Photochemical reactions of $[CH_2(\eta^5-C_5H_4)_2][Rh(C_2H_4)_2]_2$ with silanes: evidence for Si-C and C-H activation pathways[†]

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Photochemical reaction of $[CH_2(\eta^5-C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 with dmso led to the stepwise formation of $[CH_2(\eta^5-C_5H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(dmso)]$ **2a** and $[CH_2(\eta^5-C_5H_4)_2][Rh(C_2H_4)(dmso)]_2$ **2b**. Photolysis of **1** with vinyltrimethylsilane ultimately yields three isomeric products of $[CH_2(\eta^5-C_5H_4)_2][Rh(CH_2=CHSiMe_3)_2]_2$, **3a,3b** and 3c which are differentiated by the relative orientations of the vinylsilane. When this reaction is undertaken in d_6 -benzene, H/D exchange between the solvent and the α -proton of the vinylsilane is revealed. In addition evidence for two isomers of the solvent complex $[CH_2(\eta^5-C_3H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(\eta^2-toluene)]$ was obtained in these and related experiments when the photolysis was completed at low temperature without substrate, although no evidence for H/D exchange was observed. Photolysis of 1 with Et₃SiH yielded the sequential substitution products $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(C_{2}H_{4})_{2}][Rh(C_{2}H_{4})(SiEt_{3})H]$ 4a, $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(C_{2}H_{4})(SiEt_{3})H]$ 4b, $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(C_{2}H_{4})(SiEt_{3})H]$ $[Rh(C_2H_4)(SiEt_3)H][Rh(SiEt_3)_2(H)_2]$ 4c and $[CH_2(\eta^5-C_5H_4)_2][Rh(SiEt_3)_2(H)_2]_2$ 4d; deuteration of the α -ring proton sites, and all the silv protons, of **4d** was demonstrated in d_6 -benzene. This reaction is further complicated by the formation of two Si-C bond activation products, [CH2(n5-C5H4)2][RhH(µ-SiEt2)]2 5 and $[CH_2(\eta^5-C_5H_4)_2][(RhEt)(RhH)(\mu-SiEt_2)_2]$ 6. Complex 5 was also produced when 1 was photolysed with Et₂SiH₂. When the photochemical reactions with Et₃SiH were repeated at low temperatures, two isomers of the unstable C-H activation products, the vinyl hydrides $[CH_2(\eta^5-C_5H_4)_2][{Rh(SiEt_3)H}{Rh(SiEt_3)}(\mu-\eta^1,\eta^2-CH=CH_2)]$ 7a and 7b, were obtained. Thermally, 4c was shown to form the ring substituted silyl migration products $[(\eta^5-C_5H_4)CH_2(C_5H_3SiEt_3)]$ [Rh(SiEt_3)₂(H)₂]₂ 8 while 4b formed [CH₂(C₅H₃SiEt₃)₂][Rh(SiEt_3)₂(H)₂]₂ (9a and 9b) upon reaction with excess silane. The corresponding photochemical reaction with Me₃SiH yielded the expected products $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(C_{2}H_{4})_{2}][Rh(C_{2}H_{4})(SiMe_{3})H] 10a, [CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(C_{2}H_{4})(SiMe_{3})H]_{2} 10b,$ $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(C_{2}H_{4})(SiMe_{3})H][Rh(SiMe_{3})_{2}(H)_{2}]$ **10c** and $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][Rh(SiMe_{3})_{2}(H)_{2}]_{2}$ **10d**. However, three Si–C bond activation products, $[CH_2(\eta^5-C_5H_4)_2][(RhMe)(RhH)(\mu-SiMe_2)_2]$ 11, $[CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][(Rh{SiMe_{3}})(RhMe)(\mu-SiMe_{2})_{2}] 12 \text{ and } [CH_{2}(\eta^{5}-C_{5}H_{4})_{2}][(Rh{SiMe_{3}})(RhH)(\mu-SiMe_{2})_{2}] 13 \text{ were } [(Rh{SiMe_{3}})(RhMe)(\mu-SiMe_{2})_{2}] 12 \text{ and } [(Rh{SiMe_{3}})(RhMe)(\mu-SiMe_{2})_{2}] 13 \text{ were } [(Rh{SiMe_{3}})(RhMe)(\mu-SiMe_{3})(RhMe)(\mu-SiMe_{3})_{2}] 13 \text{ were } [(Rh{SiMe_{3}})(RhMe)(\mu-SiMe_{3})(RhMe)(\mu-SiMe_{3})_{2}] (Rh{SiMe_{3}})(RhMe)(\mu-SiMe_{3})(RhMe)$

Introduction

also obtained in these reactions.

Since $CpFe(CO)_2SiMe_3$ ($Cp = (\eta^5 - C_5H_5)$), the first example of a transition metal silyl complex, was reported by Wilkinson¹ in 1956, the number of such complexes has grown rapidly.² There continues to be much interest in this area because transition metal complexes are used to catalyse organosilane based transformations such as hydrosilation and polysilane formation.³ A popular route to complexes containing a silyl ligand involves the oxidative addition of the Si-H bond of a silane by a coordinatively unsaturated transition metal centre.^{2a} Harris et al.⁴ have used ultrafast IR spectroscopy and ab initio methods to investigate the process of Si-H bond activation. They studied the photochemical reactions of $CpM(CO)_3$ (where M = Mn, Re) in neat Et₃SiH. Following irradiation, these tricarbonyl complexes lose CO to generate the dicarbonyl species $CpM(CO)_2$ which were solvated by either the Si-H bond or the C-H bond of the ethyl group of the Et₃SiH (solvent) prior to forming CpM(CO)₂(SiEt₃)(H). While the Re product contains Re-H and Re-Si 2-centre 2-electron bonds, the Mn species contains a Mn-H-SiR₃, 3-centre 2-electron bond. Kubas et al.⁵ have shown that 'incomplete' and 'complete' silane oxidative addition products can exist in equilibrium with each other in the case of $Mo(SiH_4)(CO)(Et_2PC_2H_4PEt_2)_2$. One other example of the 'complete' oxidative addition of Si-H bonds is provided by the work of Graham⁶ who reported on the reaction of CpRh(CO)₂ with R_3SiH (where $R = C_6H_5$, $CH_2C_6H_5$). He observed that loss of CO led to the formation of CpRh(CO)(SiR₃)(H).

† Electronic supplementary information (ESI) available: NMR characterisation of 1-14. See http://www.rsc.org/suppdata/dt/b4/b417171c/

In 1965, Chalk and Harrod proposed a mechanism for the metal catalysed hydrosilation of olefins.7 The mechanism of this reaction involves hydride migration onto the bound alkene, in a H-M-SiR3 complex, followed by reductive elimination of the alkyl and silyl groups to form an alkylsilane. Many transition metal complexes have since been found to catalyse the hydrosilation reaction⁸ including some containing Cp or Cp* (where $Cp^* = \eta^5 - C_5 Me_5$) ligands. For example, in 1981, Maitlis et al.⁹ demonstrated that $[(Cp*RhCl)_2(\mu-Cl)_2]$ catalysed the hydrosilation and dehydrogenative silation of alkenes. During these studies, Cp*Rh(SiEt)₂(H)₂¹⁰ and Cp*Rh(C₂H₄)(SiEt₃)H were characterised.11 Extended studies then showed that $Cp*Rh(SiEt_3)_2(H)_2$ and $Cp*Rh(C_2H_4)_2$ catalysed the conversion of ethene with Et₃SiH to a 3 : 1 mixture of CH₂=CHSiEt₃ and Et₄Si.¹² At the same time, Perutz et al.¹³ showed that irradiation of $CpRh(C_2H_4)_2$ with R_3SiH (where R = Me, Et) led to $CpRh(C_2H_4)(SiR_3)H$ and $CpRh(SiR_3)_2(H)_2$, and the hydrosilation products EtSiR₃ and CH₂=CHSiR₃. In contrast to the Cp* analogues, $CpRh(C_2H_4)_2$ and $CpRh(SiR_3)_2(H)_2$ were not found to be active hydrosilation catalysts but CpRh(C2H4)(SiR3)H was shown to be involved.¹⁴ Deuterium labelling studies were used to suggest a role for CpRh(C2H4)(SiR3)H which begins with a [1,3]-H shift to generate CpRh(SiR₃)Et, and is followed by silyl migration onto the alkene. Seitz and Wrighton had earlier proposed a similar mechanism for hydrosilation by Co(CO)₄(SiMe₃).¹⁵ More recently, Brookhart et al.¹⁶ showed that the cationic Co(III) complex [Cp*Co(P(OMe)₃)CH₂CH₂- μ -H]⁺BAr'₄⁻ catalysed the hydrosilation of 1-hexene by Et₃SiH via a similar silyl migration. Brookhart et al. 17 have also reported that Cp*Co(SiPh₂H)₂(H)₂ is formed by thermal reaction of $Cp*Co(CH_2=CHR)_2$ (where R = H, SiMe₃) with Ph_2SiH_2 .

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The reported catalytic utility of related Group 9 metal systems has been expanded further in recent years, with (η^5 - C_9H_7)Rh(C_2H_4)₂ proving to catalyse the addition of aldehydes to ethene *i.e.* hydroacylation.¹⁸ Brookhart et al.¹⁹ showed that Cp*Co(CH₂=CHSiMe₃)₂ was also an active hydroacylation catalyst for the addition of aliphatic aldehydes to vinylsilanes. In the same year, Berry et al.20 reported the formation of arylsilanes via thermal dehydrocoupling of C_6H_5X (where $X = CF_3$, F, H, CH₃, Cl, Br) with Et₃SiH in the presence of 'Bu-ethylene and the Rh catalyst Cp*Rh(SiEt₃)₂(H)₂. Brookhart et al.²¹ have also revealed that $Cp*Rh(CH_2=CHSiMe_3)_2$ catalyses the addition of alkenes to aromatic ketones. A further example of the use of such complexes is provided by Hartwig et al.²² who demonstrated a role for Cp*Rh complexes in the formation of boron functionalised linear alkanes and functionalised arenes.

Approximately 20 years ago, Bergman et al.23 reported the preparation of the dicobalt complex $[CH_2(\eta^5-C_5H_4)_2][Co(CO)_2]$, via reaction of $[CH_2(C_5H_5)_2]$ with $Co_2(CO)_8$. Reduction with Na and reaction with MeI generated the M-M bond containing species $[CH_2(\eta^5-C_5H_4)_2][Co(Me)(\mu-CO)]_2$. In 1985, Werner et al.²⁴ synthesised $[CH_2(\eta^5-C_5H_4)_2][Rh(C_2H_4)_2]_2$ (1) and several related dinuclear rhodium complexes, and reported on a number of their thermal reactions.²⁵ Here we describe how the dinuclear rhodium complex $[CH_2(\eta^5-C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 reacts with dmso, CH₂=CHSiMe₃, Et₃SiH, Et₂SiH₂ and Me₃SiH under photochemical conditions. A number of novel reaction products that are formed via C-H and Si-C bond activation pathways are described.

Experimental

All the syntheses and manipulations, except where specifically stated, were carried out under inert atmosphere conditions using standard Schlenk techniques or an Alvic Scientific Gas Shield glove box equipped with freezer (at -32 °C), vacuum pump and N₂ purge facilities. Celite (Aldrich) was dried under vacuum prior to use. NMR tubes were purchased from Wilmad (5 mm 528 Grade) and fitted with a concentric PTFE Young's valve.

Chemicals were obtained from the following sources: Nondeuterated solvents: benzene, diethyl ether, dimethyl sulfoxide, pentane, toluene, hexane and THF were obtained from Fisons. Aromatic and ethereal solvents were dried by refluxing with sodium/benzophenone. Deuterated solvents: d₆-benzene and d8-toluene were stored over a potassium mirror and used via vacuum transfer. d₆-dmso was dried over 4 Å molecular sieves and stored under N₂. Sodium, magnesium (turnings and powder) and potassium were purchased from Fisons. Triethylsilane and trimethylchlorosilane were obtained from Fluka. Diethylsilane and thallium ethoxide were obtained from Aldrich.

Multinuclear NMR spectra were acquired on a Bruker DRX400 spectrometer and referenced to the residual protio solvent peaks: benzene (δ 7.15), toluene (δ 2.1) and dmso (δ 2.6). ¹³C spectra (100.62 MHz) were referenced according to: benzene (δ 128.7), toluene (δ 20.4) and dmso (δ 39.6). 1D ¹H, ¹H{³¹P}, ${}^{13}C{}^{1}H$, ${}^{31}P{}^{1}H$, ${}^{19}F$, DEPT and 2D ${}^{1}H{}^{-13}C$, ${}^{1}H{}^{-29}Si$, ${}^{1}H{}^{-31}P$, ¹H-¹⁰³Rh HMOC and ¹H-¹H COSY NMR experiments were performed using standard pulse sequences.²⁶ 1D NOESY²⁷ and 2D ¹H-¹H NOESY²⁸ were performed as described. ²⁹Si spectra (79.49 MHz) were referenced to TMS (δ 0.0). ¹⁰³Rh spectra were referenced relative to 12.64 MHz. Mass spectrometry was performed on a VG Autospec instrument in either EI or CI mode where initial GC separations were achieved on a CARBOWAX 20M column. Photochemical studies were performed using an Oriel 350 Watt High Pressure Xenon Arc Lamp.

General method for preparation of NMR samples

Approximately 20 mg (unless stated otherwise) of the appropriate complex was introduced into an NMR tube, fitted with a J. Young valve, in the glove box. Solvents were introduced by vacuum transfer.

Synthesis of Na(DME)Cp

Na(DME)Cp was synthesised according to the method of Smart and Curtis.²⁹ 300 ml of DME was added to 20 g of Na dispersion at -78 °C (dry-ice/acetone bath). To this stirred solution cyclopentadienyl (30 ml), freshly distilled from dicyclopentadienyl, was slowly added to maintain a gentle evolution of H₂. The mixture was refluxed for 2-3 h. The palepink solid was then collected by filtration on a glass frit, washed with several portions of hexane $(3 \times 10 \text{ ml})$ and dried under vacuum. Typical yield = 150-200 g.

Synthesis of CH₂(C₅H₅)₂

 $CH_2(C_5H_5)_2$ was synthesised using a modification of the method described by Schaltegger et al.,30 in which the CH2Cp2 was obtained via distillation. Na(DME)Cp (8 g) was stirred in 50 ml of THF. A solution of CH₂Cl₂ (7.5 ml) in 10 ml of THF was prepared. Half the solution was transferred, via cannula, to the main reaction vessel and the mixture was gently refluxed for 1 h. The mixture was allowed to cool prior to addition of the remaining CH₂Cl₂ solution and then refluxed for a further 3-4 h. After cooling to 0 °C, degassed distilled water (15 ml) was added via syringe and the mixture shaken. The THF layer was dried twice over MgSO₄, transferred into a clean Schlenk tube and concentrated under vacuum.

Synthesis of CH₂[(C₅H₄)Tl]₂

 $CH_2[(C_5H_4)Tl]_2$ was synthesised according to the method of Bitterwolf.³¹ TlOEt (11 g) was added, dropwise, to a stirred THF solution of $CH_2(C_5H_4)_2$. The resulting yellow suspension was stirred for a further hour. The yellow precipitate was washed with THF and hexane $(3 \times 5 \text{ ml})$ on a glass frit, dried and stored in the freezer in the glove box.

