Utilisation of an η^3-allyl hydride complex, formed by UV irradiation, as a controlled source of 16-electron (η^5-C_5Me_5)Rh(CH_2═CHMe)†

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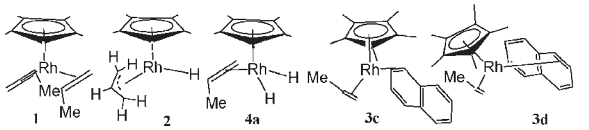
Low temperature UV irradiation of solutions of (η^5-C_5Me_5)-Rh(CH_2═CHMe)$_2$ yields (η^5-C_5Me_5)Rh(η^3-CH_2CHCH_2)(H), which provides controlled access to the 16-electron fragment (η^5-C_5Me_5)Rh(CH_2═CHMe).

NMR spectroscopy, in conjunction with UV photolysis of samples within the NMR probe, has enabled the characterisation of a number of unstable materials. Recently, this approach has been used to detect alkyl hydride complexes,[1,2] a xenon complex[3] and a number of hydride complexes.[4] Others have used photo-chemically induced dynamic nuclear polarisation (photo-CIDNP) to determine kinetic parameters for protein folding.[5] Such studies have also enabled the successful detection of materials that are unstable even at 213 K through enhanced signals resulting from the parahydrogen-induced polarisation effect (PHIP[6,7]).[8–10]

The stepwise photochemical displacement of ethene from (η^5-C_5H_5)Rh(C_2H_4)$_2$ allowed us to characterise the unstable solvent complex (η^5-C_5H_5)Rh(C_2H_4)(toluene) by NMR spectroscopy at 213 K.[11] No evidence for the formation of the corresponding aryl hydride isomer was, however, detected even though earlier H–D exchange studies suggest its existence at high temperatures.[12] In the case of the related complex (η^5-C_5Me_5)Rh(CH_2═$CHSiMe_3$)$_2$, thermolysis has been shown to result in H–D exchange with the solvent and the olefinic $SiMe_3$ and C_5Me_5 groups.[13] Indeed, when (η^5-C_5Me_5)Rh(CH_2═$CHSiMe_3$)$_2$ is warmed with benzophenone the catalytic addition of the alkene to the *ortho*-position of the activated arene is achieved.[14] A reaction mechanism involving the formation of a Rh(III)Cp*Rh(vinylsilane)(H)(aryl) complex was proposed.[15]

This paper describes a number of photolysis studies and density functional theory (DFT) calculations on the analogous C_5Me_5-containing system (η^5-C_5Me_5)Rh(CH_2═CHMe)$_2$ (**1**). **1** exists in a number of rotameric forms that are distinguished by the relative orientations of the methyl substituents of the propene ligand, as described previously by Brookart *et al.*,[16] and shows similar H–D exchange behaviour; a single isomer of **1** is illustrated in Scheme 1. As a first step, we photolysed a toluene-d_8 solution of **1** at 213 K. This led to the generation of a single metal-containing species (**2**) that yields a hydride resonance at δ −12.84 (J_{RhH} = 32 Hz) and free propene. This hydride resonance connected with a ^{103}Rh signal at δ −1059 in a 2D ^{1}H–^{103}Rh HMQC spectrum, with this rhodium centre also coupling to four other proton resonances at δ 3.61, 2.45, 2.36 and 1.87 (Cp*) for which integrations relative to the Cp* signal of 15, revealed a relative intensity of 1 (hydride) : 1 : 2 : 2, respectively. These data are therefore consistent with **2** as the η^3-allyl hydride complex (η^5-C_5Me_5)Rh(η^3-CH_2CHCH_2)(H). Bergman *et al.* obtained a similar complex by reduction of (η^5-C_5Me_5)Ir(η^3-CH_2CHCH_2)Cl.[17]



Scheme 1 Structures for **1**, **2**, **3** and **4a**.

