (r.t.) which sharpens on heating to 323 K and resolves into the expected AB quartet ( $J_{AB} = 13.5$  Hz) on cooling to 223 K, however the  $^{125}Te$  spectrum is a singlet at r.t. but resolves into a doublet at 238 K ( $J^{103}Rh-^{125}Te = 108$  Hz). It is argued that these data are only reconcilable in terms of a dissociative mechanism in which the equilibrium populations of the free species are small and where the rate of exchange at r.t. lies between that required to average the  $^{125}Te$  chemical shifts and that required to effectively decouple the  $^{125}Te-^{103}Rh$  interaction. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Telluraindane; Rhodium;  $^{125}Te$ -NMR

## 1. Introduction

The mode of binding of thiophenes to transition metals has been the subject of intense research over the last few decades with a view to elucidating mechanisms for hydrodesulfurisation processes [1,2]. More recently, Angelici and co-workers have extended their work to look at the interactions of selenophenes with transition metals, exploiting the fact that the existence of the NMR-active isotope  $^{77}Se$  (7.58% natural abundance) may make it possible to study selenophene binding to catalyst surfaces [3,4]. From this work it has emerged that  $^{77}Se$ -NMR spectroscopy is capable of distinguishing  $\eta^5$  coordination from  $\eta^1$ (Se) coordination based on chemical shift data. Less common modes of binding

such as  $\eta^2$  and  $\eta^4$  coordination have also been associated with distinct  $^{77}Se$  chemical shift ranges.

A recent publication by ourselves [5] demonstrated that  $^{125}Te$ -NMR spectroscopy (the  $^{125}Te$  nucleus has 7.03% natural abundance) may be employed in a similar fashion for determining the mode of binding of tellurium heterocycles to metal centres. A further advantage was also recognised when rhodium was used as the coordinating metal, in that the magnitude of the  $^{103}Rh-^{125}Te$  coupling constant is also useful in helping to elucidate the nature of interaction between the metal and the ligand. Thus, the tellurophene complex  $[Cp^*Rh(\eta^5-C_4H_4Te)]^{2+}$  gave a  $J(^{103}Rh-^{125}Te)$  value of 20 Hz whereas, at the other extreme, the corresponding coupling constant for the dibenzotellurophene complex  $[Cp^*RhCl_2(\eta^1-C_{12}H_8Te)]$  was found to be 142 Hz. This was explained by the direct interaction between Rh and

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Te in the  $\eta^1$ -complex in which the two atoms are associated via a  $\sigma$ -bond, whereas a much weaker interaction between rhodium and tellurium is expected in the  $\pi$ -coordinated  $\eta^5$ -complex.

The aim of the present study was to synthesise rhodium complexes of 2-telluraindane and study the nature of metal-ligand interactions in solution with NMR spectroscopy. Two possible modes of coordination can be envisaged for 2-telluraindane;  $\eta^1$ -coordination as previously described [6] in which the ligand is bound to the metal through only the heteroatom or alternatively  $\eta^6$ -coordination in which metal-ligand interaction occurs through the benzene ring.

## 2. Experimental and results

### 2.1. General

Rhodium trichloride trihydrate was provided by Johnson Matthey and used for the preparation of pentamethylcyclopentadienylrhodium dichloride dimer [7]. 2-Telluraindane was prepared by the indicated literature method [8]. Acetone was AR grade and purged with argon for an hour prior to use; hexane was distilled from  $\text{CaH}_2$  and toluene was distilled from sodium, silver triflate was a commercial specimen. All manipulations were carried out under an atmosphere of pure argon with the use of standard Schlenk techniques.

### 2.2. Physical measurements

Proton (300.133),  $^{13}\text{C}$  (75.469)- and  $^{125}\text{Te}$  (78.580)-NMR spectra were obtained at the indicated frequencies (MHz) with a Bruker AC-300 multinuclear spectrometer for  $\text{CDCl}_3$  solutions using  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and (*p*- $\text{EtOC}_6\text{H}_4$ ) $_2\text{Te}_2$ ,  $\delta$  456 [9] versus  $\text{Me}_2\text{Te}$  ( $^{125}\text{Te}$ ), as standards. IR 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. Elemental analyses were carried out by Medac, Department of Chemistry, Brunel University.