Synthesis of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1

 $[Rh(C_2H_4)_2(\mu-Cl)]_2$ was first synthesised according to the method of Cramer.³² [CH₂(C₅H₄)₂][Rh(C₂H₄)₂]₂ was synthesised using a modification of the method described by Werner et al.33 $[Rh(C_2H_4)_2(\mu-Cl)]_2$ (0.5 g) was added to a cooled (-78 °C) Schlenk tube containing CH₂[(C₅H₄)Tl]₂ (0.99 g). THF (30 ml) was slowly transferred into the Schlenk tube with continual stirring and the solvent removed after 30 minutes. The residue was then extracted into pentane, prior to filtration through Celite. Removal of the pentane yielded 1 as a yellow solid which was then stored at -30 °C. The NMR and mass spectroscopic characterisation of 1 is described in the text.

Reaction of 1 with h₆-dmso

An NMR tube containing 1 dissolved in d_6 -benzene was taken into the glove box and a 12-fold excess of h₆-dmso added by syringe. The tube was then degassed and photolysed under vacuum.

Low temperature *in-situ* photolysis of 1 in d₈-toluene

An NMR tube containing 1 (5 mg) dissolved in d_8 -toluene was degassed and introduced to the NMR probe, which was then cooled to 203 K. The tube was photolysed in-situ via the utilisation of a mirror and UV transmitting light guide in conjunction with the Oriel lamp. This system has been described previously for the case where a 325 nm laser source was employed as the photolysis source.³⁴ This approach enabled the photochemical reaction to be monitored at low temperature by multinuclear NMR spectroscopy without the sample warming up.

Et₃SiH, Et₂SiH₂ and CH₂=CHSiMe₃ were stored in ampoules under an atmosphere of N₂. Addition of the required excess of the silane to the NMR tubes containing **1** was achieved *via* a suitable syringe. The NMR tubes were subsequently degassed prior to photochemical or thermal treatment.

Photochemical reaction of 1 with Et_3SiH in d₆-benzene and d₁₂-cyclohexane

The NMR samples were prepared as described above, with the excess of Et₃SiH to 1 being varied between 5- and 12-fold. In order to generate only the Rh(III) species, a filter ($\lambda > 435$ nm) was used to allow selective irradiation of the Rh(I) precursor. The filter was removed to enable irradiation of the Rh(II) products which then produced the Rh(v) complexes. Upon completion of the photochemical reactions, the volatiles were removed on a high-vacuum line and C₆H₆ was condensed into the tube for the purposes of recording ²H NMR spectra.

Low temperature studies with Et₃SiH and Et₂SiH₂

An NMR tube containing 1 dissolved in d_8 -toluene and an excess of silane was photolysed at 213 K. This was achieved by placing the NMR tube in a partially silvered glass dewar which was cooled, *via* a flow of liquid N₂ vapour to 213 K. The lamp was situated next to this dewar to enable photolysis. Meanwhile, the NMR probe was cooled to 213 K. After 2 h irradiation, the tube was rapidly transferred into the NMR machine to ensure minimal variation in sample temperature.

Thermal reactions of 4a and 4b with Et₃SiH

An NMR tube containing 1 dissolved in d_6 -benzene and an 8-fold excess of Et₃SiH was photolysed at 296 K. After 3.5 h irradiation, ¹H NMR spectroscopy confirmed the presence of 4a and 4b as the major species. All the volatiles were removed under vacuum and d_6 -benzene was condensed into the tube followed by Et₃SiH. The resultant thermal reaction at 70 °C was then monitored (the tube was kept dark to ensure that no photochemical reaction took place). The ethene and ethane generated during this process was removed by regular degassing.

Synthesis of Me₃SiH

An ampoule containing LiAlH₄ (3 g) and 5 ml of THF was connected to the high-vacuum line and degassed. The contents were frozen and SiMe₃Cl (3 ml) condensed into this ampoule. Upon thawing, the reaction mixture was stirred at -78 °C. The valve was periodically opened to allow the pressure increase to be followed by a manometer. On completion, the resulting Me₃SiH gas was condensed into a large ampoule by liquid N₂. The vapour was then purified by passing it through a dry-ice/acetone trap, before being condensed back into the large ampoule where it was stored prior to use.

Reactions of 1 with Me₃SiH

All NMR samples were prepared using the general methods described previously, except for addition of the silane, Me_3SiH . The excess of Me_3SiH to 1 was varied between 4- and 15-fold. The NMR samples were degassed prior to study.

Descriptions of mass spectroscopic studies on the photoproducts produced during the reaction of 1 with Me_3SiH , and GCMS analysis of the organic products, can be found in the ESI.[†]

Results and discussion

Dynamic behaviour of [CH₂(C₅H₄)₂][Rh(C₂H₄)₂]₂ 1

In order to facilitate this study, **1** was first characterised by NMR spectroscopy; full NMR spectroscopic data for **1** is presented in Table 1. The 1D ¹H NMR spectrum of **1**, in d₆-benzene at 296 K,

contained five signals, which arose from two types of C_5H_4 ring protons (δ 4.93 and 4.70), two types of ethene protons (δ 2.74 and 1.21) and the apparently equivalent CH₂ bridge proton pair (δ 2.71). Both the signals at δ 4.93 and 4.70 appeared as virtual triplets ($J_{H,H} = 2.1$ Hz), with the smaller splittings of 0.38 and 0.64 Hz respectively due to rhodium coupling (¹⁰³Rh, 100%, I = $\frac{1}{2}$). The corresponding 1D $^{13}C{^{1}H}$ NMR spectrum established the presence of five different carbon environments in complex 1 and a 2D ¹H-¹⁰³Rh HMQC NMR experiment, using the ring and ethene proton couplings, located a single 103 Rh signal at $\bar{\delta}$ -929. Although these data correspond to the fundamental ¹H, ¹³C and ¹⁰³Rh signatures for 1, they are insufficient to attribute resonances to specific ligand positions. The ¹³C chemical shifts were, however, easily assigned to a ligand position via short- and long-range 2D ¹H-¹³C HMQC NMR experiments. Notably, in the long-range experiment the CH₂ bridge proton resonance (δ 2.71) showed connections to the *ipso* and α -ring carbon resonances, at δ 105.28 and δ 87.53 respectively. On the basis of these observations it can be concluded that the α -C₅H₄⁻¹H and ¹³C nuclei give rise to the signals at δ 4.93 and 87.53 respectively. This deduction was further confirmed by a 2D ¹H-¹H NOE spectrum which revealed that the ¹H resonances at δ 2.71 and 4.93 arise from groups that are close in space.

Positive cross-peaks, arising from chemical exchange, were also detected in this NOE spectrum between the proton resonances for the ethene ligands which appear at δ 2.74 and 1.21. This confirms that the ethene ligands of 1 exchange positions by rotation about the rhodium-ethene bond and, since the ¹⁰³Rh coupling remains throughout, the process can be confirmed as intra-molecular. EXSY spectroscopy allowed the rate constant for ethene rotation in 1 to be determined as a function of temperature (e.g. 13.15 $\rm s^{-1}$ at 286 K). The corresponding activation parameters, ΔH^{\ddagger} , ΔS^{\ddagger} and $\Delta G^{\ddagger}_{296}$, were determined to be $66.8 \pm 6.7 \text{ kJ mol}^{-1}$, $10.6 \pm 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$ and 63.7 ± 0.5 kJ mol⁻¹ respectively. This is consistent with the values reported by Rausch et al.35 for the ethene rotation in the analogue of 1, $[C_5H_4-C_5H_4][Rh(C_2H_4)_2]_2$, where $\Delta G^{\ddagger}_{296} = 65 \pm$ 1 kJ mol⁻¹ and by Cramer et al.³⁶ for the mononuclear analogue $CpRh(C_2H_4)_2$, where $\Delta G_{296}^{\ddagger} = 65.7 \text{ kJ mol}^{-1}$.

The fluxionality of 1 is, however, further complicated by the potential for it to exist in two extreme conformations with cis and *trans* arrangements of the rhodium centre relative to the methylene bridge (Fig. 1). Even at 177 K, however, the ¹H NMR spectrum of 1 in d₈-toluene still contains resonances for only two sets of ring protons, two sets of ethene protons and one set of CH₂ bridge protons. The CH₂ bridge proton resonance does, however, show a substantial temperature variation in its chemical shift, moving from δ 2.73 at 317 K to δ 2.35 at 177 K. Since only one set of resonances are still seen at low temperature, rapid inter-conversion of the two rotamers is necessary but the relatively large (0.38 ppm) variation in the CH₂ bridge proton chemical shift indicates that the time spent in any one orientation varies with temperature. 1D NOE spectra recorded between 242 K and 183 K, where there is no ethene rotation, revealed that the ethene protons yielding the signal at δ 1.21 (as observed at 296 K) show progressively reduced NOE interactions to the ring protons, until at 198 K no interaction is detected. In contrast, the ethene protons resonating at δ 2.74 show stronger NOE interactions to the ring protons and the CH₂ bridging group at 198 K. This suggests that the resonance at δ 2.74 arises from the ethene protons that point towards the C_5H_4 rings. Those pointing away from the rings therefore resonate at δ 1.21. The increased interaction between the *up*-ethene protons and the methylene bridge implies that the contribution of structure B increases with decrease in temperature. These data are important in the context of the work presented in this paper because they reveal that the metal centres can potentially react independently of one another (B) or show cooperative effects (A). It should be noted that in the rest of the paper compounds have been drawn with structure A, this does not mean that

 δ^{1} H (J/Hz) $\delta^{13}C{^1H}(J/Hz)$ δ^{103} Rh (J/Hz) Species δ^{29} Si{¹H} (J/Hz) 1 105.28 (d, $J_{RhC} = 3.9$, *ipso*-C₅H₄) 4.93 (vt, 4H, $J_{\rm HH} = 2.1$, α -C₅H₄) -9294.70 (vt, 4H, $J_{\rm HH} = 2.1$, β -C₅H₄) 87.53 (d, $J_{RhC} = 3.9$, α -C₅H₄) 2.74 (br, 8H, up-C₂H₄) 86.13 (d, $J_{RhC} = 4.1$, β -C₅H₄) 1.21 (br, 8H, down-C₂H₄) $38.00 (d, J_{RhC} = 13.4, C_2H_4)$ 2.71 (s, 2H, CH₂ bridge) 25.27 (s, CH₂ bridge) 2a (d₆-dmso, 5.32 (vt, 2H, $J_{\rm HH} = 2.0, \alpha - C_5 H_4^{\rm b}$) 104.84 (d, $J_{RhC} = 5.2$, *ipso*-C₅H₄^b) – -613 (Rh^a) 300 K) 101.52 (d, $J_{RhC} = 5.2$, *ipso*-C₅H₄^a) 87.40 (d, $J_{RhC} = 4.4$, α -C₅H₄^b) -929 (Rh^b) 5.23 (vt, 2H, $J_{\rm HH} = 2.0, \beta$ -C₅H₄^a) 5.08 (vt, 2H, $J_{\rm HH} = 2.0, \alpha$ -C₅H₄^a) 5.05 (vt, 2H, $J_{\rm HH} = 2.0, \beta - C_5 H_4^{\rm b}$) 85.64 (d, $J_{RhC} = 4.4$, β -C₅H₄^a) 85.58 (m, $J_{RhC} = 4.4$, β -C₅H₄^b) 2.72 (s, 2H, CH2 bridge) Me 2.62 (br, 2H, C₂H₄^b) 85.42 (d, $J_{\rm RhC} = 5.2, \alpha - C_5 H_4^{\rm a}$) Me $1.00 (br, 2H, C_2H_4^{b})$ 53.71 (s, Me) 2.49 (s, 6H, Me) 37.10 (br, C₂H₄^b) Ċ 2.28 (m, 2H, up-C₂H₄^a) $32.27 (d, J_{RhC} = 30, C_2 H_4^{a})$ $1.67 (m, 2H, down-C_2H_4^{a})$ 24.64 (s, CH2 bridge) 2b (d₆-dmso, 5.21 (vt, 4H, $J_{\rm HH} = 2.0, \beta$ -C₅H₄) 101.56 (d, $J_{RhC} = 6.0$, *ipso*-C₅H₄) -617 300 K) 5.07 (vt, 4H, $J_{\rm HH}$ = 2.0, α-C₅H₄) 2.68 (s, 2H, CH₂ bridge) 85.43 (d, $J_{RhC} = 5.0, \alpha - C_5 H_4$) 85.52 (d, $J_{\rm RhC} = 5.0$, β -C₅H₄) 2.53 (s, 12H, Me) 53.63 (s, Me) 2.27 (m, 4H, up-C₂H₄) $32.38 (d, J_{RhC} = 30, C_2H_4)$ 1.67 (m, 4H, down-C₂H₄) 25.00 (s, CH₂ bridge) 107.92 (ipso-C₅H₄) 0.30 (s, SiMe₃) -7823a 5.52 (dt, 2H, $J_{\rm HH} = 1.5, 1.2, \beta \cdot C_5 H_4^2$) 5.13 (br, 2H, α -C₅H₄⁴) 87.89 (m, α -C₅H₄⁻¹) 87.75 (m, α -C₅H₄⁴) 4.87 (q, 2H, $J_{\rm HH} = 2$, α -C₅H₄⁻¹) 4.36 (q, 2H, $J_{\rm HH} = 2$, β -C₅H₄³) 85.34 (d, $J_{RhC} = 8.0, \beta - C_5 H_4^2$) H 3.58 (s, 2H, CH₂ bridge) 85.27 (d, $J_{RhC} = 8.0, \beta - C_5 H_4^3$) Rh 2.58 (d, 4H, $J_{\rm HH} = 12$, H⁵) $53.72 (m, CH_2 = CHSiMe_3)$ 2.46 (d, 4H, $J_{\rm HH} = 10$, H⁶) 43.05 (m, CH₂=CHSiMe₃) 28.20 (s, CH2 bridge) 0.14 (s, 12H, SiMe₃) $-0.250 \,(\mathrm{dd}, 4\mathrm{H}, J_{\mathrm{HH}} = 12, 10, \mathrm{H}^7)$ 0.40 (s, SiMe₃) 3b 5.48 (dt, 2H, $J_{\rm HH} = 1.5, 1.2, \beta - C_5 H_4^2$) 108.26 (ipso-C₅H₄) 0.27 (s, SiMe₃) -7805.20 (br, 2H, α -C₅H₄⁴) 87.89 (m, α -C₅H₄⁴) 4.76 (q, 2H, $J_{\rm HH} = 2.2$, α -C₅H₄⁻¹) 87.75 (m, α -C₅H₄⁻¹) 4.41 (q, 2H, $J_{\rm HH} = 2.2$, β -C₅H₄³) 85.60 (d, $J_{RhC} = 8.0$, β -C₅H₄³) 3.74 (d, 1H, $J_{\rm HH} = 15.7$, CH₂ bridge) 85.07 (d, $J_{\rm RhC} = 8.0, \beta - C_5 H_4^2$) .Rh $3.50 (d, 1H, J_{HH} = 15.7, CH_2 \text{ bridge})$ 53.72 (m, CH₂=CHSiMe₃) 43.05 (m, CH2=CHSiMe3) 2.60 (d, 4H, $J_{\rm HH} = 12$, H⁵) 2.44 (d, 4H, $J_{\rm HH} = 10$, H⁶) 28.26 (s, CH2 bridge) Η⁷ 0.13 (s, 12H, SiMe₃) 0.40 (s, SiMe₃) -0.246 (dd, 4H, $J_{\rm HH} = 12, 10, {\rm H}^7$) 0.89 (s, Rh^b) -736 (Rh^b) 3c 5.51 (m, 1H, β -C₅H₄⁹) $87.56 (\alpha - C_5 H_4^4)$ 5.23 (br, 1H, β -C₅H₄²) 87.38 (α -C₅H₄⁻¹) 0.30 (s, Rh^a) -782 (Rh^a) 5.20 (m, 1H, α -C₅H₄⁷) 87.26 (β-C₅H₄²) 10 $5.15 (m, 1H, \beta - C_5 H_4^3)$ 87.15 (β-C₅H₄³) 4.88 (q, 1H, $J_{\rm HH} = 2.2$, α -C₅H₄¹⁰) 53.72 (trans-CH₂=CHSiMe₃) R H^{11} Rh H₁₆ 4.74 (m, 1H, α -C₅H₄¹) 50.24 (*cis*-CH₂=*C*HSiMe₃) ¹²H Rh 4.69 (m, 1H, α -C₅H₄⁴) 45.79 (cis-CH₂=CHSiMe₃) ٠R 4.40 (m, 1H, β -C₅H₄⁸) 43.05 (trans-CH₂=CHSiMe₃) _H15 H^{13} 3.55 (d, 1H, $J_{\rm HH} = 15.8$, CH₂ bridge) 0.40 (s, SiMe₃^a) $3.68 (d, 1H, J_{HH} = 15.8, CH_2 \text{ bridge})$ 85.29 (β-C₅H₄⁸) 2.77 (dd, 2H, $J_{\rm HH} = 12$, $J_{\rm RhH} = 2$, H^{14}) 84.89 $(\beta - C_5 H_4^9)$ 2.61 (d, 2H, $J_{\rm HH} = 12$, H¹¹) 2.46 (m, 2H, H¹²) 86.80 (α -C₅H₄⁷) 87.84 (α -C₅H₄¹⁰) 1.64 (ddd, 2H, $J_{\rm HH} = 14, 12, J_{\rm RhH} =$ 107.16 (ipso-C₅H₄) 2, H¹⁵) 0.145 (s, 6H, SiMe₃^a) 108.21 (ipso-C₅H₄) 0.144 (s, 6H, SiMe₃^b) $0.55 (SiMe_{3}^{b})$ 0.77 (dd, 2H, $J_{\rm HH} = 14, 12, H^{16}$) $-0.26 (m, 2H, H^{13})$ 105.10 (d, $J_{RhC} = 4.0$, *ipso*-C₅H₄-Rh(I)) 41.35 (d, $J_{RhSi} = 23.3$, SiEt₃) 4a 4.88 (br. 1H. α -C₅H₄-Rh(I)) -929 (s. Rh(I)) 87.80 (d, $J_{\rm RhC} = 4.0, \alpha$ -1483 (s, Rh(III)) 4.86 (br, 1H, α -C₅H₄-Rh(I)) $C_5H_4-Rh(I)$ 4.71 (t, 2H, $J_{\rm HH} = 1.9$, β -C₅H₄-Rh(I)) 86.56 (d, $J_{\rm RhC} = 4.0, \beta$ $C_5H_4-Rh(I)$ 2.74 (br, 4H, C_2H_4 –Rh(I)) 38.27 (d, $J_{\rm RhC} = 13.4$, Rh SiEta Rh $C_2H_4-Rh(I)$ 1.21 (br, 4H, C₂H₄-Rh(I)) 25.71 (s, CH2 bridge)