In view of the evidence that these experiments failed to facilitate the detection of the expected solvent complex, (η^5-C_5Me_5)Rh(CH_2═CHMe)(η^2-toluene), a sample of **1** was photolysed with naphthalene at the slightly higher temperature of 233 K. Naphthalene was selected because aromatic resonance stabilisation energy effects work to stabilise the corresponding η^2-arene isomers as illustrated in studies of Cp*Rh(PMe_3)(H)$_2$.[18] Now, five new Cp* resonances are observed in the corresponding ^{1}H NMR spectrum. One of these products was identified as Cp*Rh(η^4-$C_{10}H_8$); Müller *et al.* obtained an X-ray structure of a related complex.[19]

The remaining four species yield Cp* proton resonances at δ 1.07, 1.10, 1.52 and 1.53, which connect to ^{103}Rh signals that lie in a narrow 30 ppm spectral window thereby indicating their structural similarity. The formation of four isomers of the η^2-naphthalene complex Cp*Rh(CH_2═CHMe)(η^2-$C_{10}H_8$) (**3a–3d**), is indicated; the major two, as illustrated in Scheme 1, were attributed on the basis of NOE data which in turn suggest that interactions with the methyl substituent of the propene ligand control the relative ligand orientations. We present ^{1}H, ^{13}C and ^{103}Rh data for all five species in the ESI†. It should be noted that isomers **3a** and **3b**, and isomers **3c** and **3d**, interconvert on the NMR timescale according to EXSY measurements; for the interconversion **3c** and **3d** $\Delta H^‡$ = 64 ± 2 kJ mol^{-1} and $\Delta S^‡$ = 19 ± 6 J mol^{-1} K^{-1}.† Nonetheless, these spectra provide no evidence for a napthylhydride isomer, in contrast to the situation described for Cp*Rh(PMe_3)(η^2-$C_{10}H_8$), where equilibration with a Rh(III) C–H activation

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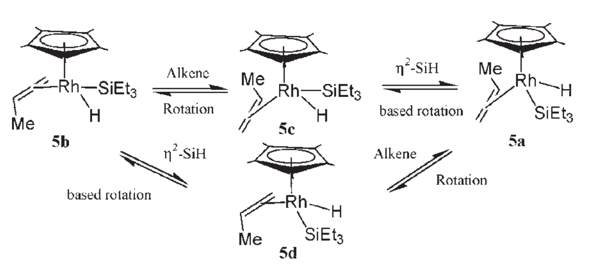
product is evident.[20] This reaction also suggests that either the formation of **2** from Cp*Rh($CH_2{=}CHMe$) is reversible or that the binding of naphthalene competes with hydride transfer.

In order to address this question, the *in situ* photolysis of **1** with *p*-H_2 at 213 K was examined. Only **2** was detected, even though the PHIP effect offers the opportunity to see species in low concentration.[6,7] This suggests that intramolecular hydride transfer from the putative 16-electron fragment Cp*Rh($CH_2{=}CHMe$) is fast relative to H_2 addition at 213 K. Upon repeating the experiment at 233 K, a secondary reaction became evident since a broad weakly polarised hydride resonance also becomes visible at δ −12.30. When this sample is cooled, this hydride signal broadens until at 196 K, two equally intense doublets based at δ −12.25 and −12.32 are observed with rhodium couplings of 26.89 and 28.42 Hz, respectively. These two hydride resonances connect to two different ^{103}Rh signals at δ −1079.1 and −1076.8, respectively, in the corresponding HMQC experiment. While these two sets of hydride resonances proved not to be coupled in the corresponding COSY experiment, they were connected by positive cross peaks in the associated EXSY experiment that are of equal intensity even with a 50 ms mixing time at 196 K. The two hydride sites that give rise to these resonances are therefore in different, albeit rapidly inter-converting, molecules. We assigned these resonances to two isomers of (η^5-C_5Me_5)Rh($CH_2{=}CHMe$)$(H)_2$ **4a** that are differentiated according to the orientation of the propene's methyl group.

When the *in situ* irradiation of **1** was repeated in the presence of *p*-H_2 and propene at 295 K, the hydride resonance for the hydride complex **4a** appears as a polarised signal at δ −12.7, supported by polarised resonances at δ 2.92 and 2.52 due scrambling of the hydride and alkenic proton sites. In addition, a further much sharper hydride signal, a polarised triplet appears at δ −16.16 where J_{RhH} = 35 Hz, as do signals at δ 0.94 and 1.31 due to propane. This hydride resonance corresponds to a kinetic isomer of the hydride bridged dimer (η^5-C_5Me_5)Rh($CH_2{=}CHMe$)(μ-H)$_2$Rh(η^5-C_5Me_5)($CH_2{=}CHMe$) (**4b**) on the basis of NMR data†.[11] In this case, the dinuclear dihydride complex is stabilised relative to **4a** because the propensity for hydride migration is reduced. These results confirm that while **2** can be prepared at 213 K, it allows controlled access to (η^5-C_5Me_5)Rh($CH_2{=}CHMe$) at 233 K.