### 2.3. Preparation of $[\text{Cp}^*\text{Rh}(\text{C}_8\text{H}_8\text{Te})][\text{O}_3\text{SCF}_3]_2$ (**1**)

An acetone solution (10  $\text{cm}^3$ ) of  $\text{Ag}(\text{O}_3\text{SCF}_3)$  (0.83 g, 3.23 mmol) was added in one portion to an acetone suspension of  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.50 g, 0.81 mmol) and 2-telluraindane (0.38 g, 1.64 mmol). Silver chloride gradually precipitated from the dark orange solution. After 2 h of stirring at r.t., the mixture was filtered through Celite in air to remove  $\text{AgCl}$  and the orange filtrate was concentrated under vacuum to half volume. Addition of an equal volume of hexane to the concen-

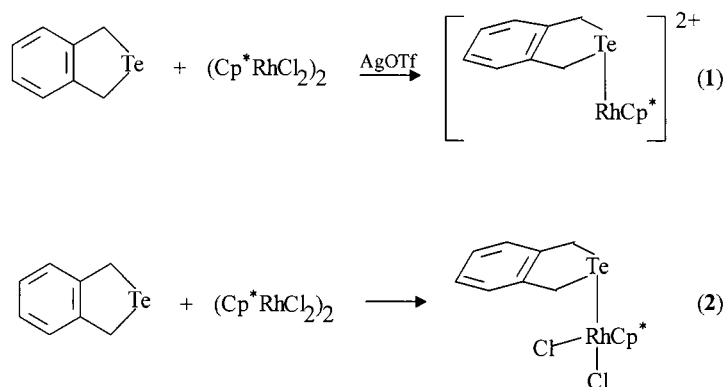
trated filtrate resulted in the precipitation of an orange solid (**1**); yield 0.59 g, 47% based on  $[\text{Cp}^*\text{RhCl}_2]_2$ . Anal. Found: C, 31.7; H, 3.4.  $\text{C}_{20}\text{H}_{23}\text{F}_6\text{O}_6\text{RhS}_2\text{Te}$  requires C, 31.3; H, 3.0%. NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  7.16 (m, 2H, ArH), 7.14 (m, 2H, ArH), 4.37 (q, 4H, CH<sub>2</sub>) [ $J_{\text{AB}} = 16.0$  Hz], 1.60 (s, 15H, Cp\*–H);  $^{13}\text{C}$ ,  $\delta$  140.2–128.2 (Ar), 20.9 (CH<sub>2</sub>), 9.97 (Cp\*);  $^{125}\text{Te}$ ,  $\delta$  74.8 (d) [ $J(^{103}\text{Rh}-^{125}\text{Te}) = 66$  Hz]. FAB mass spectrum:  $m/z = 621$ ,  $[\text{Cp}^*\text{Rh}(\text{C}_8\text{H}_8\text{Te})][\text{O}_3\text{SCF}_3]^+$ ; 472,  $[\text{Cp}^*\text{Rh}(\text{C}_8\text{H}_8\text{Te})]^+$ .