Table 1 ${}^{1}H$, ${}^{13}C{}^{1}H$, ${}^{29}Si{}^{1}H$ and ${}^{103}Rh$ NMR data for complexes 1–14 in C₆D₆ and at 296 K unless specified otherwise

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Table 1 (Continued)

| Species | δ ¹ H (J/Hz) | δ^{13} C{ ¹ H} (J/Hz) | δ^{29} Si{ ¹ H} (J/Hz) | $\delta^{103} \mathrm{Rh} \left(J/\mathrm{Hz} \right)$ |
|---------|--|---|---|---|
| | 2.73 (s, 2H, CH ₂ bridge) | 110.30 (d, $J_{RhC} = 4.0$, | | |
| | 4.91 (br, 2H, α -C ₅ H ₄ -Rh(III)) | $89.15 (d, J_{RhC} = 4.0,$ | | |
| | 5.06 (br, 2H, β -C ₅ H ₄ -Rh(III)) | α -C ₅ H ₄ -Rh(III)) 90.56 (d, $J_{RhC} = 4.0$, | | |
| | 2.36 (br, 2H, C ₂ H ₄ -Rh(III)) | α -C ₅ H ₄ -Rh(III)) 84.97 (d, $J_{RhC} = 4.0$, | | |
| | $2.16~(br,2H,C_2H_4Rh(\text{III}))$ | β -C ₅ H ₄ -Rh(III)) 33.81 (br, $J_{RhC} = 13.4$, C ₂ H ₄ -Rh(III)) | | |
| | 1.06 (t, 9H, $J_{HH} = 9$, CH ₃) 0.73 (q, 6H, $J_{HH} = 8.6$, CH ₂) -14.62 (d, 1H, $J_{RhH} = 33.5$, $J_{SH} =$ 14, Rh–H) | 11.83 (s, CH ₃) 9.83 (s, CH ₂) | | |
| 4b | 4.93 (br, 4H, α -C ₅ H ₄) 5.09 (br, 2H, β -C ₅ H ₄) 5.05 (br, 2H, β -C ₅ H ₄) 2.77 (s, 2H, CH ₂ bridge) 2.36 (br, 4H, C ₂ H ₄) 2.16 (br, 4H, C ₂ H ₄) 1.06 (t, 18H, J _{HH} = 9, CH ₃) 0.73 (q, 12H, J _{HH} = 9, CH ₂) -14.65 (d, 2H, J _{RhH} = 33.5, J _{SiH} = 14, Rh-H) | 110.00 (d, $J_{RhC} = 4.0$, $ipso-C_5H_4$) 90.60 (d, $J_{RhC} = 4.0$, $a-C_5H_4$) 88.93 (d, $J_{RhC} = 4.0$, $a-C_5H_4$) 84.84 (d, $J_{RhC} = 4.0$, $\beta-C_5H_4$) 33.81 (br, $J_{RhC} = 13.4$, C_2H_4) 25.87 (s, CH ₂ bridge) 11.83 (s, CH ₃) 9.83 (s, CH ₂) | 41.43 (d, $J_{RhSi} = 23.3$, SiEt ₃) | -1480 (s, Rh(III)) |
| 4c | 4.89 (br, 2H, α -C ₅ H ₄ -Rh(III)) | 110.00 (d, $J_{\rm RhC} = 4.0$, | 41.35 (d, $J_{RhSi} = 23.3$, SiEt ₃ -Rh(III)) | -1477 (s, Rh(III)) |
| | 5.05 (br, 2H, β -C ₅ H ₄ -Rh(III)) | $Ipso-C_5H_4-Rh(III))$ 90.60 (d, $J_{RhC} = 4.0$, | 40.05 (d, $J_{RhSi} = 16.3$, SiEt ₃ -Rh(v)) | -1872 (s, Rh(v)) |
| | 3.17 (s, 2H, CH ₂ bridge) | α -C ₅ H ₄ -Rh(III)) 88.93 (d, $J_{RhC} = 4.0$, | | |
| | 2.33 (br, 2H, C ₂ H ₄ -Rh(III)) | α -C ₅ H ₄ -Rh(III)) 84.84 (d, $J_{RhC} = 4.0$, | | |
| | 2.21 (br, 2H, C ₂ H ₄ -Rh(III)) | β -C ₅ H ₄ -Rh(III)) 33.81 (d, $J_{RhC} = 13.4$, | $H^{\text{Et}_3\text{Si}-\text{Rh}}$ $H^{\text{Rh}}_{\text{Et}_3\text{Si}}$ H^{SiEt_3} | |
| | 1.08 (t, 9H, $J_{HH} = 9$, CH ₃ -Rh(III)) 0.72 (q, 6H, $J_{HH} = 9$, CH ₂ -Rh(III)) -14.64 (d, 1H, $J_{RhH} = 33.5$, $J_{SH} =$ 14, Rh(III)-H) | C ₂ H ₄ -Rh(III)) 28.24 (s, CH ₂ bridge) 11.83 (s, CH ₃) 9.83 (s, CH ₂ -Rh(III)) | | |
| | 4.90 (br, 2H, α -C ₅ H ₄ -Rh(v)) 5.06 (br, 2H, β-C ₅ H ₄ -Rh(v)) | 110.51 (d, $J_{RhC} = 4.0$, ipso-C ₅ H ₄ -Rh(V)) 92.17 (d, $J_{RhC} = 2.18$, α | | |
| | 1.07 (t, 18H, $J_{\rm HH} = 7.8$, CH ₃ -Rh(v)) | C_5H_4 -Rh(V)) 87.67 (d, $J_{RhC} = 1.89$, | | |
| | 0.82 (q, 12H, $J_{\rm HH}$ = 7.8, CH ₂ -Rh(v)) -14.08 (d, 2H, $J_{\rm RhH}$ = 38.5, $J_{\rm SiH}$ = 14, Rh(v)-H) | $p - C_3 H_4 - Kn(V))$ 13.72 (s, CH ₂) 9.16 (s, CH ₃ Rh(V)) | | |
| 4d | 5.06 (vt, 4H, $J_{HH} = 1.89$, α -C ₅ H ₄) 4.91 (vt, 4H, $J_{HH} = 1.89$, β -C ₅ H ₄) 3.47 (s, 2H, CH ₂ bridge) 1.06 (t, 36H, $J_{HH} = 7.8$, 36H, CH ₃) 0.83 (q, 24H, $J_{HH} = 7.8$, 24H, CH ₂) -14.09 (d, 4H, $J_{RhH} = 38.5$, $J_{SH} =$ 8.9, 4H, Rh–H) | 110.51 (d, $J_{RhC} = 4.0$, $ipso-C_5H_4$) 92.17 (d, $J_{RhC} = 2.18$, α - C_5H_4) 87.67 (d, $J_{RhC} = 1.89$, β - C_5H_4) 28.11 (s, CH ₂ bridge) 13.72 (s, CH ₂) 9.16 (s, CH ₃) | 40.15 (d, $J_{RhSi} = 16.3$, SiEt ₃) | -1873 (s, Rh(v)) |
| 5 | 5.27 (vt, 4H, $J_{\rm HH} = 1.89$, β -C ₅ H ₄) | 91.52 (t, $J_{RhC} = 2.2, \alpha - C_5 H_4$) | 205.9 (t, $J_{RhSi} = 37.3$, SiEt ₂) | -2033 (m, -165) |
| | 4.79 (vt, 4H, $J_{HH} = 1.89$, α -C ₅ H ₄) 3.64 (s, 2H, CH ₂ bridge) 1.43 (q, 4H, $J_{HH} = 7.8$, CH ₂ ' up ') 1.25 (t, 6H, $J_{HH} = 7.5$, CH ₃) 1.24 (m, 6H, $J_{HH} = 7.4$, CH ₃) 1.23 (m, 4H, $J_{HH} = 7.8$, CH ₂ ' $down$ ') -14.40 (m, 2H, $J_{RhH} = 39$, 0.8, hvdride) | 85.40 (t, $J_{RhC} = 1.9$, β -C ₅ H ₄ 84.70 (t, $J_{RhC} = 1.0$, <i>ipso</i> -C ₅ H ₄) 27.84 (s, CH ₂ bridge) 26.00 (t, $J_{RhC} = 1.0$, CH ₂ ' <i>up</i> ') 18.94 (t, $J_{RhC} = 3.0$, CH ₂ ' <i>down</i> ') 10.98 (s, CH ₃) 10.51 (s, CH ₃) | | $J_{\rm RhRh} = 10.3$ |
| 6 | 4.96 (vt, 2H, $J_{\rm HH} = 1.9, \alpha$ -C ₅ H ₄ ^a) | 94.45 (m, α -C ₅ H ₄ ^a) | 220.00 (dd, $J_{RhSi} = 29.7, 37.6, SiEt_2$) | -1342 (d, |
| | 5.02 (vt, 2H, $J_{\rm HH} = 1.9$, β -C ₅ H ₄ ^a) | 92.20 (m, β -C ₅ H ₄ ^a) | | $J_{\rm RhRh} = 15, {\rm Rh}^{\rm a}$) -2019 (d, |
| | 1.43 (t, 2H, $J_{\rm HH} = 7.8$, CH ₂ (Rh–Et)) | 85.30 (m, <i>ipso</i> - $C_5H_4^a$) | | $J_{\rm RhRh} = 15, \rm Rh^b)$ |
| | 1.33 (q, 3H, $J_{HH} = 7.8$, CH ₃ (Rh–Et)) 1.60 (dq, 1H, $J_{HH} = 5.0$, 7.0, SiCH ₂ CH ₃) 1.31 (dq, 1H, $J_{HH} = 5.0$, 7.0, SiCH ₂ CH ₂ CH ₃) | 26.70 (s, CH ₂ CH ₃ (Rh–Et)) -9.80 (d, $J_{RhC} = 22$, CH ₂ CH ₃ (Rh–Et)) 25.67 (s, SiCH ₂ CH ₃) | Et Si Et | |

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Table 1 (Continued)