A preliminary DFT study (at the B3LYP level)† of the formation of the allyl complex **2** and its reactivity was used to explore this. It was found that the thermal dissociation of propene from (η^5-C_5Me_5)Rh(C_2H_3Me)$_2$ (**1**) is unfavourable by 100 kJ mol^{-1}. The corresponding *endo* isomer of 16-electron *endo*-(η^5-C_5Me_5)Rh(C_2H_3Me) (**1-me**) proved to be 1.4 kJ mol^{-1} more stable than the *exo* form, and reacted preferentially to form the allyl species (η^5-C_5Me_5)Rh(η^3-CH_2CHCH_2)(H) (**2**) in a process that is exothermic by 11.8 kJ mol^{-1} and possesses a moderate activation barrier of 48.8 kJ mol^{-1}. Equilibration between **2** and **1-me** thus allows for the reaction of the monoalkene complex with H_2 to form **4a** in a process that is favourable by 76.9 kJ mol^{-1} and competes with solvent coordination.† Oxidative addition of H_2 to 16-electron **1-me** is predicted first to yield a dihydrogen complex (**4-η^2-H_2**) in a barrier-less process (where $\Delta E_{\mathrm{overall}}$ is −59.5 kJ mol^{-1}) with further evolution to **4a** proceeding *via* the crossing of a very low energy barrier of 1.2 kJ mol^{-1}.



Scheme 2 Suggested interconversion pathways for the four isomers of Cp*Rh(H)($SiEt_3$)($CH_2{=}CHMe$).

Related Rh(III) species can also be accessed by the analogous reaction of **1** with the SiH bond of a silane.[21,22] When the reaction of **1** with Et_3SiH was initiated photochemically at 298 K, the formation of the known complex (η^5-C_5Me_5)Rh(H)$_2$($SiEt_3$)$_2$ was apparent.[23] Three additional hydride resonances were also visible in this spectrum, at δ −13.08, −14.99 and −15.31. Based on the NMR data for the species giving rise to these signals, **5a**, **5b** and **5c**, they are isomers of (η^5-C_5Me_5)Rh(C_2H_3Me)(H)($SiEt_3$).† These deductions include the assessment of multinuclear NMR data, including NOE connections at 233 K. The structures for these products are illustrated in Scheme 2; no direct evidence for **5d** was seen. The NOE measurements also revealed that the three isomers of **5** interconvert. The rate constants for these interconversions were determined between 263 and 315 K and then used to determine the associated thermodynamic parameters listed in Tables 1 and 2.

These data have been placed onto the potential energy diagram shown in Fig. 1. Species **5a** and **5c** can interconvert *via* rotation through a transition state featuring an η^2-SiH bond while **5b** and **5c** can interconvert *via* alkene rotation. The higher energy interconversion of **5b** to **5a** must proceed *via* the unseen isomer **5d** as shown in Scheme 2. This deduction is based on the fact that the measured value for alkene rotation from **5c** to **5b** exceeds the observed value for interchange of **5a** into **5b**. This means that interchange cannot proceed *via* a route involving the **5c** to **5b** transformation.

We have recently reported that the Rh(III) complex CpRh($SiEt_3$)(H)($C_2H_3CO_2{}^t$Bu) also exists as two geometrical isomers, which interconvert on the NMR timescale.[24] The activation parameters for interchange from the major to minor isomer were reported to be $\Delta H^\ddagger$ = 60.2 ± 2 kJ mol^{-1} and

Table 1 Activation parameters for the interconversion of **5**

Process	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J mol^{-1} K^{-1}	$\Delta G^\ddagger_{300}$/kJ mol^{-1}
5a → 5b	73.5 ± 1	25 ± 3	66.0 ± 0.4
5b → 5a	75.2 ± 1.5	24 ± 5	67.9 ± 0.3
5b → 5c	71.5 ± 3.5	−4 ± 12	72.7 ± 0.1
5c → 5b	66.6 ± 5	−4 ± 17	67.7 ± 1.0
5a → 5c	83.2 ± 2	47 ± 6	69.0 ± 0.2
5c → 5a	77.4 ± 0.6	38 ± 2	66.0 ± 0.2