### 2.4. Preparation of $[\text{Cp}^*\text{RhCl}_2(\text{C}_8\text{H}_8\text{Te})]$ (**2**)

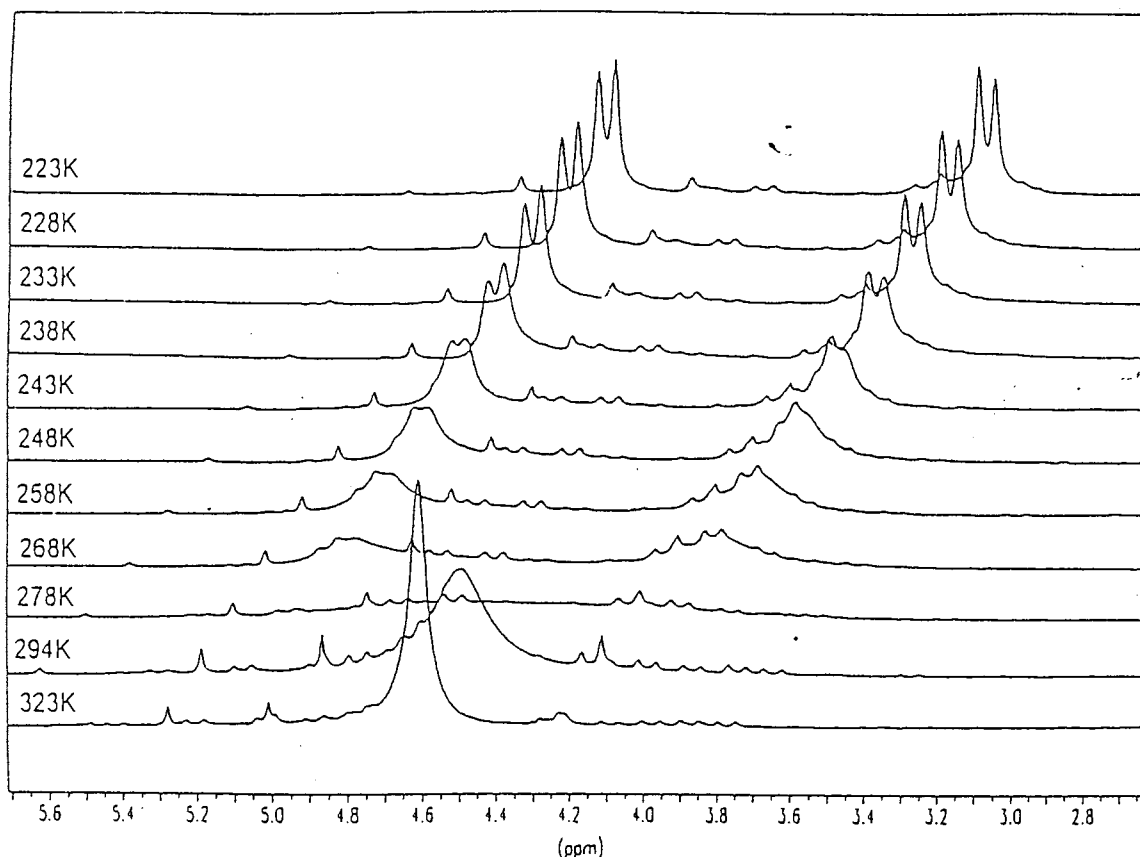
2-Telluraindane (0.38 g, 1.64 mmol) was dissolved in toluene (40  $\text{cm}^3$ ) together with  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.50 g, 0.81 mmol) and heated, with stirring, under reflux for 3 h. The reaction mixture was then filtered, affording a brown residue (0.11 g) and a deep red–brown filtrate. Removal of toluene under vacuum from the filtrate gave **2** as a dark red solid; yield 0.54 g, 62% based on  $[\text{Cp}^*\text{RhCl}_2]_2$ . Anal. Found: C, 40.2; H, 4.3.  $\text{C}_{18}\text{H}_{23}\text{Cl}_2\text{RhTe}$  requires C, 39.9; H, 4.3%. NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  7.13 (m, 2H, ArH), 7.03 (m, 2H, ArH), 4.59 [br s (r.t.) 4H, CH<sub>2</sub>;  $q < 245$  K ( $J_{\text{AB}} = 13.4$  Hz)], 1.68 (s, 15H, Cp\*–H);  $^{13}\text{C}$ ,  $\delta$  141.3–126.7 (Ar), 21.6 (CH<sub>2</sub>), 9.47 (Cp\*);  $^{125}\text{Te}$ ,  $\delta$  88.7 (s, r.t.); 86.9 (d at 238 K) [ $J(^{103}\text{Rh}-^{125}\text{Te}) = 108$  Hz (223 K)]. FAB mass spectrum:  $m/z = 507$ ,  $[\text{Cp}^*\text{RhCl}(\text{C}_8\text{H}_8\text{Te})]^+$ ; 472,  $[\text{Cp}^*\text{Rh}(\text{C}_8\text{H}_8\text{Te})]^+$ .