| Species | δ ¹ H (J /Hz) | $\delta^{13}C{1H} (J/Hz)$ | $\delta^{29}\mathrm{Si}\{^{1}\mathrm{H}\}(J/\mathrm{Hz})$ | $\delta^{103} \mathrm{Rh} \left(J/\mathrm{Hz} \right)$ |
|---|--|--|---|---|
| | 1.22 (t, 6H, $J_{HH} = 7.0$, SiCH ₂ CH ₃) 1.26 (dq, 1H, $J_{HH} = 5.0$, 7.0, | 10.13 (d, $J_{RhC} = 3$, SiCH ₂ CH ₃ ' <i>up</i> ') 15.08 (dd, $J_{RhC} = 4$, 2, SiCH ₂ CH ₃ | | |
| | $SiCH_2CH_3$) 1.07 (dq, 1H, $J_{HH} = 5.0, 7.0,$ | ^(up') 9.37 (s, SiCH ₂ CH ₃) | | |
| | SiCH ₂ CH ₃ 1.26 (t, 6H, $J_{HH} = 7.0$, SiCH ₂ CH ₃) 3.47 (s, 2H, CH ₂ bridge) 4.77 (vt, 2H, $J_{HH} = 1.9$, α -C ₅ H ₄ ^b) 5.17 (vt, 2H, $J_{HH} = 1.9$, β -C ₅ H ₄ ^b) -14.60 (d, 1H, $J_{RhH} = 40$, hydride) | 27.13 (s, CH ₂ bridge) 91.40 (m, α -C ₅ H ₄ ^b) 84.90 (m, β -C ₅ H ₄ ^b) 87.00 (m, <i>ipso</i> -C ₅ H ₄ ^b) | | |
| 7a (d_8 -toluene, | 9.58 (dd, $J_{\rm H}{}^{12}{}_{\rm H}{}^{11} = 16, J_{\rm H}{}^{13}{}_{\rm H}{}^{11} = 9,$ H ¹¹) | 146 (br, <i>C</i> H=CH ₂) | 43.45 (d, $J_{RhSi} = 35 \text{ SiEt}_3^{\text{b}}$) | $-779 (d J_{RhRh} = 13.8, Rh^{a})$ |
| 213 K) | 5.39 (m, β -C ₅ H ₄ ³) | 97.41 (m, β -C ₅ H ₄ ³) | 35.21 (d, $J_{RhSi} = 27 \text{ SiEt}_3^{a}$) | $-1407 (d J_{RhRh} =$ 13.8 R h ^b) |
| | 5.19 (m, α -C ₅ H ₄ ⁻¹) | 95.80 (m, $CH = CH_2$) | H ⁹ H ¹⁰ | 15.8, Kli) |
| | 5.03 (m, β -C ₅ H ₄ ⁷) 4.79 (m, α -C ₅ H ₄ ⁸) 4.71 (m, β -C ₅ H ₄ ⁸) 4.73 (m, β -C ₅ H ₄ ²) 4.43 (m, β -C ₅ H ₄ ⁴) 4.08 (m, α -C ₅ H ₄ ⁴) 4.08 (m, α -C ₅ H ₄ ⁴) 3.65 (m, $J_{\rm H^{11}}$ ¹³ = 9, H ¹³) 3.41 (d, $J_{\rm HH}$ = 13.70, CH ₂ bridge, H ⁹) 2.95 (d, $J_{\rm HH}$ = 13.70, CH ₂ bridge, H ⁹) | 90.80 (m, β -C ₅ H ₄ ⁷) 88.71 (m, α -C ₅ H ₄ ⁴) 88.67 (m, α -C ₅ H ₄ ⁵) 88.42 (m, β -C ₅ H ₄ ⁶) 87.02 (m, α -C ₅ H ₄ ¹) 85.38 (m, β -C ₅ H ₄ ²) 82.96 (m, α -C ₅ H ₄ ⁸) 25.64 (s, CH ₂ bridge) | $\begin{array}{c} 8 \\ 7 \\ 6 \\ \hline \\ 6 \\ \hline \\ 8 \\ \hline \\ 8 \\ \hline \\ 8 \\ \hline \\ 8 \\ \hline \\ 8 \\ \hline \\ \\ \\ 8 \\ \hline \\ \\ 8 \\ \hline \\ \\ 8 \\ \\ \\ 8 \\ \hline \\ \\ 8 \\ \\ \\ \\$ | |
| | 2.41 (m, $J_{H^{11}H^{12}} = 16$, H^{12}) 1.23 (m, CH_3 , $SiEt_3^{b}$) 1.07 (m, CH_3 , $SiEt_3^{a}$) 0.97 (m, CH_2 , $SiEt_3^{a}$) 0.74 (m, CH_2 , $SiEt_3^{b}$) -15.50 (dd, $J_{Rh^{b}H} = 35.4$, $J_{Rh^{a}H} = 3.0$, hydride) | | | |
| 7 b (d ₈ -toluene, 213 K) | 8.58 (dd, $J_{H^2H^1} = 7.6$, $J_{H^3H^1} = 12.6$, H ¹) | _ | 43.16 (d, J_{RhSi} 37 S1Et ₃ ^a) | 666 (d J_{RhRh} 14 Rh ^a) |
| | 4.19 (dd, $J_{H^{1}H^{2}} = 7.6$, $J_{H^{3}H^{2}} = 16.3$, H ²) 4.13 (dd, $J_{H^{2}H^{3}} = 16.3$, $J_{H^{1}H^{3}} = 12.6$, H ³) 3.39 (d, $J_{HH} = 13.8$, CH ₂ bridge) 3.01 (d, $J_{HH} = 13.8$, CH ₂ bridge) 1.21 (m, CH ₃ , SiEt ₃ ^a) 1.26 (m, CH ₃ , SiEt ₃ ^b) 0.85 (m, CH ₂ , SiEt ₃ ^b) 0.85 (m, CH ₂ , SiEt ₃ ^b) -15.19 (dd, $J_{Rh}^{b} = 33.3$, $J_{Rh}^{a} = 10.7$, | | 42.08 (d, J_{RhSi} 33 SiEt ₃ °) H H H H H H H H | –1399 (d <i>J</i> _{RhRh} 14 Rh ^b) |
| 8 | 10.7, hydride) 5.30 (m, 1H, α -C ₅ H ₄ ¹⁰) 5.28 (m, 1H, α -C ₅ H ₄ ⁷) 5.12 (m, 1H, α -C ₅ H ₄ ⁴) 5.10 (m, 1H, β -C ₅ H ₄ ⁹) 5.06 (m, 1H, β -C ₅ H ₄ ⁹) 5.06 (m, 1H, β -C ₅ H ₄ ³) 4.90 (m, 1H, β -C ₅ H ₄ ³) 4.90 (m, 1H, β -C ₅ H ₄ ²) 3.61 (s, 2H, CH ₂ bridge) 1.12 (m, CH ₃ , SiEt ₃ ^a) 1.096 (m, CH ₃ , SiEt ₃ ^a) 1.096 (m, CH ₂ , SiEt ₃ ^a) 0.915 (m, CH ₂ , SiEt ₃ ^a) 0.846 (m, CH ₂ , C ₃ H ₃ SiEt ₃) 0.78 (m, CH ₂ , C ₃ H ₃ SiEt ₃) -13.92 (d, 2H, J _{RhH} = 37, J _{SiH} = 11.6, hydride ^a) -14.06 (d, 2H, J _{RhH} = 38, J _{SiH} = 13.9, hydride ^b) | 111.40 (d, $J_{RhC} = 3.0$, <i>ipso</i> -C ₅ H ₄ ⁶) 110.60 (d, $J_{RhC} = 2.6$, <i>ipso</i> -C ₅ H ₄ ⁵) 98.31 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ¹⁰) 95.63 (d, $J_{RhC} = 3.0$, β -C ₅ H ₄ ⁸) 95.50 (d, $J_{RhC} = 3.0$, β -C ₅ H ₄ ⁹) 91.89 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ¹) 91.88 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ¹) 91.62 (d $J_{RhC} = 3.0$, α -C ₅ H ₄ ³) 87.50 (d, $J_{RhC} = 3.0$, β -C ₅ H ₄ ³) 87.40 (d, $J_{RhC} = 3.0$, β -C ₅ H ₄ ²) 27.72 (s, CH ₂ bridge) 13.68 (s, CH ₂ , SiEt ₃ ^a) 6.88 (s, CH ₃ , C ₅ H ₃ SiEt ₃) 6.77 (s, CH ₃ , SiEt ₃ ^b) 5.29 (s, CH ₂ , C ₅ H ₃ SiEt ₃) | 39.86 (d, $J_{RhSi} = 16.5 \text{ SiEt}_3^{\text{b}}$) 36.70 (d, $J_{RhSi} = 17, \text{ SiEt}_3^{\text{a}}$) -0.87 (s, C ₅ H ₃ SiEt ₃) 10^{0} $E_{t_3}Si = \frac{10^{0}}{10^{0}}$ $E_{t_3}Si = \frac{10^{0}}{10^{0}}$ $H = \frac{10^{0}}{10^{0}}$ $E_{t_3}Si = \frac{10^{0}}{10^{0}}$ $H = \frac{10^{0}$ | –1836 (Rh ^a) –1850 (Rh ^b) |
| 9a | 5.27 (br, 2H, α -C ₅ H ₄ ⁴) 5.26 (br, 2H, α -C ₅ H ₄ ¹) 5.07 (br, 4H, β -C ₅ H ₄ ³) 3.71 (br, 2H, CH ₂ bridge) 1.133 (t, J _{HH} = 7.3, CH ₃ , SiEt ₃) 1.040 (t, J _{HH} = 7.3, CH ₃ , C ₅ H ₃ SiEt ₃) 0.917 (q, J _{HH} = 7.3, CH ₂ , SiEt ₃) | 111.90 (d, $J_{RhC} = 3.0$, $ipso-C_5H_4^{-5}$) 98.84 (d, $J_{RhC} = 3.0$, α - $C_5H_4^{-1}$) 95.66 (d, $J_{RhC} = 3.0$, β - $C_5H_4^{-2}$) 95.48 (d, $J_{RhC} = 3.0$, β - $C_5H_4^{-3}$) 92.08 (d, $J_{RhC} = 3.0$, α - $C_5H_4^{-4}$) 27.49 (s, CH ₂ bridge) 13.62 (s, CH ₂ , SiEt ₃) | $36.52 (d, J_{RhSi} = 17 \text{ SiEt}_3)$ -0.702 (C ₃ H ₃ SiEt ₃) $\underbrace{-0.702}_{2} (C_3H_3SiEt_3)$ Et ₃ Si - Rh - H - RH - SiEt ₃ SiEt ₃ + H - RH - SiEt ₃ + H - SiEt ₃ + | -1837 t ₃ |

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 Table 1 (Continued)

| Species | δ ¹ H (J/Hz) | $\delta^{13}C{1H} (J/Hz)$ | $\delta^{29}\mathrm{Si}\{^{1}\mathrm{H}\}(J/\mathrm{Hz})$ | δ ¹⁰³ Rh (J/Hz) |
|---------|--|--|--|---|
| | 0.771 (q, $J_{\text{HH}} = 7.8$, CH ₂ , C ₅ H ₃ SiEt ₃) -13.89 (d, 4H, $J_{\text{RhH}} = 37$, $J_{\text{SiH}} =$ | 8.90 (s, CH ₃ , SiEt ₃) 5.29 (s, CH ₂ , C ₅ H ₃ SiEt ₃) | | |
| | 10.15, flyande) | 6.78 (s, CH ₃ , C ₅ H ₃ SiEt ₃) | | |
| 9b | 5.34 (t, 4H, $J_{\rm HH} = 1.5$, α -C ₅ H ₄ ¹) 5.255 (br, 2H, α -C ₅ H ₄ ⁴) 5.03 (t, 2H, $J_{\rm HH} = 2.0$, β -C ₅ H ₄ ³) | 111.70 (d, $J_{RhC} = 3.0$, <i>ipso</i> -C ₅ H ₄ ⁵) 98.94 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ¹) 95.64 (d, $J_{RhC} = 3.0$, β -C ₅ H ₄ ²) | $36.55 (d J_{RhSi} = 17, SiEt_3) -0.815 (C_3H_3SiEt_3) 3 $ | -1832 |
| | 3.76 (s, 2H, CH ₂ bridge) 1.132 (t, $J_{HH} = 7.3$, CH ₃ , SiEt ₃) 1.040 (t, $J_{HH} = 7.8$, CH ₃ , $C_3H_3SiEt_3$) 0.92 (q, $J_{HH} = 7.3$, CH ₂ , SiEt ₃) 0.778 (q, $J_{HH} = 7.8$ CH ₂ , $C_3H_3SiEt_3$) -13.92 (d, 4H, $J_{RhH} = 37$, $J_{SiH} =$ 11.6 hydride) | 95.38 (d, $J_{RhC} = 3.0$, β -C ₅ H ₄ ³) 92.14 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ⁴) 27.80 (s, CH ₂ bridge) 13.62 (s, CH ₂ , SiEt ₃) 9.00 (s, CH ₃ , SiEt ₃) 5.30 (s, CH ₂ , C ₅ H ₃ SiEt ₃) | $Et_{3}Si \xrightarrow{L^{1}} Et_{3}Si \xrightarrow{Rh} H H \xrightarrow{Rh} SiEt_{3} \\ H SiEt_{3} Et_{3}Si H$ | · |
| | 11.0, Hydride) | 6.79 (s, CH ₃ , C ₅ H ₃ SiEt ₃) | | |
| 10a | 4.87 (vt, 2H, $J_{\rm HH} = 2.0$, $q_{\rm e}C_{\rm e}H_{\rm e}-\mathbf{B}h(\mathbf{I})$) | 87.60 (d, $J_{RhC} = 4$, α -C ₅ H ₄ -Rh(I)) | 23.64 (d, $J_{RhSi} = 23.29$, SiMe ₃) | -929 (Rh(I)) |
| | $4.69 \text{ (vt, 2H, } J_{\text{HH}} = 2.0,$ | 86.22 (d, $J_{RhC} = 4$, β -C ₅ H ₄ -Rh(I)) | | -1450 (Rh(III)) |
| | $\begin{array}{l} p-C_{3}H_{4}-Rh(l))\\ 2.74 (br, 4H, C_{2}H_{4}-Rh(l))\\ 1.20 (br, 4H, C_{2}H_{4}-Rh(l)) \end{array}$ | 104.85 (<i>ipso</i> -C ₅ H ₄ -Rh(I)) 38.05 (d, $J_{RhC} = 13.5$, C ₂ H ₄ -Rh(I)) | | |
| | 2.74 (s, 2H, CH ₂ bridge) 5.01 (br, 1H, α -C ₃ H ₄ -Rh(III)) 4.85 (br, 1H, α -C ₃ H ₄ -Rh(III)) 4.76 (br, 2H, β -C ₃ H ₄ -Rh(III)) 2.40 (br, 2H, C ₂ H ₄ -Rh(III)) 2.16 (br, 2H, C ₂ H ₄ -Rh(III)) 0.37 (s, 9H, CH ₃) -14.57 (d, 1H, J _{RhH} = 34.1, hydride) | 25.64 (s, CH ₂ bridge) 89.24, 90.56 (m, α -C ₃ H ₄ -Rh(III)) 87.38 (m, β -C ₃ H ₄ -Rh(III)) 110.03 (<i>ipso</i> -C ₃ H ₄ -Rh(III)) 34.23 (br, C ₂ H ₄ -Rh(III)) 8.18 (s, CH ₃) | Rhi KiMe ₃ | |
| 10b | 5.01 (br, 2H, α -C ₃ H ₄) 4.85 (br, 2H, α -C ₃ H ₄) 4.76 (br, 4H, β -C ₃ H ₄) 2.78 (s, 2H, CH ₂ bridge) 2.38 (br, 4H, C ₂ H ₄) 2.16 (br, 4H, C ₂ H ₄) 0.37 (s, 18H, CH ₃) -14.60 (d, 2H, J _{RhH} = 34.1, hydride) | 109.95 (<i>ipso</i> -C ₅ H ₄) 89.10 (m, α -C ₅ H ₄) 90.50 (m, α -C ₅ H ₄) 87.30 (m, β -C ₅ H ₄) 34.20 (br, C ₅ H ₄) 25.85 (s, CH ₂ bridge) 8.18 (s, CH ₃) | 23.64 (d, $J_{RhSi} = 23.29 \text{ SiEt}_3$) | -1449 |
| 10c | 5.01 (m, 2H, α -C ₅ H ₄ -Rh(III)) | 90.44 (m, α -C ₅ H ₄ -Rh(III)) | 23.64 (d, $J_{RhSi} = 23.3$, SiMe ₃ , | -1450 (Rh(III)) |
| | 4.76 (m, 2H, β -C ₃ H ₄ -Rh(III)) 3.07 (s, 2H, CH ₂ bridge) 2.39 (br, 2H, C ₂ H ₄) 2.16 (br, 2H, C ₂ H ₄) 0.40 (s, 9H, CH ₃ -Rh(III)) -14.59 (d, 1H, J _{RhH} = 34.1, hydride-Rh(III)) 4.96 (m, 2H, α -C ₃ H ₄ -Rh(v)) 4.87 (m, 2H, β -C ₃ H ₄ -Rh(v)) | 89.24 (m, β -C ₅ H ₄ -Rh(III)) 110.18 (<i>ipso</i> -C ₅ H ₄ -Rh(III)) 34.20 (m, C ₂ H ₄) 26.88 (s, CH ₂ bridge) 8.18 (s, CH ₃ , Rh(III)) 110.90 (<i>ipso</i> -C ₅ H ₄ -Rh(V)) 91.94 (m, α -C ₅ H ₄ -Rh(V)) 88.00 (m, β -C ₅ H ₄ -Rh(V)) | $\begin{array}{c} \text{Kn(III))} \\ 19.83 \text{ (d, } J_{\text{RhSi}} = 23.4, \text{ SiMe}_3, \text{ Rh}(\text{v})) \\ \hline \\ \text{Me}_3 \text{Si}^{-\text{Rh}} & H^{-\text{Rh}} & \text{SiMe}_3 \\ H & \text{Me}_3 \text{Si}^{-\text{H}} & H^{-\text{Rh}} \\ \end{array}$ | -1731 (Rh(v)) |
| | 0.51 (s, 18H, CH ₃ , Rh(v)) -13.74 (d, 2H, $J_{RhH} = 39.9$, hydride-Rh(v)) | $12.00 (s, CH_3 - Rh(v))$ | | |
| 10d | 4.98 (vt, 4H, $J_{HH} = 1.9$, α -C ₅ H ₄) 4.87 (vt, 4H, $J_{HH} = 1.9$, β -C ₅ H ₄) 3.34 (s, 2H, CH ₂ bridge) 0.51 (s, 36H, CH ₃) -13.75 (d, 4H, $J_{RhH} = 39.9$, hydride) | 91.98 (m, α -C ₅ H ₄) 87.59 (m, β -C ₅ H ₄) 111.12 (<i>ipso</i> -C ₅ H ₄) 27.80 (s, CH ₂ bridge) 12.18 (s, CH ₃) | 19.83 (d, $J_{RhSi} = 23.39 \text{ SiMe}_3$) | -1732 |
| 11 | 4.90 (m, 2H, α -C ₅ H ₄ ^a) | 93.68 (d, $J_{RhC} = 2.0, \alpha - C_5 H_4^a$) | 204.67 (dd, $J_{RhSi} = 34.9, 46.0, SiMe_2$) | -1424 (d, |
| | 4.93 (m, 2H, β -C ₅ H ₄ ^a) | 91.41 (d, $J_{RhC} = 2.0, \beta - C_5 H_4^{a}$) | | $J_{\rm RhRh} = 15, {\rm Rh}^{\rm a})$ -2008 (d, |
| | 0.20 (s, 3H, Rh–Me) | 85.83 (<i>ipso</i> -C ₅ H ₄ ^a) | ATTA | $J_{\rm RhRh} = 15, \rm Rh^b)$ |
| | 1.13 (m, 6H, SiCH ₃ ' μp ') 0.77 (m, 6H, SiCH ₃ ' $down$ ') 3.54 (s, 2H, CH ₂ bridge) 4.77 (m, 2H, α -C ₃ H ₄ ^b) 5.21 (m, 2H, β -C ₃ H ₄ ^b) -14.19 (m, 1H, $J_{RhH} = 40.8$, hydride) | 26.96 (s, CH ₂ bridge) 20.18 (m, SiCH ' up ') 12.54 (m, SiCH ' $down$ ') -31.23 (d, $J_{RhC} = 27.5$, Rh–Me) 91.81 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ^b) 86.68 ($ipso$ -C ₅ H ₄ ^b) 85.49 (d, $J_{RhC} = 4.0$, β -C ₅ H ₄ ^b) | Me Me Me H Si Me | |
| 12 | 4.73 (m, 2H, α -C ₃ H ₄ ^a) | 94.30 (m, α -C ₅ H ₄ ^a) | 212.39 (dd, $J_{RhS} = 35.65, 46.18,$ SiMe ₂) | $-1957 (d, J_{RhRh} = 14.7, Rh^{a})$ |

