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Photochemical studies of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Me$: formation of Si–H and C–H bond activation products†

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Studies examining the photochemical reactivity of $CpRu(PPh_3)_2Cl$ and $CpRu(PPh_3)_2Me$ towards the two electron donor ligands PEt_3, C_2H_4, DMSO, the CH bond activatable reagents tetrahydrofuran, toluene, and pyridine, and the SiH bond activatable reagents $HSiEt_3$ and $HSi(Me)_2CH{=}CH_2$) are presented. Broadband UV irradiation of $CpRu(PPh_3)_2Cl$ leads to the formation of mono-substitution products such as $CpRu(PPh_3)(PEt_3)Cl$ which are inert to further photochemical reaction, although thermally bis-substituted products such as $CpRu(PEt_3)_2Cl$ can be formed. Room temperature irradiation of the related complex $CpRu(PPh_3)_2Me$ with L = PEt_3, C_2H_4, and DMSO also produces $CpRu(PPh_3)(L)Me$. However, when these reactions are followed by *in situ* laser irradiation (325 nm source) at low temperature, three solvent activated isomers (*ortho*, *meta* and *para*) of $CpRu(PPh_3)_2(C_6H_4Me)$ are detected in toluene in addition to η^1- and η^3-coordinated benzyl species. Furthermore, photolysis in THF leads to both the C–D bond activation product $CpRu(PPh_3)_2(OC_4D_7)$ and the labile coordination complex $CpRu(PPh_3)(THF)Me$. Now CH_4 rather than CH_3D is liberated which suggests the involvement of an *ortho*metallated species. The photochemically driven reaction of $CpRu(PPh_3)_2Me$ with $HSiEt_3$ at 198 K generates $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(SiEt_3)H$ and thereby confirms a role for an *ortho*metallated complex is this process. Irradiation in cyclohexane produces the known *ortho*metallated complex, $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)$, and CH_4 in accordance with this reactivity.

Introduction

The bis-phosphine complex, $CpRu(PPh_3)_2Cl$ (**1**), was first discovered by Wilkinson *et al.*[1] as a side product of the reaction of $RuCl_2(PPh_3)_3$ with cyclopentadiene. This was confirmed by Stone *et al.* who presented data on its characterisation and reactivity.[2] The method by which $CpRu(PPh_3)_2Cl$ can be synthesised has been revised a number of times over the past thirty years,[3,4] and it is now prepared most commonly by the high yielding route of Bruce *et al.*[5] The resulting availability of $CpRu(PPh_3)_2Cl$ makes it an ideal starting point in the synthesis of other cyclopentadienyl ruthenium complexes. Over the last half century, this class of complex has been used to study the activation of small molecules and to facilitate a number of catalytic transformations.[6–9]

Studies of the thermal reactivity of $CpRu(PPh_3)_2Me$ (**2**) have demonstrated that it is more reactive than **1**, undergoing intramolecular C–H bond activation at 363 K in decalin to form the *ortho*metallation product $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)$ (**3**).[10,11] Similarly, the C–H bond activation of benzene by **2** or **3** produces $CpRu(PPh_3)_2Ph$ while toluene leads to $CpRu(PPh_3)_2(CH_2C_6H_5)$ and *meta* and *para* tolyl derivatives $CpRu(PPh_3)_2(C_6H_4Me)$.[12,13]

While thermal reactivity studies of these types of ruthenium complex have been widely explored, examples of their photochemical reactivity are not common. Cyclopentadienyl iron derivatives of these types of complex have however been widely examined, both thermally and photochemically.[14–17] Notable examples of such work include studies by Pannell *et al.*,[18–22] who over several decades probed the photochemical activity of bis-carbonyl cyclopentadienyl iron complexes towards silanes. They discovered that isomerisation of the silyl moiety in $CpFe(CO)_2(CH_2(SiMe_2)_2SiMe_3)$ proceeds through the silene intermediate $CpFe(CO)(SiMe_2SiMe_3)(\eta^2\text{-}CH_2{=}SiMe_2)$.[18] Ruthenium bimetallic carbonyl complexes have been examined and compared to their iron analogues.[23,24] Here Farrow and Knox[25] showed how $(Cp^*Ru(CO)_2)_2$ photolysis in $CHCl_3$ led to $Cp^*Ru(CO)_2Cl$. In contrast, photochemical reaction with ethene and hydrogen retains a bimetallic product structure, with monocarbonyl substitution resulting, while with H_2 the bridging carbonyls are replaced by bridging hydrides and a ruthenium–ruthenium double bond.

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† Electronic supplementary information (ESI) available: Synthetic and characterisation details, example NMR traces, and further product/irradiation time evolution plots. See DOI: 10.1039/c3dt52069b

Indeed, one of the major benefits of photochemically induced reactions, over thermal studies, is the opportunity to introduce product selectivity. For example, while the thermal substitution of a carbonyl ligand in $CpMn(CO)_3$ by THF requires high temperatures, the same reaction proceeds photochemically at room temperature.[26] The product of this reaction, $CpMn(CO)_2THF$, is relatively labile[27] and can be used as a precursor to many other $CpMn(CO)_2L$ type complexes (where for example L = N_2, η^1 P–P (dmpm = bis(dimethylphosphinomethane) or dmpp = 1,3-bis(dimethylphosphinopropane), piperidine or 4-acetylpyridine).[28–32]

Low temperature photolysis may also be employed to generate and stabilise 16-electron intermediates, which subsequently undergo coordination of an incoming ligand to form a coordinatively saturated 18-electron complex. The net effect of this process is to promote ligand exchange at the metal centre which is useful in cases where the parent complexes do not undergo ready thermal ligand loss. Haddleton and Perutz used this method to generate $[CpRh(C_2H_4)]$ from the parent complex $CpRh(C_2H_4)_2$ in an argon/methane matrix at 12 K through $\lambda > 200$ nm irradiation.[33–35] They subsequently showed that in a CO containing matrix the formation of $CpRh(C_2H_4)(CO)$ was possible. This photochemical route has since been used to form a range of novel and previously inaccessible CpRh complexes.

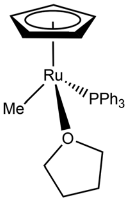
Photochemistry has also been used in conjunction with irradiation within an NMR probe to generate unstable species at low temperature and then characterise them. Geftakis and Ball first demonstrated this method using a fibre optic cable[36] and successfully formed $CpRe(CO)_2$(cyclopentane) *in situ*.[37–39] At York, a similar *in situ* irradiation apparatus uses a laser beam, provided by a He–Cd laser in this study.[40–42] This *in situ* technique allowed the monitoring of the photochemical reactivity of the N-heterocyclic carbene complex, $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (IEt_2Me_2 = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene) with the result that H_2 and PPh_3 loss was demonstrated.[43] It was also used to follow the formation of $CpCo(C_2H_4)(SiEt_3)H$ from $CpCo(C_2H_4)_2$.[44]

Here we describe a series of studies on the photochemical reactivity of $CpRu(PPh_3)_2R$ (where = Cl or Me) using broadband UV irradiation, and/or the laser *in situ* irradiation method. This approach allows access to both C–H and Si–H bond activation pathways, while producing definitive mechanistic information. In this case, we hoped to answer the question of whether direct CH bond activation or *ortho*metallation play a defining role in the reaction chemistry of **2**.