## 3. Discussion

In our previous study [5], complexes containing  $\text{Cp}^*\text{Rh}$  and dibenzotellurophene (dbt) were prepared, the structural formulae of which were elucidated as  $[\text{Cp}^*\text{Rh}(\text{C}_{12}\text{H}_8\text{Te})][\text{O}_3\text{SCF}_3]_2$  (**3**) and  $[\text{Cp}^*\text{RhCl}_2(\text{C}_{12}\text{H}_8\text{Te})]$  (**4**). The present work was concerned with the preparation of analogous complexes of 2-telluraindane and two stoichiometrically very similar compounds were isolated;  $[\text{Cp}^*\text{Rh}(\text{C}_8\text{H}_8\text{Te})][\text{O}_3\text{SCF}_3]_2$  (**1**) and  $[\text{Cp}^*\text{RhCl}_2(\text{C}_8\text{H}_8\text{Te})]$  (**2**) (see Scheme 1). As for the dbt complexes, the proton and  $^{13}\text{C}$ -NMR spectra provide no evidence for anything other than  $\eta^1$ -coordination. The fact that the  $^{125}\text{Te}$ -NMR signal is split into a doublet for complex **1** at r.t. and for complex **2** at 223 K further supports the presence of  $\eta^1$ -coordination. Complex **1** gives a tellurium-125 coordination shift ( $\Delta\delta$ ) of +260 ppm and a  $^{103}\text{Rh}-^{125}\text{Te}$  coupling constant of 66 Hz. The related dbt complex has  $^{125}\text{Te}$ -NMR parameters of  $\Delta\delta = -56.5$  ppm and  $J(^{103}\text{Rh}-^{125}\text{Te}) = 88$  Hz. Complex **2** shows a  $\Delta\delta$  value of +276 ppm and a  $J(^{103}\text{Rh}-^{125}\text{Te})$  value of 108 Hz with the analogous dbt complex displaying values of -67.2 ppm and 142 Hz, respectively. Hence, in contrast to the aromatic tellurophene complexes, the tellurium atom in the 2-telluraindane complexes is greatly deshielded relative to



Scheme 1. Synthesis of coordination complexes of 2-telluraindane and rhodium.

Fig. 1. Temperature variation in  $^1\text{H-NMR}$  signal for methylene protons of  $[\text{Cp}^*\text{RhCl}_2(\text{C}_8\text{H}_8\text{Te})]$ .

the free heterocycle, implying that it acts as a simple two-electron donor (Lewis base). Furthermore, in the 2-telluraindane complexes, the ligand is less strongly bound to the metal, as reflected by the smaller values of  $J(^{103}\text{Rh}-^{125}\text{Te})$  compared with the related dbt complexes. It is also clear that greater values of coupling constants are observed for the dichloro-complexes than for the triflate salts.

Complexes **1** and **2**, which failed to produce crystals suitable for X-ray diffraction studies of the solids, show distinct differences in their behaviour in solution at r.t.. The observation of an AB quartet for the 2-tellurain-

dane methylene protons of **1** ( $J_{\text{AB}} = 16.0$  Hz,  $\Delta\nu = 49.8$  Hz) is as expected for pyramidal coordination about tellurium; however, compound **2** shows a broad singlet for these methylene protons in  $\text{CDCl}_3$  solution at r.t.. This singlet sharpens on heating to 323 K and resolves into the expected AB quartet ( $J_{\text{AB}} = 13.4$  Hz,  $\Delta\nu = 311$  Hz) on cooling to 223 K (see Fig. 1) thus simplistically implying inversion about coordinated tellurium in this complex (further minor peaks are also present which are most likely to be due to impurities). Structural studies on telluronium salts derived from 2-telluraindane [10] suggest that when the tellurium atom is