Table 1(Continued)

| m, 2H, β -C ₃ H ₄ ^a) s, 2H, CH ₂ bridge) m, 6H, SiCH ₃ ' <i>up</i> ') m, 6H, SiCH ₃ ' <i>down</i> ') s, 9H, Rh–SiMe ₃) m, 2H, α -C ₃ H ₄ ^b) m, 2H, β -C ₃ H ₄ ^b) s, 3H, Rh–Me) | 90.58 (m, β -C ₅ H ₄ ^a) 95.33 (m, <i>ipso</i> -C ₃ H ₄ ^a) 26.05 (s, CH ₂ bridge) 21.71 (s, SiCH ₃ ' <i>up</i> ') 12.91 (s, SiCH ₃ ' <i>down</i> ') 10.43 (d, $J_{RhC} = 2.0$, Rh–SiMe ₃) 93.62 (m, α -C ₃ H ₄ ^b) 91.01 (m, β -C ₅ H ₄ ^b) | 15.41 (d, $J_{\text{RbSi}} = 40.53$, SiMe ₃) Me ₃ Si Me Me Me Me | $-1350 (d, J_{RhRh} =$ 14.7, Rh ^b) |
|---|---|---|---|
| s, 2H, CH ₂ bridge) m, 6H, SiCH ₃ ' up ') m, 6H, SiCH ₃ ' $down$ ') s, 9H, Rh–SiMe ₃) m, 2H, α -C ₃ H ₄ ^b) m, 2H, β -C ₃ H ₄ ^b) s, 3H, Rh–Me) | 95.33 (m, <i>ipso</i> -C ₃ H ₄ ^a) 26.05 (s, CH ₂ bridge) 21.71 (s, SiCH ₃ ' <i>up</i> ') 12.91 (s, SiCH ₃ ' <i>down</i> ') 10.43 (d, $J_{RhC} = 2.0$, Rh–SiMe ₃) 93.62 (m, α -C ₃ H ₄ ^b) 91.01 (m, β -C ₃ H ₄ ^b) | Me ₃ Si Me Me ₃ Si Me | |
| ., , | 87.96 (m, <i>ipso</i> -C ₅ H ₄ ^b) -27.51 (d, $J_{RhC} = 27.5$, Rh–Me) | we | |
| vt, 2H, $J_{\rm HH} = 2.2, \alpha - C_5 H_4^{\rm a}$) | 93.86 (d, $J_{RhC} = 2.0, \alpha - C_5 H_4^{a}$) | 197.44 (dd, $J_{\text{RhSi}} = 29.1, 46.6, \text{SiMe}_2$) | $-1965 (d, J_{RhRh} = 14.8, Rh^{a})$ |
| vt, 2H, $J_{\rm HH} = 2.2, \beta \cdot C_5 H_4^{\rm a}$) | 92.65 (<i>ipso</i> - $C_5H_4^{a}$) | 13.74 (d, $J_{RhSi} = 34.7$, SiMe ₃) | $-1952 (d, J_{RhRh} = 14.8, Rh^{b})$ |
| s, 2H, CH ₂ bridge) s, 6H, SiCH ₃ 'up') s, 6H, SiCH ₃ 'down') s, 3H, Rh–SiMe ₃) vt, 2H, $J_{HH} = 2.0, \beta$ -C ₅ H ₄ ^b) vt, 2H, $J_{HH} = 2.0, \alpha$ -C ₅ H ₄ ^b) l9 (m, 1H, $J_{RhH} = 40.8,$ de) | 90.79 (d, $J_{RhC} = 2.5$, β -C ₅ H ₄ ^a) 26.76 (s, CH ₂ bridge) 20.83 (s, SiCH ₃ 'up') 17.83 (s, SiCH ₃ 'down') 11.70 (d, $J_{RhC} = 2.0$, Rh–SiMe ₃) 91.61 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ^b) 85.99 (<i>ipso</i> -C ₅ H ₄ ^b) | Me ₃ Si Me Me | |
| m 2H α -C _e H ^a) | 85.34 (d, $J_{RhC} = 4.0, \beta \cdot C_5 H_4^\circ$) 98.57 (<i>inso</i> -C ₅ H ₄ ^a) | 20.91 (d. $J_{\text{phys}} = 23.71 \text{ SiMe}_{2}$) | -1052 (Rh ^a) |
| m, 2H, β-C ₅ H ₄ ^a) br, 2H, up-C ₂ H ₄) br, 2H, up-C ₂ H ₄) br, 2H, down-C ₂ H ₄) 07 (dd, 2H, J _{RhH} = 17.4, hydride) s, 2H, CH ₂ bridge) m, 2H, α C ₅ H ₄ ^b) | 89.32 (m, α -C ₅ H ₄ ^a) 88.55 (m, β -C ₅ H ₄ ^a) 36.67 (m, C ₂ H ₄) 32.41 (s, CH ₂ bridge) 92.89 (m, α -C ₅ H ₄ ^b) 112.9 (<i>ipso</i> -C ₅ H ₄ ^b) 112.9 (<i>ipso</i> -C ₅ H ₄ ^b) | h h h h h h siMe ₃ | -1608 (Rh ^b) |
| | $f_{t}, 2H, J_{HH} = 2.2, α-C_{5}H_{4}^{a})$ $f_{t}, 2H, J_{HH} = 2.2, β-C_{5}H_{4}^{a})$ $f_{s}, 2H, CH_{2} \text{ bridge})$ $f_{s}, 6H, SiCH_{3} 'up')$ $f_{s}, 6H, SiCH_{3} 'down')$ $f_{s}, 3H, Rh-SiMe_{3})$ $f_{t}, 2H, J_{HH} = 2.0, β-C_{5}H_{4}^{b})$ $f_{t}, 2H, J_{HH} = 2.0, α-C_{5}H_{4}^{b})$ $g (m, 1H, J_{RhH} = 40.8, le)$ $n, 2H, α-C_{5}H_{4}^{a})$ $n, 2H, β-C_{5}H_{4}^{a})$ $n, 2H, α-C_{2}H_{4})$ $f_{t} (down-C_{2}H_{4})$ $f_{t} (down-C_{2}H_{4})$ $f_{t} (down-C_{2}H_{4})$ $f_{t} (down-C_{2}H_{4})$ $f_{t} (dd, 2H, J_{RhH} = 17.4, low + C_{5}H_{4}^{b})$ $f_{t} (2H, CH_{2} bridge)$ $n, 2H, β-C_{5}H_{4}^{b})$ $n, 2H, β-C_{5}H_{4}^{b})$ $f_{t} (2H, GC_{5}H_{4}^{b})$ | s, 3H, Rh–Me)91.01 (m, β-C ₃ H ₄ ^a) 87.96 (m, <i>ipso</i> -C ₅ H ₄ ^b) -27.51 (d, $J_{RhC} = 27.5$, Rh–Me)vt, 2H, $J_{HH} = 2.2$, α -C ₅ H ₄ ^a)93.86 (d, $J_{RhC} = 2.0$, α -C ₅ H ₄ ^a)vt, 2H, $J_{HH} = 2.2$, β -C ₅ H ₄ ^a)92.65 (<i>ipso</i> -C ₅ H ₄ ^a)s, 2H, CH ₂ bridge)90.79 (d, $J_{RhC} = 2.5$, β -C ₅ H ₄ ^a)s, 6H, SiCH ₃ 'up')26.76 (s, CH ₂ bridge)s, 6H, SiCH ₃ 'up')20.83 (s, SiCH ₃ 'up')s, 6H, SiCH ₃ 'down')20.83 (s, SiCH ₃ 'up')s, 3H, Rh–SiMe ₃)17.83 (s, SiCH ₃ 'up')s, 3H, Rh=SiMe ₃)17.80 (a, SiCH ₃ 'up')s, 3H, Rh=SiMe ₃)17.80 (a, SiCH ₃ 'up')s, 3H, Rh=SiMe ₃)17.80 (a, SiCH ₃ 'up')s, 3H, Rh=10, β-C ₅ H ₄ ^b)11.70 (d, $J_{RhC} = 2.0$, Rh -SiMe ₃)t, 2H, J _{HH} = 2.0, α -C ₅ H ₄ ^b)91.61 (d, $J_{RhC} = 3.0$, α -C ₅ H ₄ ^b)g (m, 1H, $J_{RhH} = 40.8$,85.99 (<i>ipso</i> -C ₅ H ₄ ^a)s85.34 (d, $J_{RhC} = 4.0$, β -C ₅ H ₄ ^b)n, 2H, β -C ₅ H ₄ ^a)89.32 (m, α -C ₅ H ₄ ^a)or, 2H, <i>down</i> -C ₂ H ₄)36.67 (m, C ₂ H ₄)or, 2H, <i>down</i> -C ₂ H ₄)36.67 (m, C ₂ H ₄)or, 2H, <i>down</i> -C ₂ H ₄)32.41 (s, CH ₂ bridge)ydride)92.89 (m, α -C ₅ H ₄ ^b)n, 2H, α -C ₃ H ₄ ^b)112.9 (<i>ipso</i> -C ₅ H ₄ ^b)n, 2H, β -C ₅ H ₄ ^b)11.65 (SiMe ₃)< | |

form **A** dominates but rather it simply reflects a useful pictorial representation.



Fig. 1 Extreme conformations of 1.

Photochemical reaction of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 with dmso

In order to investigate the photochemical reactivity of 1, a solution of 1 in d₆-dmso was photolysed using broad band UV irradiation from a 350 W Xe arc and the reaction monitored by 1D and 2D NMR spectroscopic methods. After 15 min irradiation, a ¹H NMR spectrum recorded at 300 K revealed the presence of free ethene (δ 5.41) and two new peaks at δ 2.72 (major) and 2.68 (minor) corresponding to the CH₂ bridge protons of two metal-based photoproducts; such CH₂ bridge proton resonances proved to be a firm indicator of the number of products that were produced in the reactions described here. It should be noted at this stage, that when the mononuclear analogue of 1, $CpRh(C_2H_4)_2$, is photolysed with dmso the mono-substituted product CpRh(C2H4)(dmso) is obtained.41 It was therefore expected that products corresponding to the successive loss of one ethene ligand from each metal centre, namely $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(dmso)]$ 2a and $[CH_2(C_5H_4)_2][Rh(C_2H_4)(dmso)]_2$ 2b, would be formed. Complex 2a contains two distinct C_5H_4 rings, in agreement with the fact that the CH₂ bridge ¹H resonance for this species at δ 2.72 connects to two *ipso* carbon resonances, at δ 101.52 and 104.84, and two α -C₅H₄ carbons, at δ 85.42 and 87.40 in the long-range ¹H–¹³C NMR spectrum. Upon extended photolysis [CH₂(C₅H₄)₂][Rh(C₂H₄)(dmso)]₂ **2b** became the sole product. This product yields ¹H NMR peaks at δ 5.07 and 5.21 (for the two sets of C₃H₄ protons), 2.68 (for the CH₂ bridge) and, 2.27 and 1.67 (for the ethene protons). Furthermore, a single ¹⁰³Rh signal was observed at δ –617. Full NMR data for these two species are presented in Table 1.

A key feature in the ¹H NMR spectra of both 2a and 2b was the observation of fine structure for the ethene signals (at δ 2.28 and 1.67, **2a**; δ 2.27 and 1.67, **2b**). This indicates that there is now a substantial barrier to alkene rotation in the dmso substituted centre. In order to determine the orientation and binding mode of the dmso ligands in 2a and 2b a d₆-benzene solution of 1 was photolysed in the presence of a 12-fold excess of h₆-dmso until ¹H NMR spectra recorded at 300 K revealed the formation of both the mono- and di-substituted products. A 2D ¹H–¹³C NMR experiment then connected the methyl ¹H and ¹³C resonances of free dmso (δ 1.78, 39.59), the monosubstituted product (δ 2.49, 53.71) and the disubstituted product (δ 2.53, 53.63). The downfield shift of the ¹³C resonances (with respect to the free dmso) has previously been shown to be indicative of dmso binding through the S atom in both products.³⁷ These observations demonstrate that UV irradiation of 1 in solution provides a facile route to complexes resulting from the loss of a single ethene molecule per rhodium centre.