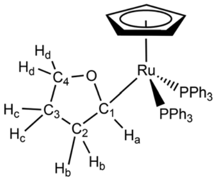
Experimental

Details of the synthetic and NMR procedures used can be found in the ESI.† Full NMR data for species **1–23** can also be found there. Partial data is presented in this section for complexes **11** and **12** for illustration. Throughout this work, UV photochemical studies were carried out using either a Oriel 200 W Hg–Xe arc lamp or a Kimmon 63 mW He–Cd laser (operating at 325 nm).

$CpRu(PPh_3)Me(THF)$ (**11**): ^{1}H NMR 0.16 (d, 3H, Ru–CH_3), 4.59 (s, 5H, η^5-C_5H_5), 7.08 (m, *p*-$P(C_6H_5)_3$), 7.12 (m, *m*-$P(C_6H_5)_3$), 7.53 (m, $|^3J_{PH}|$ = 5.9 Hz, *o*-$P(C_6H_5)_3$). $^{31}P\{^1H\}$ NMR 61.3 (s, $P(C_6H_5)_3$).



$CpRu(PPh_3)_2(2\text{-}C_4H_7O)$ (**12**): ^{1}H NMR 1.75 & 1.94 (t, $|^3J_{HH}|$ = 6.2 Hz, H_c), 2.19 & 2.41 (q, 2, $|^3J_{HH}|$ = 5.4 Hz, H_b), 3.70 & 3.86 (q, $|^3J_{HH}|$ = 5.4 Hz, H_d), 4.23 (s, 5H, η^5-C_5H_5), 5.37 (dt, 1, $|^3J_{HH}|$ = 1.7 $|^3J_{PH}|$ = 16.3 Hz, H_a), 7.09 (m, *p*-$P(C_6H_5)_3$), 7.16 (m, *m*-$P(C_6H_5)_3$), 7.38 (m, 12H, *o*-$P(C_6H_5)_3$). $^{31}P\{^1H\}$ NMR 41.9 (s, $P(C_6H_5)_3$).



Results and discussion

Thermal reaction of $CpRu(PPh_3)_2Cl$ (1) with PEt_3

In order to investigate the thermal reactivity of **1**, a d_8-toluene solution of the complex was first heated to 353 K with a 7 fold excess of PEt_3 for 24 hours. Subsequent NMR monitoring revealed the complete conversion of **1** into $CpRu(PEt_3)_2Cl$ (**4**) which yields a ^{31}P NMR signal at δ 46.8, and $CpRu(PPh_3)(PEt_3)Cl$ (**5**) which yields a pair of doublets at δ 27.8 and 45.5 that are indicative of mono-substitution. The ratio of **4** : **5** proved to be 2 : 1 at this point. Upon further heating at 353 K for 24 h the complete conversion to **4** was achieved.

Photochemical reaction of 1 with PEt_3

As a starting point, the photochemical reactivity of $CpRu(PPh_3)_2Cl$ was examined at 198 K using the *in situ* laser irradiation method. No evidence for any reaction was evident in the associated NMR spectra after 18 h irradiation using the 325 nm source. A 200 W He–Xe arc lamp (broad-band UV) was then employed. This method required the sample to be irradiated outside the NMR spectrometer. The sample was then transferred into the probe of the NMR spectrometer, precooled as required, to record the ^{1}H and $^{31}P\{^1H\}$ NMR spectra that were required to follow the reaction.

An analogous solution of **1** containing PEt_3 was therefore prepared and irradiated at 198 K using this *ex situ* setup. Only the mono-substituted reaction product **5** was formed and after

18 hours of UV irradiation full conversion to it was achieved. The sample was then washed with ethanol to remove the excess PEt_3 and liberated PPh_3 and re-dissolved in d_8-toluene. A 5-fold excess of PMe_3 was then added and the resulting sample re-photolysed using *ex situ* at 233 K. No change in sample composition was observed. The product complex **5** is therefore photoinsensitive under these conditions. It should be noted that when **5** is warmed with PMe_3, the previously characterised complex $CpRu(PMe_3)_2Cl$[45] is formed. We therefore conclude that the preparation of such mono-substituted complexes can be achieved selectively photochemically.