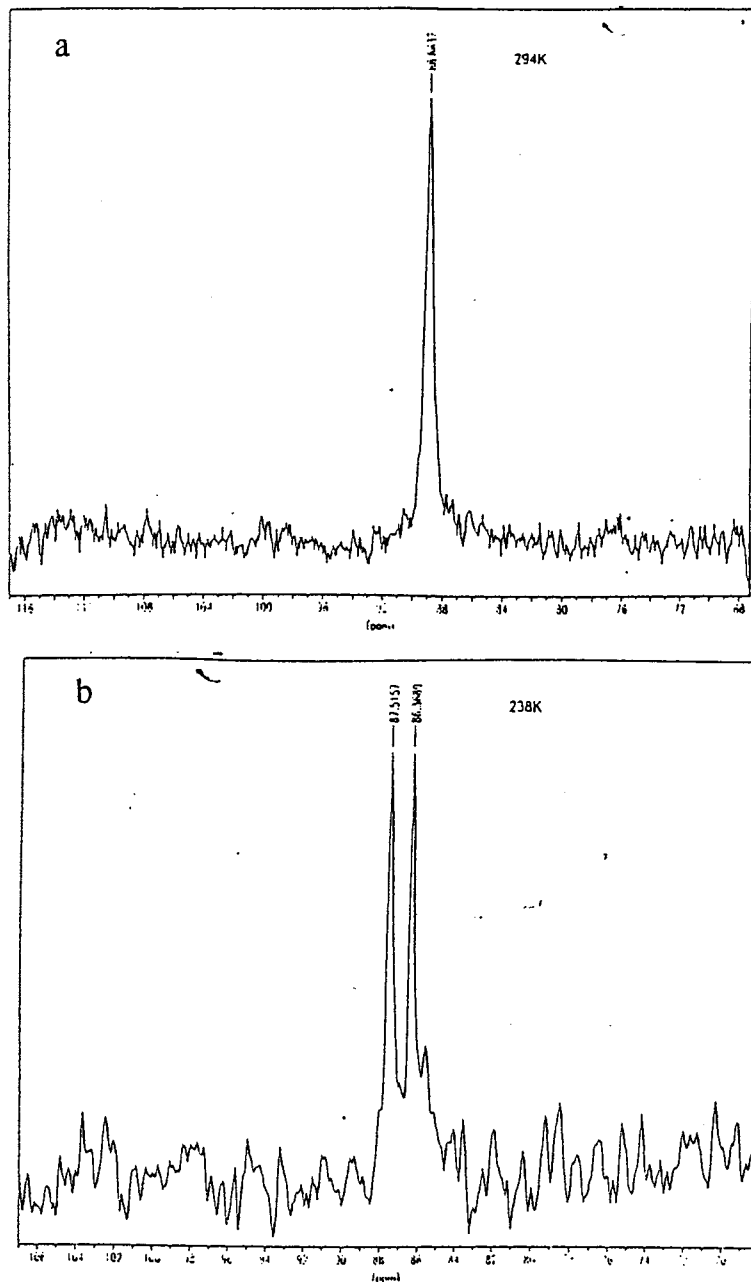
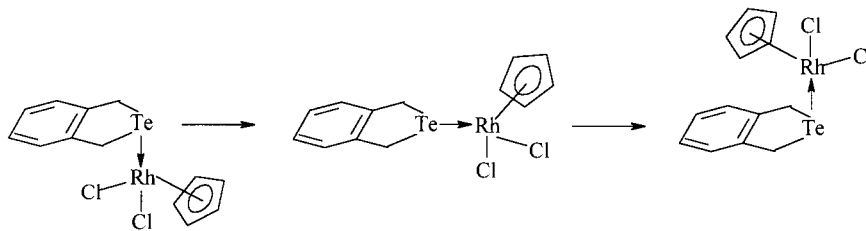


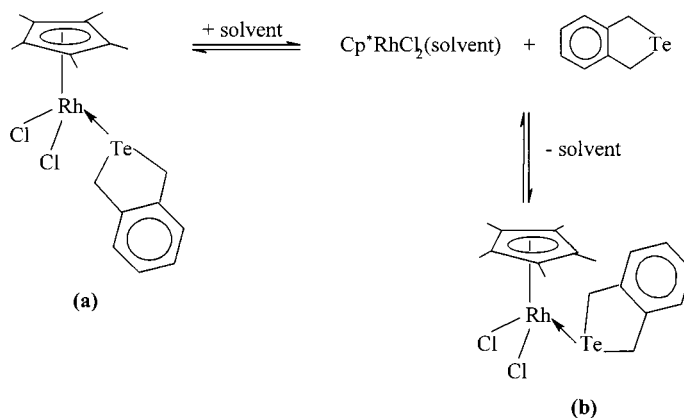
Fig. 2.  $^{125}\text{Te}$ -NMR spectra of  $[\text{Cp}^*\text{RhCl}_2(\text{C}_8\text{H}_8\text{Te})]$  at (a) 294 and (b) 238 K.