Low temperature *in-situ* photolysis of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 in d₈-toluene

Perutz *et al.* used laser flash photolysis to demonstrate the existence of two transient intermediates, $[CpRh(C_2H_4)]$ and

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 $CpRh(C_2H_4)(solv)$ (where solv = solvent), following irradiation of $CpRh(C_2H_4)_2$ in cyclohexane and benzene. 34,38 The same group has also reported evidence for the solvent complexes $CpRh(C_2H_4)(MeCN)$ and $CpRh(C_2H_4)(\eta^2$ -toluene).⁴¹ The substitution products that are formed by photolysis of CpRh(C2H4)2 in the presence of a suitable ligand therefore originate from either $CpRh(C_2H_4)$ or $CpRh(C_2H_4)$ (solv). We recently expanded on these studies by completing an NMR based in-situ photolysis study of this system at 193 K.³⁴ This revealed that the photoproduct $CpRh(C_2H_4)(\eta^2$ -toluene) exists in two isomeric forms that interconvert on the NMR timescale. It should be noted that the related species $CpIr(C_2H_4)(C_6F_6)$ has also been shown to exist in two isomeric forms, where the metal binds to the π -face in an $\eta^2\mbox{-}fashion$ and the C_6 plane points towards or away from the cyclopentadienyl ring.³⁹ We now expand on the previously communicated data obtained from the low temperature in-situ photolysis of 1 with d_8 -toluene.

A sample of complex 1 (5 mg) was dissolved in d₈-toluene, in a 5 mm NMR tube, and placed into the NMR spectrometer. The sample was then photolysed *in-situ* at 203 K and ¹H NMR spectra recorded at regular intervals. After 18 h of irradiation, there was evidence for a single new species in the ¹H NMR spectrum, most notably *via* the observation of a CH₂ resonance, corresponding to the bridging methylene group, at δ 2.35 with equal intensity to the analogous resonance of 1. Free ethene was detected at δ 5.31, but no hydride resonances were observed in the region δ -5 to -25. On the basis of these data, the new species was expected to be the solvent complex $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(\eta^2-toluene)]$. Two rotamers, as drawn in Fig. 2, would be expected for this species and hence sixteen ring proton resonances could potentially be observed. In the ¹H NMR spectrum, only seven peaks at δ 4.08, 4.14, 4.54, 4.61, 4.85, 5.05 and 5.12, corresponding to C_5H_4 ring protons, and δ -0.18, 1.42, 2.53 and 2.89, attributed to ethene protons respectively were readily visible. It was noted that the peak at δ 4.54 was twice as intense as the other ring proton resonances.

$\begin{array}{c} 4.61 \\ \hline \\ R \\ R \\ \hline \\ R \\ \\ R \\ \hline \\ R \\ \\ R \\ \\ R \\ \\ \\ R \\ \\ R \\ \\ \\$

[Rh(C₂H₄)₂]-[Rh(C₂H₄)₂]-[Rh(C₂H₄)(η^2 -toluene)] (where R = CD₃) with key ¹H resonances indicated.

Ring-walk of the unsymmetrical arene, in a series of $\eta^2 - \eta^2$ steps, would lead to an apparent plane of symmetry in each of these rotamers and hence halve the number of ring proton resonances expected for each isomer to four. The observation of eight ring proton resonances is consistent with this hypothesis. Positive cross-peaks were observed between signals at δ 4.08 and 4.61, δ 4.14 and 4.85, and δ 5.05 and 5.12 in the corresponding EXSY spectrum. These data correspond to the observation of the pairwise interconversion of the six distinct ring proton sites at 203 K and prove that the two proposed rotamers interconvert by arene rotation.⁴⁰ The observation of further EXSY connections between the four ethene proton signals at δ 1.42 and -0.18, and δ 2.89 and 2.53 further complicates these spectra, but indicates that the alkene ligands bound to the substituted rhodium centre also rotate. These NOE spectra enabled the location of two further ethene resonances, at δ 1.34 and 2.81 (which correspond to ligand sites that also interchanged positions) due to the $Rh(C_2H_4)_2$ units of the unsubstituted ring. (Overlap with the corresponding ethene resonances in the starting material masked these signals in the initial 1D ¹H NMR spectrum.) These

NOE connections were consistent with the chemical shift data included in Fig. 2. It should be noted that the actual orientation of the d_8 -toluene ligand in these species cannot be determined *i.e.* it is not possible to distinguish the *up* or *down* isomers.

Photochemical reaction of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 with vinyltrimethylsilane

Perutz *et al.*⁴¹ have previously reported that photolysis of the mononuclear analogue of **1**, CpRh(C₂H₄)₂, with vinyltrimethylsilane led to the formation of CpRh(C₂H₄)(CH₂=CHSiMe₃)₂, and the double substitution product CpRh(CH₂=CHSiMe₃)₂, where the latter complex exists in *cis* and *trans* forms that are differentiated by the relative orientations of the vinyl ligands. Exhaustive photolysis of a solution of **1** in d₆-benzene in the presence of an 8-fold excess of vinyltrimethylsilane yielded three major products which were subsequently assigned to the disubstituted species [CH₂(C₅H₄)₂][Rh(CH₂=CHSiMe₃)₂]₂**3a,3b** and **3c** (Fig. 3). This observation demonstrates that the substitution of both the ethene ligands on each rhodium centre in **1** is possible.



Fig. 3 Structures of $[CH_2(C_3H_4)_2][Rh(CH_2=CHR)_2]_2$ **3a**, **3b** and **3c** as indicated by NMR spectroscopy (where $R = SiMe_3$).

A brief description of how the NMR data supports this deduction follows (Table 1). The dominant products 3a and **3b** yield vinyl ¹H signals at δ -0.250, 2.46 and 2.58, for **3a**, and δ -0.246, 2.44 and 2.60, for **3b** and are indicative of the ligand orientations. Previously, the relative orientation of the vinylsilane ligands in CpRh(CH2=CHSiMe3)2 was shown to affect the chemical shift of H^{α}, which appears at δ 0.68 in the cis form and δ -0.40 in the trans form.⁴¹ This implies that the vinylsilane ligands on each rhodium centre in 3a and 3b are orientated trans to one another. There are two possible ways of achieving this; the pairs of vinylsilane ligands can themselves be either in a cis or trans arrangement. The distinction between these two forms was simple to achieve since the symmetrical product **3a** yields a single CH₂ bridge proton resonance at δ 3.58 while the unsymmetrical form 3b gives rise to an AB pattern for the CH₂ group with resonances at δ 3.50 and 3.74; this is achieved by a trans arrangement of the pairs of vinyl ligands. Species 3a and 3b each yield four ring ¹H resonances with NOE measurements confirming that the SiMe₃ groups point towards the C₅H₄ rings. Unambiguous assignment of **3a** and **3b** was achieved via 1H-13C, 29Si and 103Rh 2D correlations.

In contrast, complex **3c** yields six ¹H resonances due to the vinylsilane core, with the three at δ 2.61, 2.46 and -0.26 corresponding to a pair of *trans* vinylsilane ligands on one metal centre, and the remaining three, at δ 2.77, 1.64 and 0.77, corresponding to a pair of *cis* ligands on the second metal centre. Thus, **3c** possesses a *trans/cis* arrangement of the vinylsilane ligand pairs and has the structure shown in Fig. 3. The ratio of **3a : 3b : 3c** was 4 : 1.7 : 1.

It is important to note that these spectra were complicated by the fact that H/D exchange was observed between the solvent, d₆-benzene, and free and bound vinyltrimethylsilane. Free vinyltrimethylsilane yields NMR signals at δ 6.16 (dd, $J_{\rm H,H} = 14.7, 20.3, H^{\circ}$), 5.90 (dd, $J_{\rm H,H} = 3.9, 14.7, H^{\beta}$), 5.65 (dd, $J_{\rm H,H} = 3.9, 20.3, H^{\gamma}$) and 0.05 (s, SiMe₃), however, after 5 h photolysis, signals with a doublet of 1 : 1 : 1 triplet multiplicity were present at δ 5.90 and 5.65. The δ 6.16 resonance then proved



Scheme 1 Structures of products formed during photochemical reactions of 1 with HSiEt₃, HSiMe₃ and H₂SiEt₂.

to be reduced in intensity by 50% of the expected integral value; the ²H couplings are 2.2 $(J_{D,H}^{\beta})$ and 3.2 $(J_{D,H}^{\gamma})$ Hz respectively. A 1 : 1 : 1 triplet, centred at δ 139.8 $(J_{D,C} = 21 \text{ Hz})$, was observed in the corresponding ¹³C NMR spectrum in accord with the fact that H^{α} becomes deuterated. GCMS and ¹H NMR integrations both agreed with 50% ²H incorporation into the alpha proton site of both free and bound vinyltrimethylsilane. Similar H–D exchange has been seen with Cp*Rh(CH₂=CHSiMe₃).⁴²

This reaction should be noted for three reasons, (i) the dominant species **3a** possesses a *trans/trans* arrangement of vinylsilane ligands, with the silyl groups orientated such that they are furthest away from each other-presumably due to steric reasons, (ii) in contrast to the reaction with dmso, exhaustive photolysis of **1** with vinylsilane now results in the substitution of all four ethene ligands and (iii) evidence for a C–H bond activation pathway has been obtained.

Photochemical reactions of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 with Et₃SiH and Et₂SiH₂

When a solution of 1 in d₆-benzene was photolysed at 296 K, using a $\lambda > 400$ nm filter, in the presence of a 5-fold excess of Et₃SiH, the ¹H NMR spectrum recorded after 30 min irradiation contained a signal at δ 5.24, corresponding to free ethene, and two new hydride resonances at δ –14.62 (major) and δ –14.65 (minor). Both these resonances were split into doublets of 33.5 Hz due to coupling to ¹⁰³Rh; this value proved to be indicative of a Rh(III) centre in the analogous CpRh system.^{13b} Thus the species giving rise to these hydride signals were assigned as [CH₂(C₅H₄)₂][Rh(C₂H₄)₂][Rh(C₂H₄)(SiEt₃)H] **4a**, the primary photoproduct, and [CH₂(C₅H₄)₂][Rh(C₂H₄)(SiEt₃)H]₂ **4b**, the secondary product, respectively. The structures of these species are indicated in Scheme 1.

While the resultant ¹H NMR spectrum is extremely complex between 4 and 6 ppm, three resonances that were attributable to the CH₂ bridge protons of **1** and the photoproducts **4a** and **4b** were easily distinguished at δ 2.71, 2.73 and 2.77 respectively. The 0.04 ppm separation of the latter two signals proved sufficient to enable the identification of **4a** and **4b** *via* long-range 2D ¹H– ¹³C and 2D NOE measurements. Significantly, the CH₂ bridge protons of the major product resonate at δ 2.73 and connect to two *ipso* carbons at δ 105.10 and 110.30, and three α -ring carbons at δ 87.80, 89.15 and 90.56. This confirms that the associated complex contains two distinct C5H4 rings. The remaining bridge proton resonance at δ 2.77 for **4b** connects to a single *ipso* carbon at δ 110.00, and two distinct α -ring carbons at δ 88.93 and 90.60, which confirms that 4b is a symmetrical product. This information, in conjunction with the corresponding NOE data, enabled the complete assignment of the ¹H resonances for the corresponding Rh(I) and Rh(III) rings in these species. The corresponding 2D 1H-29Si NMR spectrum located the 29Si chemical shifts for the silvl ligands in 4a (δ 41.35) and 4b (δ 41.43) via connections to the corresponding hydride and ethyl proton signals, while the 2D 1H-103Rh NMR spectrum located the corresponding ¹⁰³Rh resonances at δ –929 and –1483 in 4a, and $\delta - 1480$ in **4b** via connections to the ethene ¹H resonances. The remaining ¹³C resonances were located via connections in a short-range ¹H-¹³C 2D correlation. The full NMR spectroscopic data for complexes 4a and 4b obtained in this way are presented in Table 1.

Upon further irradiation, the ¹H resonances due to 4b were observed to consistently grow in intensity whilst those arising from 4a initially grew and were then depleted. Subsequently, resonances for 4b began to disappear, and new signals for four new hydride containing species, identified by NMR spectroscopy as $[CH_2(C_5H_4)_2][Rh(C_2H_4)(SiEt_3)H][Rh(SiEt_3)_2(H)_2]$ $SiEt_2)]_2$ 5 and $[CH_2(C_5H_4)_2][(RhEt)(RhH)(\mu\text{-}SiEt_2)_2]$ 6 were observed. NMR resonances for these products were unambiguously assigned using the methods described for complexes 4a and 4b (see ESI[†] and Table 1). The formation of 4c and 4d is consistent with the expected stepwise photochemical displacement of ethene from 4a and 4b, as illustrated in Scheme 2, however, the generation of 5 and 6, corresponding to Si-C bond activation products, was somewhat unexpected (structures indicated in Scheme 1).

The ratio of 4d: 5:6 observed after 4 h of photolysis proved to be 72: 16: 12, although, inspection of the ¹H NMR spectra as a function of irradiation time revealed that 6 was generated prior to 5. Interestingly, the proportion of 5 and 6 relative to 4d increased in experiments where the initial excess of Et₃SiH used relative to 1 was reduced. Upon exhaustive photolysis of these



Scheme 2 Conversion of 1 to 4a, 4b, 4c, 4d, 5 and 6.

samples only complexes **4d** (71%) and **5** (29% in the case above) remain; this confirms that **6** transforms into **5** upon photolysis (Scheme 2). Complex **5** could be generated independently when **1** was photolysed with a 4-fold excess of Et_2SiH_2 in d₆-benzene at 296 K.

It should be noted that when this reaction was completed in d₆-benzene, only one ring proton resonance, at δ 4.91, was observed for 4d. However, when the irradiation of 1 was repeated on an NMR scale in neat Et₃SiH, ¹H NMR spectroscopy revealed peaks corresponding to a single product, 4d. Under these conditions, the formation of 5 was suppressed and two resonances of equal intensity were observed for the two types of C_5H_4 ring protons of 4d at δ 5.06 and 4.91. Ultimately this effect was explained by the observation in a long-range 2D $^{1}H^{-13}C$ correlation spectrum that the signal at δ 4.91 connected to a β ¹³C resonance which appeared as a 1 : 1 : 1 triplet of 28 Hz in the ¹³C domain. This is consistent with deuteration of the α -ring positions in 4d. The ¹H NMR spectrum for the reaction product formed in d₆-benzene contained a peak at δ 5.06 with only 10% of the expected intensity suggesting that 90% deuteration of the α-ring proton site was achieved. Examination of this sample by ²H NMR spectroscopy revealed broad peaks at δ 5.06, 1.08, 0.83 and -14.10 that are consistent with ²H labeling of the α -ring position, the ethyl groups of the silvl ligands and the hydride site. In order to explore this effect further we photolysed 1 with Et₃SiH in d₁₂-cyclohexane rather than d₆-benzene. Under these conditions the level of deuteration of the α -ring site fell to 80%. These observations suggest that while aromatic C-H/D activation and exchange is more facile, aliphatic C-H/D activation and exchange occurs with only slightly less propensity.

Descriptions of how the structures of **5** and **6** fit with their NMR data can be found in the ESI.[†] However, important features worthy of note for **5** are the appearance of the corresponding hydride, ²⁹Si and ¹⁰³Rh resonances. The hydride signal of **5**, at δ –14.40, is the most diagnostic feature since a second order pattern, corresponding to an [AX]₂ spin system is observed (from simulation $J_{Rh,H} = 39$ and -0.8 Hz, while $J_{H,H} = -1.2$ Hz and $J_{Rh,Rh} = 16.5$ Hz). In addition, the ²⁹Si resonance for this species appears as a rhodium coupled triplet at δ 205.9 ($J_{Rh,Si} = 37.3$ Hz) which is characteristic of a bridging silyl group.⁴³ The corresponding ¹⁰³Rh resonance for **5** was located at δ –2033. Significantly, NOE measurements confirmed

the presence of two inequivalent ethyl groups on each of the $SiEt_2$ units; one pointing towards and one pointing away from the rings (Scheme 1).