Photochemical reaction of 1 with ethane

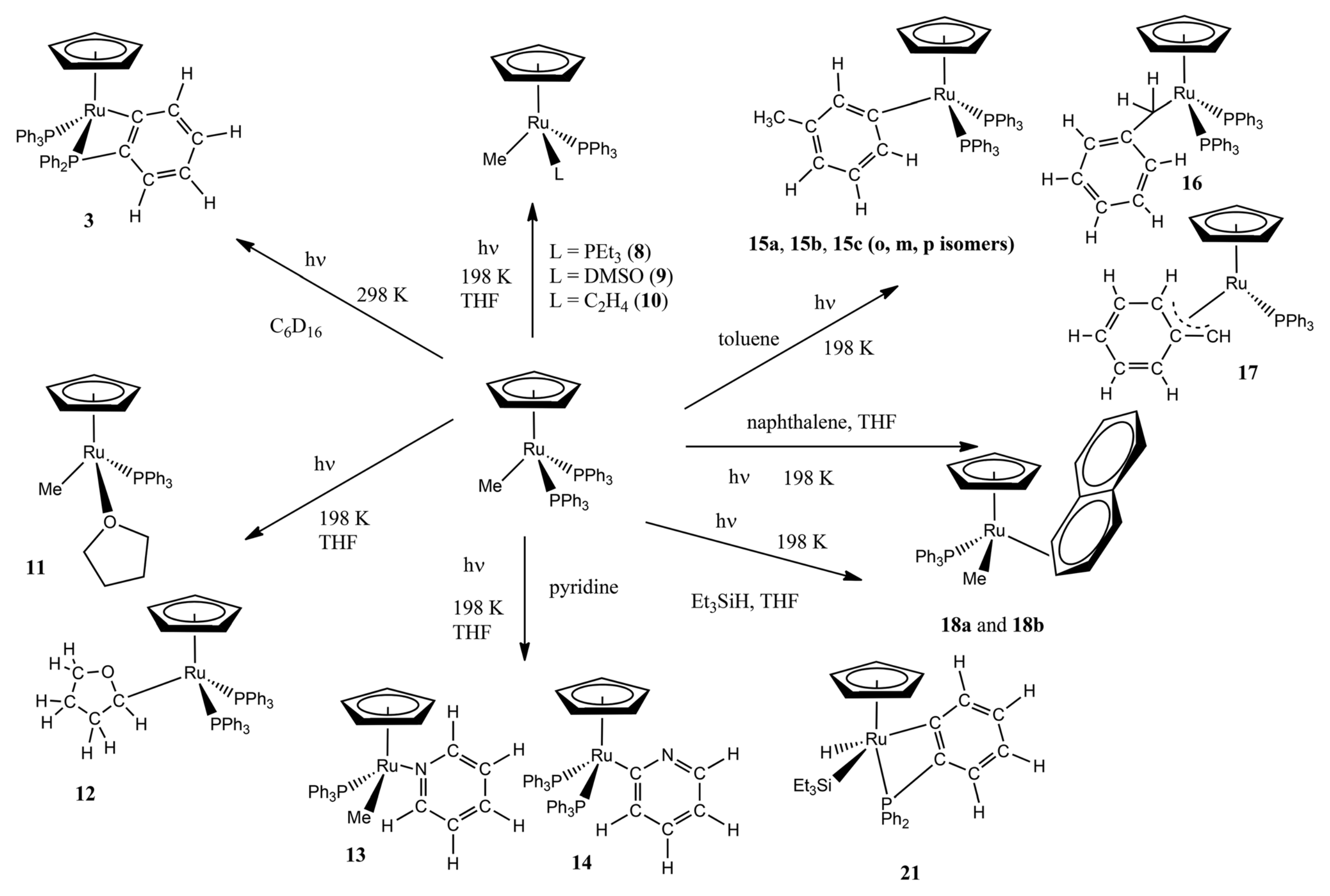
A second substitution reaction was tested in order to assess whether the photolysis of **1** with ethene (pressurised to 1.5 bar) in d_8-toluene led to the formation of the η^2-ethene coordination complex $CpRu(PPh_3)(\eta^2\text{-}C_2H_4)Cl$ (**6**) or the corresponding C–H activation product $CpRu(PPh_3)(C_2H_3)(H)Cl$. This photolysis reaction was undertaken *ex situ* at 198 K. The resulting ^1H NMR spectrum recorded after 12 hours of photolysis contained a new resonance at δ 4.23 which is consistent with the formation of a η^5-Cp containing complex. Four new peaks, broad multiplets at δ 0.56, 1.18, 2.23 and 2.64 were also detected which correspond to the inequivalent protons of an η^2-bound ethene ligand. Following the NMR characterisation of **6**, the temperature of the solution was raised to 298 K in order to appraise the thermal stability of **6**. The corresponding ^1H and $^{31}P\{^1H\}$ NMR spectra revealed that **6** reverted back to **1** before measurement could be made. No reaction was evident when thermal initiation was employed.

These results demonstrate that **1** does not activate the C–H bonds of these reagents, nor the solvent C–D bonds under irradiation in the presence of ethene or PEt_3. More importantly, no evidence was found for any *ortho*metallation products that might result from involvement of the putative 16-electron intermediate $CpRu(PPh_3)Cl$. This situation contrasts with that found for the methyl analogue of **1**, $CpRu(PPh_3)_2Me$ (**2**) which has been shown previously to activate the C–H bonds of benzene and to undergo *ortho*metallation of the aryl ring of the phosphine.[11] These reported observations suggest that **2** possesses a significantly different reactivity that of **1**.

Studies where the photochemical reactivity of **2** is examined are now presented. In this case, 325 nm irradiation using the *in situ* method was employed. Scheme 1 details the main reaction products that are detected and characterised in this work.

Thermal and photochemical reactions of $CpRu(PPh_3)_2Me$ (2) with PEt_3

These studies were completed to assess the ability of **2** to undergo a substitution reaction with a suitable 2-electron



Scheme 1 Reaction products formed when **2** is subject to UV irradiation as specified.

donor. To achieve this, a d_8-THF solution of **2** containing a 7-fold excess of PEt_3 was prepared and heated to 353 K for 24 hours. Related spectral changes to those described earlier for the reaction of **1** with PEt_3 were found. For example, the resulting $^{31}P\{^1H\}$ NMR spectra now contain a major signal at δ 40.5 due to $CpRu(PEt_3)_2Me$ (**7**) and minor signals for $CpRu(PPh_3)(PEt_3)Me$ (**8**). Upon further heating for 16 h, the complete conversion of **2** into **7** was demonstrated by NMR spectroscopy.

When a second sample was prepared and the corresponding *in situ* photochemical reaction monitored at 198 K over 18 h, only **8** was formed. The progress of this reaction was followed during this period by ^1H and $^{31}P\{^1H\}$ NMR methods. New proton resonances at δ 0.39, 0.83, 1.39, 1.50 and 4.49 are diagnostic of **8**. Specifically, the peak at δ 4.49 is consistent with that expected for a cyclopentadienyl ring while the triplet at δ 0.39 (J_{PH} = 5.6 Hz) is consistent with the proton resonance of a ruthenium-bound methyl group. The triplet splitting indicates that two phosphine ligands couple to this group and are hence are bound to the metal. Two doublets of equal intensity, that share a common splitting of 39.3 Hz, are observed in the corresponding $^{31}P\{^1H\}$ NMR spectrum at δ 35.2 and 62.9. These resonances represent the two ^{31}P nuclei of the phosphines of **8**. A large singlet resonance at δ −6.4 which is characteristic of free triphenylphosphine is also detected.

2D $^1H/^{31}P$ HMQC, $^1H/^{13}C$ HMQC and ^1H-COSY spectra were then used to fully characterise this product. Specifically, the two ^{31}P resonances connect to common ^1H resonances at δ 0.39, 1.39, 1.50, 4.49 and 7.61. While the ^{31}P resonance at δ 62.9 couples strongly to ^1H resonances at δ 7.61, 7.06 and 6.97 of the *ortho*, *meta* and *para* phenyl protons of the bound triphenylphosphine ligand of **8**. Signals at ^1H δ 0.83, 1.39 and 1.50 were found to couple strongly to the ^{31}P resonance at δ 35.2. The proton resonances at δ 1.39 and 1.50 correspond to the inequivalent CH_2 protons of the triethylphosphine ligand (confirmed by their mutual coupling to a common carbon at δ 23.4 in the corresponding $^1H/^{13}C$ HMQC experiment) while that at δ 0.83 corresponds to the Me group.

The plot shown in Fig. 1 illustrates the change in relative intensities of these ^{31}P signals as a function of irradiation time. The time taken to achieve 50% conversion of **2** is 7.4 h. The corresponding ^1H NMR spectra contained characteristic C_5H_5 resonances which vary in intensity in a similar way. There are no signals in the high field region (δ 0 to −20 range) of the ^1H NMR spectrum where metal-hydride resonances are commonly observed.