Table 2 Equilibrium parameters for the interconversion of **5**

Process	ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}	ΔG°_{300}/kJ mol^{-1}
5a → 5b	−0.4 ± 0.5	5 ± 1	−1.9 ± 0.1
5b → 5c	4.9 ± 1	0 ± 4	4.9 ± 0.1
5a → 5c	4.4 ± 0.8	5 ± 3	3.0 ± 0.1

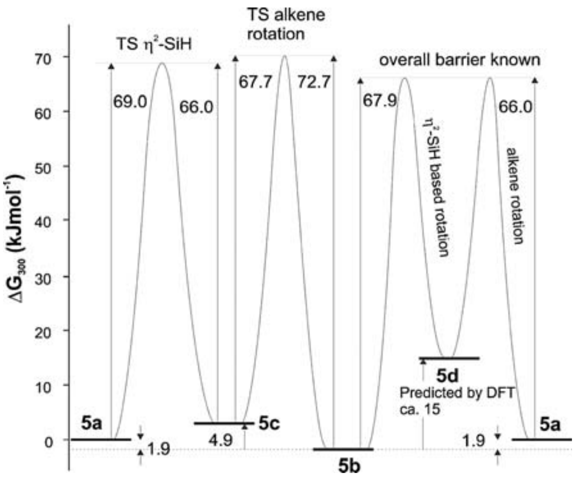


Fig. 1 Potential energy diagram for the interconversion of **5**.

$\Delta S^‡ = 8 \pm 9$ J mol^{-1} K^{-1} for this process. They are substantially smaller than those found here in agreement with the suggestion the Cp* ring activates the system and stabilises the Rh(III) form.

When a sample of **1** is photolysed at 213 K, in the presence of a 25 fold excess of $HSiEt_3$, while **2** dominates, **5a** : **5b** : **5c** are also observed in the ratio 1 : 0.73 : 0.32. The proportion of **5b** is therefore reduced when compared to 298 K where the corresponding ratio is 0.46 : 1 : 0.14. These data allow us to conclude that there is a kinetic preference for the formation of **5a**; overall **5b** is the preferred thermodynamic product, perhaps because in **5b** the interaction of the Me substituent of the alkene with the Cp* ring and the silyl ligand is minimised.

The DFT study is consistent with these data since formation of **2** competes effectively *via endo*-(η^5-C_5Me_5)Rh(C_2H_3Me) while *exo*-(η^5-C_5Me_5)Rh(C_2H_3Me) in which methyl group points away from the metal centre forms **5a**. The relative energies of the silyl hydride isomers have also been considered for the $SiMe_3$ analogue. This revealed that there are indeed four local minima for (η^5-C_5Me_5)Rh(C_2H_3Me)(H)($SiMe_3$) (**6a**, **6b**, **6c** and **6d**) where **6b** is lowest in energy isomer, with **6a** and **6b** being less stable by 2.4 and 5.1 kJ mol^{-1}, respectively (Table 3). Species **6d** proved to lie 16.8 kJ mol^{-1} in energy above **6b**. While we have not been able to locate a TS for the Rh-η^2-H-Si based species necessary to convert **5a** to **5c** for the Cp* system, we have located one for the analogous Cp system.†

In this paper we have described how the reversible interconversion of an 18-electron allyl hydride and a 16-electron alkene enables the controlled formation of unstable η^2-arene complexes. In addition, this enabled the NMR characterisation of the elusive (η^5-C_5Me_5)Rh(alkene)$(H)_2$ complex. The p-H_2 enhancements seen for the alkene and hydride protons of **4a** illustrate a rapid and reversible hydride transfer step. These PHIP results were made possible because replacing ethene with propene breaks the symmetry of the hydride ligands in **4a**. This effect was further utilised in **5** where it facilitated the examination of a racemisation processes that would be invisible with C_2H_4. The use of laser irradiation to promote ligand exchange could allow these symmetry breaking methods to be applied to a wider range of photochemical problems spanning organic, inorganic and biological areas with the opportunity to see substantial PHIP effects in normally invisible species.

Table 3 DFT (BL3YP) relative gas-phase energies, enthalpies and entropies for model complexes **6**

	ΔE/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	ΔG_{300}/kJ mol^{-1}
6a	2.4	2.0	6.6	0.0
6b	0.0	0.0	0.0	0.0
6c	5.1	6.3	−3.7	7.4
6d	16.8	16.3	4.8	14.8

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