Key features arising from the unsymmetrical silylene bridged complex **6**, include eight CH ¹³C resonances, corresponding to the α and β positions of two distinct C₅H₄ rings, and two *ipso* carbon signals. A single hydride resonance, a rhodium coupled doublet, was observed at δ –14.60 while the corresponding ²⁹Si resonance appears as a doublet of doublets at δ 220 ($J_{\text{siRh}} =$ 29.7, 37.6 Hz). This confirms that **6** contains a hydride ligand, and silicon centre that bridges two inequivalent ¹⁰³Rh nuclei, which were subsequently found to yield signals at δ –2019 and –1342. The remaining site was identified *via* the observation of a methylene ¹³C signal for a RhEt ligand that was split by a direct, one bond, ¹⁰³Rh coupling of 22 Hz. Both **5** and **6** contain Rh–Rh bonds, as demonstrated by values for J_{RhRh} of 16.5 and 15 Hz determined for these species respectively.

The reactions with Et₃SiH revealed that the corresponding 16electron fragments formed by ethene loss were able to break a Si–H bond and form the corresponding $Rh(III)(C_2H_4)(SiEt_3)(H)$ products. The corresponding ${}^2J_{\rm SiH}$ coupling constants for 4a and 4b proved to be 14 Hz in each case (Table 1) which suggests that there is no 3-centre bonding interaction in these species. These Rh(III) centres also proved to undergo photochemically driven ethene loss to yield formal Rh(v) centres of the type Rh(SiEt₃)₂(H)₂ by the addition of a second molecule of silane. Again, the size of the ${}^{2}J_{SiH}$ couplings observed for 4c and 4d suggested that there were no 3-centre-2-electron interactions present in these complexes. This is consistent with the fact that the 16-electron fragment $Rh(III) [(C_5H_4)R][Rh(SiEt_3)H]$ (where $\mathbf{R} = [CH_2(C_5H_4)][Rh(C_2H_4)(SiEt_3)H])$ appears to be sufficiently electron rich to be able to activate both the Si-C bonds of bound silvl groups and the C-D bonds of aromatic and aliphatic solvents. A similar deduction has been made by Berry on a related Cp*Rh system.20

Low temperature studies with Et_3SiH and Et_2SiH_2 : Generation of σ,π vinyl complexes

In order to probe the C-H activation potential of these binuclear rhodium systems further, a series of photochemical studies were performed using the *in-situ* photochemical approach described earlier at low temperature where any C-H/C-D bond activation products might be stabilised.³⁴ A solution of **1** in d₈-toluene was therefore photolysed at 213 K in the presence of a 4-fold excess of Et₃SiH. ¹H NMR spectra recorded at 213 K after 2 h irradiation revealed the presence of free ethene and 4a as the dominant species, while 4b was observed as a minor component. Two further photoproducts were generated during this reaction as demonstrated by the observation of hydride signals at δ –15.50 (dd, $J_{\rm Rh,H} = 3.7$, 35.4 Hz) 7a and δ -15.19 (dd, $J_{\rm Rh,H} = 10.7$, 33.3 Hz) 7b which were approximately 10% of the intensity of the hydride signals arising from 4a. Additional ¹H signals were also visible at δ 9.58, 8.58, 4.19, 4.13, 3.65 and 2.41, with the corresponding integrals suggesting that the resonances at δ 9.58, 3.65 and 2.41 arose from one species while those at δ 8.58, 4.19 and 4.13 corresponded to a second product. Based on integrals of the δ 9.58 and δ 8.58 signals these materials were initially produced in a 1 : 1 ratio, although 7b proved to be dramatically less stable than 7a with the associated NMR signals disappearing over night at -50 °C. Similar resonances have been reported for the vinyl-bridged binuclear iridium complexes $[(C_5H_5)Ir(\mu-\eta^1, \eta^2-CH=CHtBu)]_2$ and $[CH_2(C_5H_4)_2][Ir_2(\mu-\eta^1, \eta^2-H_2)]_2$ $CH=CHtBu)_2$, which suggested that 7a and 7b also contain μ - η^1 , η^2 -vinyl ligands.⁴⁴ This was subsequently confirmed, with the complexes being shown by NMR spectroscopy to have identical ligand spheres, differing only in the relative vinyl group orientations as determined by NOE spectroscopy. The structures of 7a and 7b and a suggested route to their formation are shown in Fig. 4. These species differ according to the relative



Fig. 4 Generation of vinylic C-H activation products 7a and 7b.

orientations of the silyl and hydride ligands on the higher oxidation state rhodium centre.

It should be noted, the 103Rh spectra of these complexes proved to be very helpful in their characterisation. The doublet of doublet multiplicity of each hydride resonance required both these species to contain inequivalent rhodium centres, which were subsequently shown to yield signals at δ -779 and -1407 for **7a** and δ -666 and -1399 for **7b**. The ¹⁰³Rh spectra subsequently revealed Rh-Rh splittings of ca. 14 Hz which indicates the products contain metal-metal bonds, with the large chemical shift difference between the ¹⁰³Rh signals further indicating that the two metal centres have different environments. Full NMR spectroscopic data for 7a and partial data for 7b are included in Table 1, a description of their detailed NMR assignments is presented in the ESI.† The relative amount of 7a and 7b formed in this reaction proved to increase as the initial excess of Et₃SiH relative to 1 was reduced. Furthermore, both these complexes proved to be thermally unstable, apparently transforming into 4a and 4b on warming. Interestingly, the analogous low temperature reaction with Et_2SiH_2 generated 5 alone.

Thermal reactions of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)-(SiEt_3)H]$ 4a and $[CH_2(C_5H_4)_2][Rh(C_2H_4)(SiEt_3)H]_2$ 4b with Et₃SiH

It has been reported that $CpRh(C_2H_4)(SiR_3)H$ reacts thermally with R_3SiH (where R = Me, Et) to generate the tri(silyl)hydride complex CpRh(SiR₃)₃H and ethane.⁴⁵ However, the CpRh(SiR₃)₃H product proved to be unstable and reacted further to generate the ring-substituted product [C₅H₄(SiR₃)][Rh $(SiR_3)_2(H)_2$ via silvl migration to the capping cyclic polyene. It was therefore expected that thermal reactions of 4a and 4b might provide access to the corresponding trisilyl hydride or silyl ring substitution products, or even the Si-C bond activation products 5 and 6. A solution was therefore prepared that contained both 4a and 4b in d₆-benzene and a greater than 5-fold excess of Et₃SiH. The resulting thermal reaction was then monitored by ¹H NMR spectroscopy which revealed that all resonances arising from 4a and 4b disappeared, with new signals for 4d, 5 and 6 (in a ratio of 59 : 24 : 17) becoming visible; the most diagnostic features seen in these spectra were the corresponding hydride resonances at δ –14.09, -14.40 and -14.60 respectively. On the basis of these observations it can be concluded that the formation of the Si-C bond activation products is possible under thermal conditions. This situation is, however, complicated by the observation of further hydride resonances at δ -14.06 (d, $J_{\text{Rh,H}}$ = 38 Hz), -13.92 (d, $J_{\rm Rh,H} = 37$ Hz) and -13.89 (d, $J_{\rm Rh,H} = 37$ Hz).

These signals were subsequently shown to arise from the ringsubstituted products $[(C_5H_4)CH_2(C_5H_3SiEt_3)][Rh(SiEt_3)_2(H)_2]_2$ 8 and $[CH_2(C_5H_3SiEt_3)_2][Rh(SiEt_3)_2(H)_2]_2$, with the latter species existing as isomers 9a and 9b. The structures of these materials are shown in Scheme 1.

A full description of the NMR spectroscopic characterisation of 8, 9a and 9b is given in the ESI,[†] and their NMR data are presented in Table 1. Key resonances for these new species appeared in the CH₂ bridge region of the ¹H NMR spectrum at δ 3.61, 3.71 and 3.76. Tracing the $^1\mathrm{H},~^{13}\mathrm{C},~^{103}\mathrm{Rh}$ and $^{29}\mathrm{Si}$ resonance connectivity within these products was achieved via appropriate high-resolution ¹H-¹³C, ¹H-¹⁰³Rh and ¹H-²⁹Si 2D HMQC correlations, coupled with appropriate ¹H-¹H NOE data. In the case of the complex giving rise to the methylene bridge proton resonance at δ 3.61, two *ipso* carbon signals were located at δ 110.60 and 111.40. This required the corresponding product to contain two distinct rings. Four sets of α ^{13}C and ¹H resonances were identified for these rings at δ 91.89/5.06, 91.62/5.12, 91.88/5.28 and 98.31/5.30 respectively. Further connections within the 2D 1H-13C NMR spectrum revealed that the pair of inequivalent α protons resonating at δ 5.06 and 5.12 in one ring were next to β -ring ¹³C nuclei that resonated at δ 87.40 and 87.50 which in turn coupled directly to β -ring protons at δ 4.90 and 4.93. In the second ring, ¹H resonances at δ 5.30 and 5.28 were found to connect to β -ring carbon signals at δ 95.50 and 95.63. However, direct ¹³C detection demonstrated that the carbon resonance at δ 95.50 arose from a CH group while that at δ 95.63 proved to arise from a carbon centre with no protons attached. This situation would exist if an SiEt₃ group replaced the proton and hence this species corresponded to a silylated ring substitution product.

The presence of this silyl group was confirmed by three separate NMR spectroscopic procedures. First, in the long-range 2D ¹H–¹³C NMR spectrum, a connection between the CH₂ (δ 0.78) proton signal of the SiEt₃ group and the ring carbon (δ 95.63) was observed. In the second method, a ¹H–¹H NOESY spectrum revealed NOE interactions between the ring protons and two distinct ethyl group resonances at δ 0.915 (CH₂) and 1.12 (CH₃), for one type of ethyl, and δ 0.78 (CH₂) and 1.044 (CH₃) for the second. In the third procedure, a ¹H–²⁹Si correlation was found to contain resonances that connected these ethyl proton resonances to ²⁹Si signals at δ 36.70 ($J_{RhSi} = 17$ Hz, Rh–*Si*Et₃) and –0.87 (C₅H₃*Si*Et₃) respectively. The full NMR spectroscopic data for complex **8**, identified as [(C₅H₄)CH₂(C₅H₃SiEt₃)][Rh(SiEt₃)₂(H)₂]₂, are listed in Table 1.

The remaining two methylene bridge ¹H signals, located at δ 3.71 (br) and 3.76, coupled to single *ipso* carbon signals in the long-range 2D ¹H–¹³C NMR spectrum at δ 111.99 and 111.70 respectively. This reveals that both these products are symmetrical about the CH₂ bridge. Using the same NMR spectroscopic methods described for **8**, these two species were deduced to correspond to the ring-substituted products [CH₂(C₅H₃SiEt₃)₂][Rh(SiEt₃)₂(H)₂]₂ **9a** and **9b** which differ only in the relative orientations of the ring substituents (Scheme 1). It should be noted that, in isomer **9a**, the CH₂ bridge protons should be slightly inequivalent in accordance with the correspondingly broad CH₂ bridge proton signal at δ 3.71.

In a further reaction, where the isolation of **4d** was attempted, a 5 mm NMR tube containing 20 mg of **1** in neat Et₃SiH was photolysed for 5 h. Upon removal of the volatiles, redissolving in d_6 -benzene, and recording a ¹H NMR spectrum, the apparently selective formation of **4d** was confirmed. This reaction was then scaled up, with a 100 mg sample of **1** being dissolved in neat Et₃SiH and photolysed for 10 h. The sample was then dried under vacuum, dissolved in d_6 -benzene and a ¹H NMR spectrum obtained. Examination of the hydride region of the NMR spectrum revealed the presence of the three hydride containing products **8**, **9a** and **9b** as the major products. The formation of **4d** was therefore suppressed in this system when the conditions

Photochemical reactions of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 with Me₃SiH

In order to explore whether these reactions depended on the identity of the silane, a d_6 -benzene solution of 1 was photolysed at 296 K, using a $\lambda > 400$ nm filter, in the presence of a 9-fold excess of Me₃SiH. ¹H NMR spectra recorded after 30 min revealed the presence of free ethene $(\delta$ 5.24) and two rhodium coupled hydride resonances at δ -14.57 (major) and -14.60 (minor). These observations suggest that this reaction follows an analogous path to that described previously with Et₃SiH and hence the species yielding these signals are $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(SiMe_3)H]$ 10a and $[CH_2(C_5H_4)_2][Rh(C_2H_4)(SiMe_3)H]_2$ 10b. As expected, extended irradiation did result in the formation of $[CH_2(C_5H_4)_2][Rh(C_2H_4)(SiMe_3)H][Rh(SiMe_3)_2(H)_2]$ 10c and $[CH_2(C_5H_4)_2][Rh(SiMe_3)_2(H)_2]_2$ 10d. The NMR characteristics of complexes **10a–10d** are listed in Table 1 and a description of the assignment process can be found in the ESI.† Three new bridged species, identified as [CH₂(C₅H₄)₂][(RhMe)(RhH)(µ- $SiMe_2_2$ 11, $[CH_2(C_5H_4)_2][(Rh{SiMe_3})(RhMe)(\mu-SiMe_2)_2]$ 12 and $[CH_2(C_5H_4)_2][(Rh{SiMe_3})(RhH)(\mu-SiMe_2)_2]$ 13 were also formed in this reaction. The structures of these materials are shown in Scheme 3. At the point when all the Rh(I) and Rh(III) centres were consumed, the ratio of 10d: 11: 12: 13 in solution proved to be 18:34:27:21.



Scheme 3 Additional products formed during the photochemical reactions of 1 with HSiMe₃.

Species **11, 12** and **13** all contain two distinct C_5H_4 rings, and produce signals in the corresponding ²⁹Si NMR spectrum at δ 204.67 (dd, $J_{Rh,Si}$ = 34.9, 46.0 Hz), 212.39 (dd, $J_{Rh,Si}$ = 35.7, 46.2 Hz) and 197.44 (dd, $J_{Rh,Si}$ = 29.1, 46.6 Hz) respectively which are characteristic of bridging silyl ligands. These products are differentiated by their terminal 1-electron donor ligands, which correspond to Me/H, SiMe₃/Me and SiMe₃/H respectively. A full description of how the NMR spectroscopic characterisation of **11, 12** and **13** was achieved can be found in the ESI.[†]

In view of the observations made during the analogous reaction with Et₃SiH, exhaustive photolysis of **1** with Me₃SiH was expected to yield the Rh(v) species **10d** alone. However, the silylene-bridged complex **13** containing SiMe₃ and H terminations was generated when a sample of **1** was photolysed in d₆-benzene with a 10-fold excess of silane for 4 h. Upon replacing the d₆-benzene with C₆H₆, and examining the sample by ²H NMR spectroscopy, signals in the methyl region revealed ²H labelling of the SiMe₃ and SiMe₂ groups in **13**. There was no evidence for ²H incorporation in the rings, which was confirmed in the ¹H NMR spectrum—the signals at δ 4.71, 4.77, 5.02 and 5.13 were all of equal intensity.