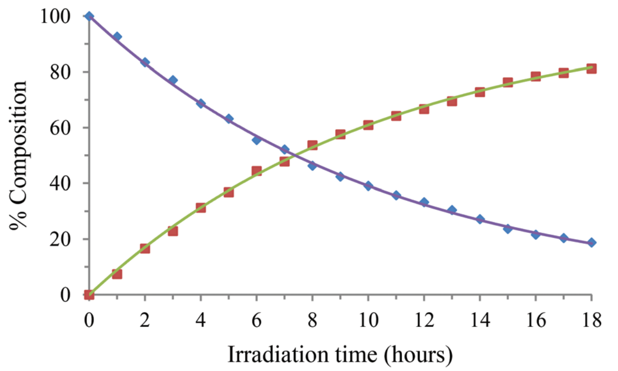


Fig. 1 Plot of the relative ^{31}P signal intensities as a function of irradiation time (325 nm, in d_8-THF) during the reaction of **2** (◆) with PEt_3 at 198 K leading to the formation of **8** (■).

The observation of **8** suggests that the 16-electron reaction intermediate $[CpRu(PPh_3)Me]$ can be formed under photolysis and that rapid reaction with PEt_3 ensues. Under thermal conditions, the dominance of $CpRu(PEt_3)_2Me$ suggests complete phosphine exchange is possible. Under irradiation however, the selective formation of **8** is achieved even after 30 hours of photolysis with the 325 nm source.

Photochemical reaction of 2 with DMSO

In view of the fact that PEt_3 is highly reactive, a further reaction with the milder reagent dimethylsulfoxide was undertaken. Previous studies have shown that DMSO may interact with metal centres, as a two electron donor, through either M–S (*e.g.* $[Ru(NH_3)_5(DMSO)](PF_6)_2)$[46] or M–O (*e.g.* $[CuBr_2(DMSO)_3)$[47] coordination modes. The coordination mode that DMSO adopts may be determined by X-ray crystallography,[48] observation of the change of the $\nu(O{=}S)$ relative to free DMSO using IR methods,[49] or as confirmed more recently, through the use of NMR techniques.[50] Here we describe the formation of the products for reaction between **2** with DMSO, and determine the coordination mode of the bound DMSO moiety. Accordingly, a sample of **2** was prepared in d_8-THF that contained 5 µl of DMSO. UV irradiation led to the loss of PPh_3 and a new ^{31}P signal was observed at δ 59.0 in addition to notable ^1H methyl signals at δ 0.02, 2.57 and 2.37. These data confirm that the selective formation of the mono-substituted complex $CpRu(PPh_3)(DMSO)Me$ (**9**) was achieved. The CH_3 moieties of the coordinated DMSO ligand are inequivalent and show a strong connection to the Cp ring protons according to nOe data. The DMSO ligands coordination mode was confirmed as arising through a Ru–S link by the downfield shift of the CH_3–^{13}C signal relative to that of free DMSO.[50] These results also confirm that the reaction is selective to mono substitution with no hydride or *ortho*metallation products being indicated. The plot shown in ESI Fig. 1† presents the change in relative intensities of the species in solution as a function of irradiation time. The time taken to achieve 50% conversion of **2** into **9** was 15.5 h.

Photochemical reaction of 2 with ethane

An analogous reaction to that described earlier between **1** and ethene was then monitored; $CpRu(PPh_3)(\eta^2\text{-}C_2H_4)Me$ (**10**), has been previously synthesised under forcing conditions (50–150 bar of ethene at 373 K).[51] It was intended that this photochemically initiated reaction would yield **10** under mild conditions thereby allowing us to probe its reactivity in a rigorous way. In order to achieve this, a sample of **2** in d_8-THF was pressurized with 1.5 bar of ethene gas. This sample was then cooled to 198 K and subjected to 325 nm irradiation for 18 hours using the *in situ* laser set-up. The reactions progress

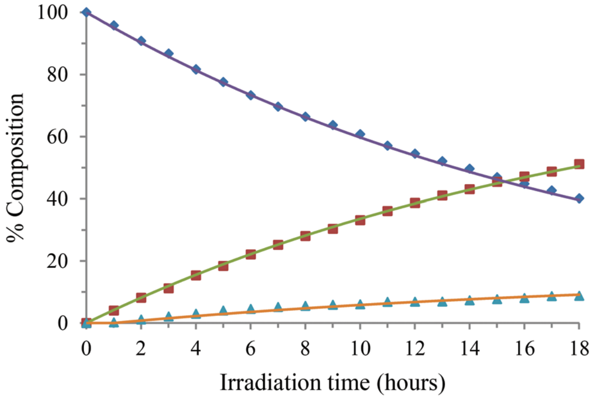


Fig. 2 Plot of the relative proportions of **2** (◆), **10** (■) and **11** (▲) as a function of irradiation time (325 nm, in d$_8$-THF) for the reaction of **2** with ethene at 198 K.

was monitored during this period by recording ^{1}H and ^{31}P{^{1}H} NMR spectra every 12 minutes. In the ^{31}P NMR spectra, the singlet at δ 55.3 for **2** reduced in intensity while three new peaks grew in at δ −6.4, δ 67.7 and δ 61.3. The latter of these ^{31}P resonances is due to the THF adduct CpRu(PPh$_3$)(THF)Me (**11**) which will be described later in this manuscript, while the former is due to free PPh$_3$. Fig. 2 shows how the proportion of these products varies over the 18 hour irradiation period. Under these conditions, 14.2 h was taken to achieve 50% conversion of **2**.

Comparison of the initial ^{1}H NMR spectrum with that recorded after 4 hours of photolysis shows the formation of a new resonance at δ 4.63 in the "Cp region". Four new peaks at δ 0.67, 1.28, 2.54 and 2.81 (multiplets) were also found. A ^{1}H COSY experiment demonstrated coupling between these four proton resonances. A final proton resonance was found at δ 0.43 (d, 6.7 Hz) due to the methyl protons of this product. These six resonances are consistent with those expected for **10** if alkene rotation is restricted by the low temperature.

Data collected in a ^{1}H/^{31}P HMQC experiment revealed connections between the δ 67.7 ^{31}P signal and the four ethene protons resonances, the methyl resonance, the Cp signal, and a new *ortho* phenyl proton signal at δ 133.2. A ^{1}H/^{13}C HMQC experiment located the corresponding ^{13}C resonances while examination of COSY data revealed the remaining the phenyl group signals.

When this sample was warmed to 233 K, the ethene proton signals started to broaden, indicating that the two *trans* proton pairs undergo site exchange due to η^2-ethene ligand rotation. In order to confirm this, a series of selective nOe measurements were undertaken. In such an experiment, when the signal at δ 0.67 is probed, magnetisation transfer into the signal at δ 2.54 is observed. These data confirm that the protons giving rise to these resonances are *trans* to each other and while no link to the Cp resonance was observed, one to the RuMe resonance was seen.

This suggests that the δ 0.67 yielding proton points away from the Cp ring and is on the same side as the RuMe in **10**. No evidence for products resulting from methyl migration was found.