Scheme 2. A possible model for the behaviour of  $[\text{Cp}^*\text{RhCl}_2(\text{C}_8\text{H}_8\text{Te})]$  (2) at room temperature.

trigonally coordinated, the five-membered heterocyclic ring is virtually coplanar with the aromatic ring and rigid. Thus, a relatively high barrier to inversion might

be expected for the coordinated ligand. A difference is also noted in the  $^{125}\text{Te}$ -NMR spectra of the two complexes (1 and 2) at r.t.. Complex 1 shows the expected

Scheme 3. Alternative mechanism to explain the dynamic behaviour of complex **2**.

doublet for  $\eta^1$ -coordination arising from direct  $^{125}\text{Te}$ – $^{103}\text{Rh}$  coupling (both nuclei have a nuclear spin of a half), whilst complex **2** displays only a singlet. This singlet is resolved into a doublet on cooling to 238 K (see Fig. 2) which corresponds to the temperature at which the  $\text{CH}_2$  quartet resolution begins in the  $^1\text{H}$ -NMR spectrum (Fig. 1) The doublet (Fig. 2 b) no doubt arises from the  $^{103}\text{Rh}$ – $^{125}\text{Te}$  coupling and does not indicate the existence of two different isomers. The fact that two quartets are not observed in the low temperature  $^1\text{H}$ -NMR spectrum dismisses any possibility of the latter being the case. These observations can be explained by considering the nature of the dynamic process taking place in solution. One possibility is that the tellurium and the rhodium are permanently bonded at r.t., and their relative positions are constantly fluctuating, as for example, depicted in Scheme 2. In such a case the  $^{103}\text{Rh}$ – $^{125}\text{Te}$  coupling constant could follow a rapidly fluctuating cycle so that only an average of the coupling constant would be observed at r.t.. However, for the coupling constant to be averaged to zero, and result in the observed singlet, it would be necessary for the coupling constant to undergo an unlikely change of sign and also to quite fortuitously result in the average coupling constant approximating to zero. That this explanation is improbable is further supported by the temperature dependence of the  $^{125}\text{Te}$  spectrum. If Scheme 2 is valid it would be expected that as the temperature is decreased the various conformers would become populated, possibly to different extents, and it would be expected that several  $^{125}\text{Te}$  doublets might be resolved.

Another possible explanation for the dynamic behaviour of complex **2** in solution is that a dissociative mechanism is operative, although this is surprising for a  $4d^6$  complex it is possible that the components do not become solvent separated. Without specifying the mechanistic nature of this mechanism pro temp, the

temperature dependence of the  $^1\text{H}$  and  $^{125}\text{Te}$  spectra will depend on the relative concentrations of the free and complexed  $^{125}\text{Te}$  species and on the rate of exchange between these.

Using classical exchange theory, the experimental observations can be rationalised by:

$$\Delta\delta_{\text{Te}}(10^4) \geq R_{\text{HT}} \geq \Delta\delta_{\text{H-H}} (2 \times 10^3) \geq J_{\text{Rh-Te}} (7 \times 10^2) \\ \geq J_{\text{H-H}} (10^2) \geq R_{\text{LT}}$$

The implication is that the rate of exchange at the higher temperature ( $R_{\text{HT}}$ ) lies between  $10^4$  and  $2 \times 10^3 \text{ s}^{-1}$ , and that, as expected, this decreases with temperature to give a lower temperature value ( $R_{\text{LT}}$ ) of  $< 10^2 \text{ s}^{-1}$ .

The crux of the above explanation is that the concentration of the uncomplexed Te species in the dissociative mechanism is always very low so that resonances at its chemical shift are not detected.

Although it is not possible to definitively establish the mechanism of the dissociative process two broad categories are possible. The first is similar to that suggested in Scheme 3 where the solvent plays an important role. In this case it is possible that the solvent might stabilise the free species, which would be significantly populated, contrary to the above-mentioned requirements of the exchange process. The second might involve the breaking and making of the Te–Rh bond utilising the two available lone pairs in the free moiety. In this case it would be reasonable to imagine that the Rh and Te species would remain in close proximity, almost as a lowly populated encounter pair, during the exchange process. On balance the second mechanism is to be favoured because it would be expected to involve a relatively faster exchange rate than a process hindered by the solvent, and also a smaller temperature dependence of the population of the free species.

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