Low temperature studies with Me₃SiH

In order to probe these reactions at low temperature, a solution of 1 in d_8 -toluene was photolysed at 213 K in the presence of

a 4-fold excess of Me₃SiH. ¹H NMR spectra recorded after 3 h irradiation revealed the presence of free ethene and resonances corresponding to **10a** (major), **10b**, **10c** and **10d**. Two additional photoproducts were also observed in this reaction—one yielding a hydride signal at $\delta - 12.97$ (dd, $J_{Rh,H} = 17.4$, 25.7 Hz), and tentatively assigned as $[CH_2(C_5H_4)_2][Rh(C_2H_4)][Rh(SiMe_3)_2](\mu-H)_2$ **14**, and the second yielding a second order resonance at $\delta - 19.00$, and hence assigned as $[CH_2(C_5H_4)_2][RhH(\mu-SiMe_2)]_2$ **15**. The ratio of **10a** : **14** : **15** at this point proved to be 88 : 4 : 8. A description of the NMR characterisation of **14**, which has the structure shown in Scheme 3, is given in the ESI.[†] However, important features that should be noted include the

However, important features that should be noted include the doublet of doublet multiplicity (17.42 and 25.65 Hz) seen for the hydride signal. This confirms the presence of two distinct rhodium centres and a pair of equivalent bridging hydrides. In the long-range 2D $^{1}H^{-13}C$ NMR spectrum, the CH₂ bridge protons couple to two *ipso* carbons, which confirms the presence of two distinct C₅H₄ rings, and two α -ring carbons, which supports a symmetrical ligand arrangement about each (C₅H₄)Rh moiety. Furthermore, 2D NOE and $^{1}H^{-29}Si$ experiments provide unambiguous evidence for the presence of bound ethene and Rh–SiMe₃ ligands in 14.

In the 2D ¹H–¹⁰³Rh NMR spectrum, the hydride signal at δ –19.00 due to **15** couples to a single rhodium centre resonating at δ –1420, and the corresponding 2D ¹H–²⁹Si NMR spectrum contains a triplet at δ 204.96 in the ²⁹Si dimension. These observations suggested the formation of an analogous species to **5**, with bridging silylene and hydride ligands which couple to two magnetically distinct rhodium centres. Furthermore, the ²⁹Si resonance couples to two peaks in the ¹H dimension at δ 1.16 and 0.86, which indicates the presence of two inequivalent methyl groups in the SiMe₂ ligands. However, **15** was found to be unstable, and hence the full NMR based characterisation of this species was not possible. These data however serve to indicate that the reactivity of **1** towards silanes is highly dependent on the identity of the silane.

Hydrosilylation

The mononuclear CpRh(C_2H_4)(SiR₃)H Rh(III) systems have been shown to be precursors to catalytically active species involved in the hydrosilation of ethene with R₃SiH.¹⁴ Following irradiation of complex 1 in d₆-benzene in the presence of Et₃SiH, the volatiles were subjected to GCMS analysis which revealed that Et₃SiH, Et₄Si and CH₂=CHSiEt₃ were present. The same analysis was carried out on the volatiles from the analogous reaction of complex 1 with Me₃SiH. The GCMS results now detected EtSiMe₃, CH₂=CHSiMe₃ and the double insertion product SiMe₃CH₂CH₂SiMe₃. Hydrosilation of CH₂=CHSiMe₃ would explain the generation of SiMe₃CH₂CH₂SiMe₃.

Conclusions

The work presented in this paper has employed 1D and 2D NMR methods to unambiguously characterise a number of dinuclear rhodium complexes that were formed when $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2]_2$ 1 was photolysed in the presence of dmso, CH_2 =CHSiR₃ and R₃SiH [R = Me, Et]. These reactions proved to be relatively unselective, with the presence of two independent metal centres dramatically increasing the complexity of the situation over that found when the corresponding mononuclear systems have been examined. The preliminary NMR spectroscopic studies on 1 revealed dynamic behaviour *via* the observation of dramatic variations in the ¹H chemical shift of the CH₂ bridge protons with temperature. This was attributed to rotation about the CH2-C5H4 bond and suggested that the populations of the two extreme conformations available in solution changed with temperature. Fig. 1 illustrates the two situations and would suggest that the two metal centres might react totally independently of one another (B) or show Published on 18 January 2005. Downloaded by University of Prince Edward Island on 25/10/2014 04:43:23.

cooperative effects (A). Evidence for both these situations has been obtained during these studies.

Photochemical studies on the reaction of 1 in dmso have revealed that one of the ethene ligands of each rhodium centre in 1 can be readily replaced with dmso. This led to the stepwise formation of $[CH_2(C_5H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(dmso)]$ 2a and $[CH_2(C_5H_4)_2][Rh(C_2H_4)(dmso)]_2$ 2b, where the dmso ligand is bound through the sulfur atom. This deduction was based on the downfield shift of the corresponding ¹³C methyl resonances (with respect to that of free dmso) which matches the findings in related species.³⁷

Low temperature *in-situ* photochemical studies where **1** was irradiated in d₈-toluene in the absence of substrate enabled the detection of the labile solvent complex $[CH_2(C_3H_4)_2][Rh(C_2H_4)_2][Rh(C_2H_4)(\eta^2-toluene)]$ which was found to exist in two interconverting isomeric forms that differ only in the relative orientation of the η^2 -toluene ligand. The photochemical substitutions are therefore likely to first involve the generation of an unstable solvent complex. No evidence for H/D exchange with the solvent was observed in this experiment.

The photochemical reaction of 1 with vinyltrimethylsilane demonstrated that three isomeric forms of the double substitution product $[CH_2(C_5H_4)_2][Rh(CH_2=CHSiMe_3)_2]_2$ (3a, 3b and 3c) could be obtained after exhaustive photolysis. These differ in the relative orientations of the SiMe₃ substituents as illustrated in Fig. 3. Examination of the NMR spectra obtained for these samples revealed H/D exchange between the solvent, d₆benzene, and the a proton of free vinyltrimethylsilane. Brookhart et al. have previously observed deuterium incorporation into the vinylic sites of the olefin ligands of $Cp*Co(CH_2=CHR)_2$ (where R = H, SiMe₃) following heating of these complexes in d₆-benzene.⁴⁶ Earlier studies by Seiwell⁴⁷ found similar H/D exchange with $(\eta^5-C_5R_5)Rh(C_2H_4)_2$ (where R = H, Me) when they were heated in d₆-benzene. In both cases, a mechanism involving solvent coordination to the coordinatively unsaturated $[C_5R_5M(olefin)]$ fragment, followed by H/D exchange with the olefin and subsequent elimination of C_6D_5H was proposed. Brookhart et al.42 have also prepared the analogous rhodium complexes $Cp*Rh(CH_2=CHR)_2$ (where $R = SiMe_3$, $SiMe_2OEt$, Si(OⁱPr)₃, SiMe(OSiMe₃)₂, SiPh₂OⁱPr) and seen similar effects, as have Perutz et al. during their photochemical studies of $CpRh(C_2H_4)_2.^{41}$

The photochemical studies with Et₃SiH and Me₃SiH have demonstrated that upon ethene loss, complex 1 is able to activate the Si-H bonds of the trialkylsilanes as shown in Scheme 2. The primary photoproducts of these reactions contain both Rh(I) and Rh(III) centres but upon extended photolysis, the stepwise replacement of ethene is observed. This enabled the corresponding Rh(III)/(III), Rh(III)/(V) and Rh(V)/(V) species, to be characterised. The small values of the ${}^{2}J_{Si-H}$ hydride coupling constants determined for the SiEt3 containing complexes 4a $(J_{\text{SiH}} = 14 \text{ Hz})$, 4b $(J_{\text{SiH}} = 14 \text{ Hz})$ and 4d $(J_{\text{SiH}} = 9 \text{ Hz})$ imply that full oxidative addition of the Si-H bond has occurred. In addition, the value of $J_{\rm RhH}$ in 4a is 33.5 Hz and 4d is 38.5 Hz which allows the Rh(III) and Rh(v) centres to be readily distinguished. There is also a systematic shift in the ¹⁰³Rh chemical shifts found for these complexes to higher field on increasing the oxidation state from Rh(I) to (III) to (V). For example, the values found for 1, 4a and 4d are δ –929 (Rh(I)), -1483 (Rh(III)) and -1873 (Rh(v)).

The 16-electron fragment $[(C_5H_4)R][Rh(SiEt_3)H]$ (where $R = [CH_2(C_5H_4)][Rh(C_2H_4)(SiEt_3)H]$), formed by photolysis in these reactions, has also been shown at low temperature to activate the C–H bonds of the ethene ligand attached to the second Rh centre (Fig. 4). Two geometries of the corresponding vinyl hydride product 7 were detected in solution. This information demonstrates that the proximity of the second Rh centre can lead to novel reaction chemistry. Here, activation of a ligand which is remotely coordinated to the metal centre is demonstrated. Although these reactions were undertaken at low temperature

in toluene, no phenyl hydride or η^2 -arene containing complexes were detected. However, deuterium incorporation into **4d** and **10d** provided evidence for the transient existence of such products. The enhanced stability of **7a** over **7b** is most likely a result of the relative orientations of the hydride and silyl ligands on the rhodium centre with the higher oxidation state.

Similar H/D exchange processes have been observed before. For example, Maitlis et al. observed H/D exchange when Cp*Rh(SiEt₃)₂(H)₂, a known thermal source of [Cp*Rh-(SiEt₃)H], was heated in d₆-benzene.¹¹ Later, Berry et al.²⁰ revealed that this complex was an active catalyst for the formation of arylsilanes. However, it should be noted that there was no evidence to suggest that similar functionalised aryl species were generated here. The detection of the silvlene-bridged species 5 and 6, following the photochemical reaction of 1 with Et₃SiH is, however, significant since it confirms that not only is $[CH_2(C_5H_4)_2][Rh(C_2H_4)(SiEt_3)H][Rh(SiEt_3)H]$ able to C-H and Si-H bond activate, but that Si-C bond activation is also possible. Notably, when the photolysis was completed at low temperature, these silvlene bridged complexes are not observed, but the corresponding vinyl activation species are produced. This indicates that there is a higher activation barrier for Si-C cleavage and the products of this process are relatively stable. The ¹H resonances corresponding to free ethene and ethane generated in these experiments showed no signs of splitting due to deuterium incorporation.

It is interesting to note the variability in the bridged silylene products that were formed at room temperature. With Et_3SiH , two silylene bridged complexes are generated; $[CH_2(C_5H_4)_2][Rh(\mu-SiEt_2)H]_2$ **5** and $[CH_2(C_5H_4)_2][(RhH)-(RhEt)(\mu-SiEt_2)_2]$ **6**. While for Me₃SiH, three silylene bridged species are observed; $[CH_2(C_5H_4)_2][(RhMe)(RhH)(\mu-SiMe_2)_2]$ **11**, $[CH_2(C_5H_4)_2][(Rh{SiMe_3})(RhMe)(\mu-SiMe_2)_2]$ **12** and $[CH_2(C_5H_4)_2][(Rh{SiMe_3})(RhH)(\mu-SiMe_2)_2]$ **13**. The formation of the (H)(Et) and (H)(Me) analogues suggests that the source of the Rh–Et ligand in $[CH_2(C_5H_4)_2][(RhH)(RhEt)(\mu-SiMe_2)_2]$



Scheme 4 Pathways to the Si–C bond activation products observed during the reactions of **10b** with Me₃SiH.

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 $SiEt_2$] is therefore Et_3SiH , and not an ethene ligand, as indicated in Scheme 4.

The ratio of Rh(v) products to Si-C cleavage products obtained in these reactions proved to be influenced by the excess of silane relative to the corresponding unsaturated fragment. Thus when 1 was photolysed on an NMR scale in neat Et₃SiH, neither 5 nor 6 were observed—only the product of ethene loss and Si-H activation, 4d, was generated. Consequently, as the concentration of Et₃SiH rises, the reaction pathways that lead to the formation of the silylene bridged species are suppressed because the rate of intra-molecular Si-C activation no longer competes with inter-molecular Si-H activation of the free silane. When the original excess of Et₃SiH relative to 1 was between 8 and 12-fold, the ratio of Rh(v) to silylene bridged species proved to be approximately 7:3. However, when 1 was photolysed in the presence of between a 6- and 8-fold excess of Me₃SiH, the corresponding ratio proved to be approximately 2 : 8 in favour of the Si-C activation products. This demonstrates that intramolecular Si-C bond activation of a Si-Me bond is more facile than that of a Si-Et bond.

The low temperature photochemical studies with Me₃SiH also suggested that while the formation of similar vinyl hydride species to those observed in the presence of Et₃SiH was possible, they were observed at only a 1% level, with Si-C bond activation products dominating. This suggests that a substantial contribution to the Si-C bond activation barrier is steric in origin. The detection of the bridging hydride complex $[CH_2(C_5H_4)_2][Rh(C_2H_4)][Rh(SiMe_3)_2](\mu-H)_2$ 14, and the unstable silylene bridged species $[CH_2(C_5H_4)_2][Rh(\mu-SiMe_2)H]_2$ 15, that is analogous to 5, supports this view.

A review by Ogina and Tobita43 reveals numerous examples of similarly bridged silylene complexes which are generally formed by the reaction of di-, tri- and tetra-hydrosilanes with coordinatively unsaturated metal centres, although an alternative approach involves the oxidative addition of both the Si-H and Si-Si bonds of disilanes to metal centres. It appears that the formation of such species via Si-C bond activation is less common, although, Suzuki et al.48 have published data on the reactions of $(Cp^*Ru)_2(\mu-H)_4$ with vinyltrimethylsilane. They observed the µ-dimethylsilylene, µ-ethylidyne species $(Cp*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$, generated by double Si-C bond activation. While Oskada et al.49 have reported that the reaction of tris(2-phenylethyl)silane with $[RhClL_2]$ (where L = $P(^{i}Pr)_{3}$ generated the species $[Rh(H)_{2}L(\mu-SiR_{2})]_{2}$ as a result of both Si-H and Si-C bond activation. Redistribution reactions where silane substituents are exchanged represent an important organosilicon based reaction that involves Si-C bond cleavage and reformation. Sabo-Etienne et al. have used this approach to generate novel bridging silanes in $Ru_2H_4(\mu-\eta^2:\eta^2:\eta^2:\eta^2:\eta^2$ SiH_4)(PCy₃)₄ and Ru₂H₂(μ - η^2 : η^2 -SiH₂(Me)₂)₃(PCy₃)₂.⁵⁰ The catalytic formation of SiC bonds from CH and SiH containing substrates provides an exciting opportunity for efficient catalytic CH bond functionalisation.^{51,52}

Thermal reactivity studies on the Rh(III) complexes 4a and 4b showed that they react to form 4c, 4d, 5 and 6 when the excess of silane relative to the precursor is restricted to 10-fold or less. However, this situation is complicated by the observation of the SiEt₃ ring-substituted products 8 and 9 when a large excess of silane is present. During studies on the analogous mononuclear systems, Perutz *et al.* observed that, $CpRh(C_2H_4)(SiEt_3)(H)$ formed CpRh(SiEt₃)₃(H) on reaction with two equivalents of silane, and that species ultimately yielded the analogous complex $(C_5H_4SiEt_3)Rh(SiEt_3)_2(H)_2$ as the only reaction product.⁴⁵ The role of a similar, but undetected, tri(silyl)hydride complex is therefore suspected here.

Collectively, these observations reveal the accessibility of intermolecular Si-H and C-H activation pathways, and intramolecular Si-H, Si-C and C-H activation pathways. In view of these findings, and consideration of the relative bond dissociation energies (e.g. Si-H 318 kJ mol⁻¹, C-H 435 kJ mol⁻¹

and Si-C 384 kJ mol⁻¹), it would seem plausible that reactions involving C-C (368 kJ mol-1) or Si-Si (226 kJ mol-1) bond cleavage should also become feasible in these systems if suitable groups can be brought together. We are currently exploring these reactions.

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