Table 1 Rate constant for ethene rotation in **10**

T/K	k/s^{-1}
253	2.96×10^{-2}
243	8.24×10^{-3}
233	1.66×10^{-3}
223	1.96×10^{-4}
213	4.30×10^{-5}
203	4.80×10^{-6}

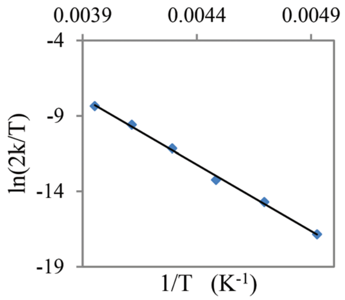


Fig. 3 Eyring plot as used to determine the barrier to ethene rotation in **10**.

Alkene rotation was then examined over the temperature range 203–253 K through a series of EXSY measurements and appropriate rate constant data obtained. These data are presented in Table 1 while Fig. 3 illustrates the corresponding Eyring plot which yielded $\Delta H^‡ = 72.9 \pm 3.0$ kJ mol^{-1}, $\Delta S^‡ = 21.7 \pm 4.0$ J K^{-1} mol^{-1} and $\Delta G^‡_{300} = 66.4 \pm 0.8$ kJ mol^{-1}. It should be noted that the Eyring plot used rate constants which were multiplied by two in order to account for the possibility of the equally likely reverse-reaction.[52] Similar $\Delta G^‡$ values of ethene rotation have been reported for cyclopentadienyl rhodium complexes: CpRh(CH$_2$=CH(CO$_2{}^t$Bu))$_2$ $\Delta G^‡_{295} = 72.5 \pm 0.1$ kJ mol^{-1} [53] and Cp*Rh(CH$_2$=CH(Me)) (SiEt$_3$)(H) $\Delta G^‡_{300} = 72.7 \pm 0.1$ kJ mol^{-1}.[54] It should be noted that there was no evidence for any CH bond activation of the ethene ligand and upon warming to room temperature **2** was reformed.

Photochemical reaction of 2 in cyclohexane

The introduction has already detailed how the *ortho*metallation product CpRu(κ^2-2-C$_6$H$_4$PPh$_2$)(PPh$_3$) (**3**) and the C–H activation product CpRu(PPh$_3$)$_2$Ph can be formed from **2**. Furthermore, the reactions with the added ligands, DMSO, PEt$_3$ and ethene have established that the corresponding substitution products can be formed. However, no evidence for any CH bond activation was observed in the reactions presented so far. In order to monitor more clearly the C–H/C–D bond activation potential of **2**, a d$_{12}$-cyclohexane solution was prepared where the only source of ligation for a photoproduct is the solvent itself or a C–H bond within the initial photoproduct. When this sample was irradiated for 12 h a reaction was evident according to NMR. In this case the ^{31}P{^{1}H} NMR signal of **2** was replaced by two doublets at δ −16.9 (J_{PP} = 33.8 Hz) and 63.5 (J_{PP} = 33.8 Hz). The absence of the expected ^{31}P{^{1}H}

NMR signal at δ −6.4 for free phosphine in this reaction indicates that both phosphine ligands remain bound to the ruthenium centre. The lack of a ruthenium–methyl moiety and observation of methane were also evident in these spectra. These data confirm that the known product **3** is readily formed, and confirm the existence of a CH bond activation pathway in the photochemistry of **2**. Owing to the relatively high freezing point of cyclohexane (280 K), low temperate irradiation of such a sample was not feasible. Additionally, no activation of the solvent was indicated. The presented NMR data for **3** is in agreement with that reported.[11]

Photochemical reaction of 2 with THF

In order to probe this *ortho*metallation reaction, a d_8-THF solution of **2** was prepared and irradiated at 198 K. Two new species were formed under these conditions which yielded ^{31}P NMR signals at δ 41.9 and 61.3. ESI Fig. 2† shows how the intensity of these signals varies over the 18 hour irradiation period. After 18 hours only 30% of **2** was converted into product and this lower conversion is taken to suggest that **2** must reform during this process (we estimate it would take 36.2 h for 50% conversion). ^{1}H NMR signals at δ 0.19[57] due to methane and at δ 0.16 due to a RuMe are also observed, although no signals attributable to **3** are seen (see Fig. 4).

In order to confirm the identity of these species an analogous solution consisting of **2** in a 2 : 1 mixture of d_8- and h_8-THF was examined. In the d_8-THF experiment, only the two ^{1}H NMR signals at δ 4.23 and 7.38 connected to the dominant ^{31}P signal at δ 41.9. This changed for the d_8–h_8 mixture as connections to signals at δ 5.37, 3.86, 3.70, 1.75, 1.94, 2.41 and 2.19 were also observed. These resonances arise from a tetrahydrofuryl group and while there was no methyl proton resonance, further *ortho*-, *meta*- and *para*-PPh_3 resonances were located at δ 7.38, 7.16 and 7.09. The ^{1}H signal at δ 5.37 was confirmed as arising from the α-proton of the ruthenium-bound tetrahydrofuryl group through the observation of a one-bond carbon coupling to a ^{13}C signal at δ 145.7 which exhibited a triplet splitting to phosphorus of 17.8 Hz. The presence of two triphenylphosphine ligands in **12** is therefore confirmed and these data identify it as $CpRu(PPh_3)_2(2\text{-}C_4H_7O)$. No hydride signals were observed during these studies.

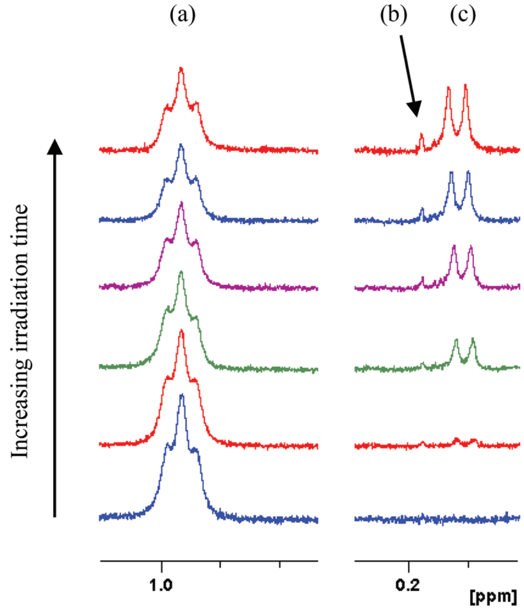
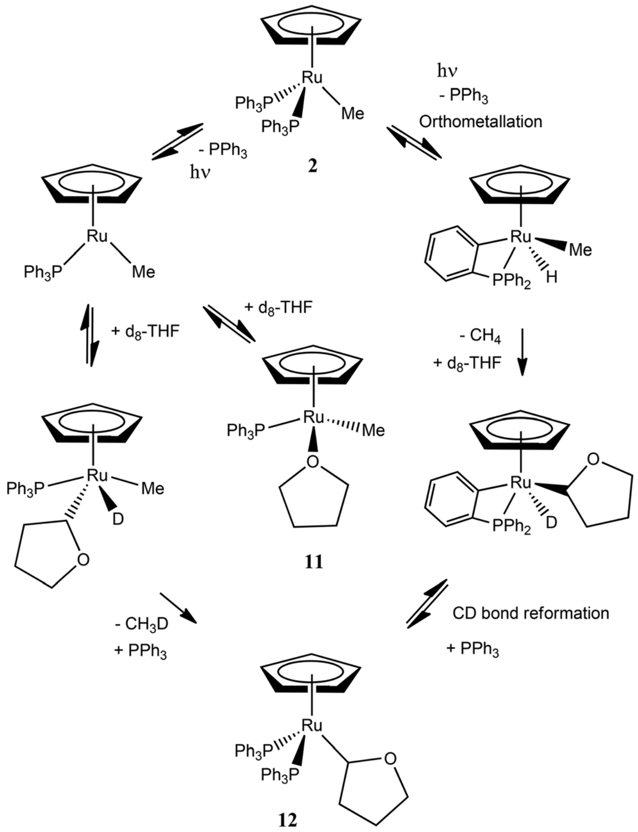


Fig. 4 Change in ^{1}H NMR intensities for: (a) the methyl resonance of $CpRu(PPh_3)_2Me$ (**2**), (b) the free methane signal and (c) the methyl signal for $CpRu(PPh_3)(THF)Me$ (**11**) with increasing irradiation time.

The minor product **11** which yielded the ^{31}P signal at δ 61.3 proved to connect with a ^{1}H signal at δ 4.59 due to a Cp ring. This ^{31}P signal also coupled to a ^{1}H peak at δ 0.16 which appeared as a doublet of 5.91 Hz thereby confirming **11** possesses a RuMe group and corresponds to a mono phosphine complex. The phosphine that is released in this reaction produced the expected singlet ^{31}P resonance at δ −6.4. These data suggest that **11** corresponds to the solvent coordination complex, $CpRu(PPh_3)Me(THF)$, although it should be noted that the THF moiety was too labile to be detected, even at 198 K. Similar THF-coordination complexes are known[26,55,56] and in this case **11** is unstable above 218 K. There are two potential routes to the **12**, as outlined in Scheme 2.

Photochemical reaction of 2 with pyridine

Following the demonstration that both **11** and **12** form when **2** is irradiated in THF solution, the reactivity of **2** towards



Scheme 2 Potential UV initiated reaction pathways leading to $CpRu(PPh_3)Me(THF)$ (**11**) and $CpRu(PPh_3)_2(2\text{-}C_4H_7O)$ (**12**) from **2** in d_8-THF solution.

pyridine was examined. Irradiation of **2** with pyridine in d_8-THF solution led to the conversion of **2** into a single product **13** which yielded a ^{31}P NMR signal at δ 68.3 (17.4 h for 50% conversion of **2**). The lack of any signals for **11** confirmed that the coordination strength of the pyridine is greater than that of THF. NMR data for CpRu(PPh$_3$)(pyridine)Me (**13**) is presented in the ESI.†

Upon warming this solution, the formation of a new product **14**, yielding a ^{31}P{^{1}H} NMR resonance at δ 54.7 resulted. This ^{31}P signal was found to couple to ^{1}H NMR signals at δ 4.64, 7.00 and 7.51, through a ^{1}H/^{31}P HMQC NMR experiment. The signals at δ 4.64 and 7.51 have relative integrals of 5 : 12, which indicates that they arise from a cyclopentadienyl group and the *ortho*-phenyl protons of **14**, CpRu(PPh$_3$)$_2$(2-pyridyl).

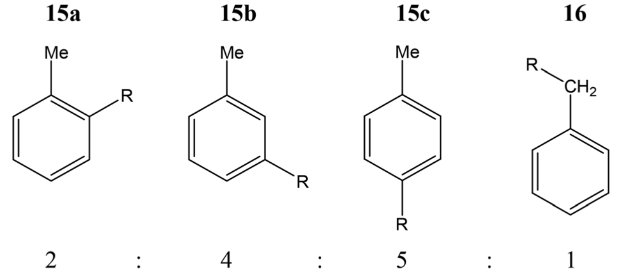
Photochemical reaction of 2 with toluene

The activation of the CH bond of an arene is now a relatively common reaction in inorganic chemistry.[58,59] Evidence has been already presented here for both *ortho*metallation and THF and pyridine CH bond activation products during studies on the reactivity of **2**.

When a d_8-toluene solution of **2** was irradiated for 6 hours the formation of five products was revealed by NMR methods. These data include the detection of new ^{31}P resonances at δ 51.6, 52.0, 52.3, 52.6 and 60.3. However, the corresponding ^{1}H NMR spectra revealed little information that could be used to identify these species.

In order to fully characterise them, a second sample was prepared containing protio toluene alone and it was then irradiated for 20 hours. At this point, the protio toluene was removed and the sample dissolved in d_8-toluene and the resulting ^{31}P NMR spectrum contained the five original signals observed in the d_8-toluene reaction. Using a combination of ^{1}H/^{31}P HMQC and ^{1}H COSY NMR experiments, it proved possible to characterise these species, **15a**, **15b**, **15c**, **16** and **17**. Scheme 3 reveals the site at which C–H bond activation has occurred in order to form these species. Notably, no hydride signals were present in any of these ^{1}H NMR spectra. The NMR characteristics of these products are presented in the ESI.†

It should be noted that the ^{31}P signals at δ 51.6 and 60.3 arise from CpRu(PPh$_3$)$_2$(CH$_2$Ph) (**16**) and CpRu(PPh$_3$)(η^3-CH$_2$Ph) (**17**) respectively. A small ^{1}H NMR peak at δ 0.17 was observed in these NMR samples due to liberated methane. No evidence was found for any η^2-coordinated toluene complexes nor was any evidence found for the *ortho*metallation complex **3** in these spectra. The characterisation of CpRu(PPh$_3$)$_2$(σ-CH$_2$C$_6$H$_5$) (**16**) and CpRu(PPh$_3$)(η^3-CH$_2$C$_6$H$_5$) (**17**) is detailed in the ESI.† Previously the thermal reactivity of CpRu(PPh$_3$)$_2$Me with toluene was been explored by Lehmkuhl *et al.*[12,13] who observed **15b**, **15c** and **16**.



Scheme 3 *Ortho*, *meta*, *para* and benzyl C–H activation products with their relative composition where R = RuCp(PPh$_3$)$_2$.

Photochemical reaction of 2 with naphthalene

Following the successful reaction with toluene, naphthalene was considered as a potential substrate. Surveys of the literature show that naphthalene can bind in an η^2-fashion to 16-electron fragments through a 1,2 interaction;[60–62] the 2,3 coordination mode is less common.[63] In the case of CpRh(PMe$_3$)(η^2-naphthalene), diagnostic proton resonances are seen at δ 3.49 (qd, J = 5.6, 2.4 Hz) and δ 4.09 (td, J = 6.6, 2.6 Hz) for the η^2-bound olefinic protons.[64] A solution containing 8 mg of naphthalene and **2** was therefore prepared and irradiated *in situ* at 198 K.

The resulting ^{31}P{^{1}H} NMR showed the formation of two product signals at δ 63.2 and δ 62.8 in the ratio of 20 : 8. In the corresponding ^{1}H/^{31}P HMQC NMR experiment, the δ 63.2 resonance connected to ^{1}H NMR signals at δ 4.55 and 0.95 (d, 5.8 Hz) which are consistent with the resonances expected for protons of a coordinated cyclopentadienyl ring and a ruthenium bound methyl group (respectively). Further connections to diagnostic η^2-bound olefinic protons were visible at δ 3.72 and 4.13. The smaller ^{31}P resonance at δ 62.8 was observed to couple to proton signals at δ 4.51, 4.06, 3.67 and 0.89 (d, 5.8 Hz). The nature of the doublet splitting for the two methyl resonances reveals that each of these complexes possesses only one coordinated triphenylphosphine ligand.

Analysis of the recorded ^{1}H NMR spectra during the photochemical reaction also revealed the growth of a series of new peaks in the range δ 6.4 and δ 6.9 that are also diagnostic of a bound naphthalene ring. However, the overlap of these signals with those of the triphenylphosphine and free naphthalene resonances made the characterisation of these complexes using ^{1}H COSY and 2D NOE experiments difficult. 2D NOE spectra did, however, reveal two small, connected, signals between δ 4.13 and δ 4.55 resonances that are consistent with an interaction between the Cp ring and an η^2-bound naphthalene proton.

It has been shown in a number of instances that when an arene binds to a metal centre to form a complex such as CpRh(PMe$_3$)(η^2-arene), the pi face of the aromatic ring can point either up or down. Two rotamers therefore often exist which can interconvert.[64] Warming this solution above 230 K led to the decomposition of the resultant complexes rather than further reaction to form the corresponding naphthyl product.

Photochemical reaction of 2 with HSiEt$_3$

Until now, the reactions discussed have focused on exploring the potential for C–H bond activation. The following sections outline how **2** reacts with a silane in a further attempt to observe RuH-bond containing species. Photolysis of a d_8-toluene solution of **2** containing $HSiEt_3$ at room temperature resulted in extremely complicated ^1H and $^{31}P\{^1H\}$ NMR spectra. A number of hydride resonances were seen in the range δ −11.5 and −13.0. Notably, ^1H NMR signals were also seen for the Cp and ethyl groups of the known complex $CpRu(PPh_3)_2SiEt_3$[65] (**19**) at δ 4.53, 1.19 and 1.31. Furthermore, $CpRu(PPh_3)(SiEt_3)_2H$ (**20**) provided a hydride resonance at δ −11.89 that coupled to a single ^{31}P centre with J_{PH} = 9.7 Hz. Upon prolonged UV photolysis of this solution, $CpRu(PPh_3)_2H$ was formed and found to increase in concentration until after 4 hours it became dominant.

Photochemical reaction of 2 with $HSiEt_3$ at 198 K

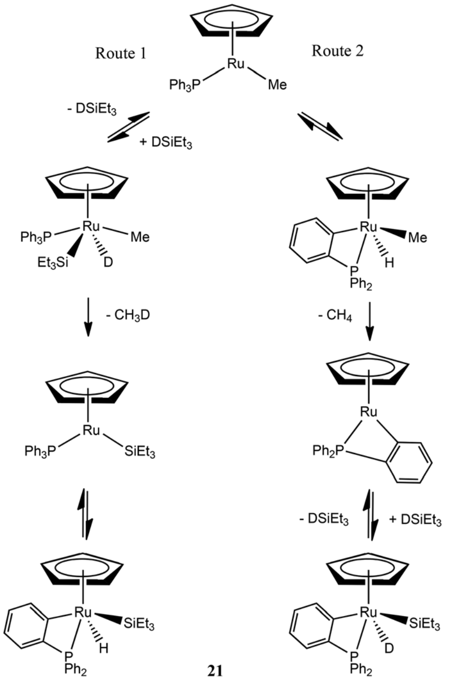
The reaction between **2** and $HSiEt_3$ was then initiated by *in situ* laser irradiation in d_8-THF at 198 K. The resulting $^{31}P\{^1H\}$ NMR spectrum now clearly showed the presence of a new species (**21**) which yields a singlet at δ −16.2. A ^1H–^{31}P HMQC experiment connected this resonance to further proton signals at δ 7.07, 7.37, 7.74, 7.55, 7.62, 7.74, 8.09, 4.82 and δ −9.13 (d, 23.0 Hz). The δ 4.78 signal is characteristic of a cyclopentadienyl ring while those at δ 7.09, 7.07 and 7.01 are due to *ortho*, *meta* and *para* protons of a phenyl ring. The remaining four signals, at δ 7.55, 7.62, 7.74, 7.18, were also observed to couple in a ^1H–^1H COSY experiment and are characteristic of those in an *ortho*metallated ring of triphenylphosphine. This is confirmed by the fact the δ −16.2 ^{31}P signal of **21** is similar in position to that of *ortho*metallated **3** which was seen at δ −16.9. As the δ −9.13 hydride signal of **21** appears as a doublet, where J_{PH} = 23.0 Hz, it is which established as a mono-phosphine complex.

Connections between the cyclopentadienyl ^1H resonance of **21** and signals at δ 0.38, 0.54 and 0.81 in a 2D NOE experiment were observed. The protons giving rise to three peaks were shown to couple and hence they are attributed to CH_2 (δ 0.38 and 0.54) and CH_3 (δ 0.81) groups in a ruthenium-bound triethylsilyl ligand; the two CH_2 protons couple to a single carbon resonance at δ 13.8. **21** is therefore identified as $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(SiEt_3)H$ and upon warming it decomposes to form an array of products including those described earlier.

Deuterotriethylsilane ($DSiEt_3$) was then employed to confirm how **21** forms. With $DSiEt_3$, while signals for **21** were seen, no hydride signal was visible at δ −9.13 in the corresponding ^1H NMR spectrum. This suggests that **21** possesses a RuD group and that the *ortho*metallation step, which yields a RuH, must precede SiD bond activation. This sequence is illustrated in Scheme 4.

Photochemical reaction of 2 with dimethylvinylsilane

A reaction with dimethylvinylsilane was also examined. Low temperature *in situ* irradiation led to the formation of both $CpRu(PPh_3)(\eta^3\text{-}Si(Me)_2\text{–}CH{=}CH_2)$ (**22**) and $CpRu(PPh_3)_2(Si(Me)_2\text{–}CH{=}CH_2)$ (**23**). The reactions progress was again tracked using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. ESI Fig. 3† shows how the proportion of these species varies with photolysis time. Such reactivity is expected.[66]

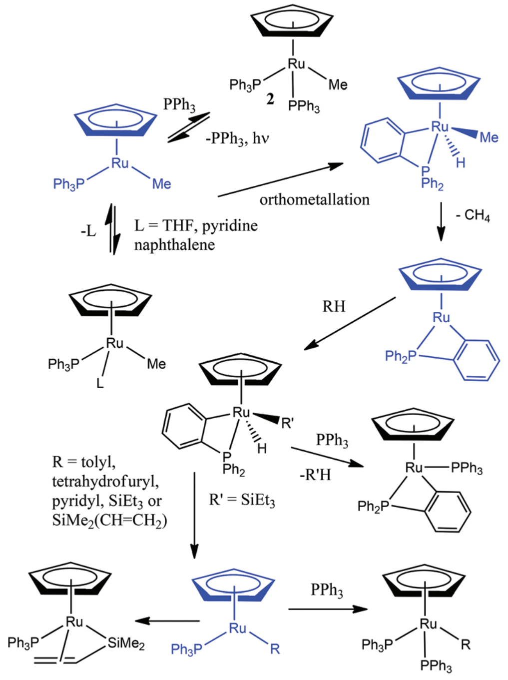


Scheme 4 Reaction pathways for the formation of the *ortho*metallation product **21**. Deuterium labelling indicates $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(SiEt_3)D$ is formed *via* route 2.

Conclusions

The reactivity of **1** and **2** towards PEt_3, ethene and DMSO has been examined. Thermally, for the reaction with PEt_3, the bis-substituted products $CpRu(PEt_3)_2Cl$ (**4**) and $CpRu(PEt_3)_2Me$ (**7**) are readily formed *via* their mono-substituted counterparts $CpRu(PPh_3)(PEt_3)Cl$ (**5**) and $CpRu(PPh_3)(PEt_3)Me$ (**8**). In contrast, under broad-band UV irradiation, **1** and **2** react to selectively produce **5** and **8**. This conversion can be achieved with 325 nm irradiation for **2** but not **1**. This suggests that the first reaction step in this sequence is the loss of phosphine, to form the corresponding 16-electron intermediate, which is trapped by PEt_3, or DSMO. When ethane is used and the reaction examined at low temperature, $CpRu(PPh_3)(C_2H_4)Cl$ (**6**) and $CpRu(PPh_3)(C_2H_4)Me$ (**10**) are readily formed in a similar process. Under these conditions, no evidence for CH bond activation of the alkene was seen, and upon warming the reformation of **1** and **2**, respectively, was observed.

In contrast, when **1** was irradiated in C_6D_{12} with no added ligand no reaction was found. Under the same conditions, **2** was observed to undergo a reaction where the activation of a C–H bond of the phosphine led ultimately to the known complex $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)$ (**3**).[10,12] This suggests that the implicated 16-electron intermediate $CpRu(PPh_3)Me$ is able to react with an internal CH bond as there is no suitable trapping ligand present to form $CpRu(\kappa^2\text{-}2\text{-}C_6H_4PPh_2)(Me)(H)$.



Scheme 5 Reaction mechanism as revealed through low temperature photochemical studies on **2**. Species in blue are not detected but inferred from the observed reaction products.

Subsequently MeH elimination and phosphine recoordination to what is CpRu(κ^2-2-$C_6H_4PPh_2$) are expected to lead to **3**.

In contrast, when the UV irradiation of **2** is completed in THF at low temperature, the proposed 16-electron intermediate is trapped as **11**. The THF-activation product CpRu(PPh_3)$_2$-(2-C_4H_7O) (**12**) is also observed in this reaction and **3** is not seen. Based on these observations it would appear that the reaction of CpRu(PPh_3)Me with the solvent is faster than the rate of intra-molecular CH bond activation. The formation of **12** could, however, proceed *via* either CpRu(PPh_3)Me or CpRu-(κ^2-2-$C_6H_4PPh_2$) as neither CpRu(κ^2-2-$C_6H_4PPh_2$)(D)(2-C_4H_7O) nor CpRu(PPh_3)Me(D)(2-C_4H_7O) are observed; Lehmkuhl's thermally initiated deuterium labelling studies would suggest CpRu(κ^2-2-$C_6H_4PPh_2$)(D)(2-C_4H_7O) is involved.[13] The ability of the solvent to compete with the CH bond activation step is further supported by the fact that when pyridine is employed as the incoming ligand, the selective formation of **13** is observed at low temperature. Upon warming the pyridyl complex CpRu-(PPh_3)$_2$(2-C_5H_4N) (**14**) was formed and no **3** was evident.

In order to probe for a RuH species directly in these reactions, toluene and a THF–naphthalene mixture were examined. While we observed no evidence for η^2 coordination of the arene in the case of toluene, the C–H bond activation products **15**, **16** and **17** were detected. CH bond activation was therefore evident without the detection of either CpRu(κ^2-2-$C_6H_4PPh_2$)-(D)(tolyl) or CpRu(PPh_3)Me(D)(tolyl). In contrast, with naphthalene, trapping did result in the detection of two η^2-arene containing complexes (**18a** & **18b**) but upon warming decomposition resulted and no characterisable ruthenium species were produced.

The reaction of **2** with $HSiEt_3$ did however enable the low temperature detection of a hydride containing *ortho*metallated product in the form of CpRu(κ^2-2-$C_6H_4PPh_2$)($SiEt_3$)H (**21**). Studies with $DSiEt_3$ suggest that the elusive species CpRu(κ^2-2-$C_6H_4PPh_2$)(Me)H rapidly eliminates MeH before adding $HSiEt_3$ to 16-electron CpRu(κ^2-2-$C_6H_4PPh_2$) because CpRu(κ^2-2-$C_6H_4PPh_2$)($SiEt_3$)D and not CpRu(κ^2-2-$C_6H_4PPh_2$)($SiEt_3$)H is formed. Furthermore, upon monitoring the analogous reaction of **2** with HSi(Me_2)CH=CH_2), the production of a 2 : 1 mixture of CpRu(PPh_3)(η^3-Si(Me_2)CH=CH_2) (**22**) and CpRu(PPh_3)$_2$-(Si(Me_2)CH=CH_2) (**23**) was achieved. This is consistent with the suggestion that CpRu(κ^2-2-$C_6H_4PPh_2$) is indeed involved in these reactions, as CpRu(κ^2-2-$C_6H_4PPh_2$)(Si(Me_2)CH=CH_2)H can readily form both **22** or **23**. These observations are summarised in Scheme 5 and add to the earlier findings of Stone and Lehmkuhl.[4,12,13]

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