**Contrasting Photochemical and Thermal Catalysis by Ruthenium Arsine Complexes Revealed by Parahydrogen Enhanced NMR Spectroscopy**

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Dedication to celebrate the 65th birthday of Professor Rinaldo Poli

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**Abstract:** The thermal and photochemical reactivity of Ru(CO)3(dpae) (**1**) and Ru(CO)2(dpae)(PPh3) (**2**) towards H2 and diphenylacetylene is described. These reactions are monitored by NMR spectroscopy in conjunction with the *para*hydrogen induced polarisation (PHIP) effect, spatially resolved chemical shift imaging and the Only Parahydrogen Spectroscopy (OPSY) signal filtering method. The results are supported by DFT. The thermal and photochemical reactions of **1** with H2 proceed by CO loss and form Ru(H)2(CO)2(dpae) (**3**). **1** catalyses the formation of 1,2 diphenylethane, *cis*- and *trans*-stilbene, and 1,2,3,4 tetraphenylbutadiene under 325 nm irradiation at 295 K in a reaction where Ru(CO)2(dpae)(2-CHPh=CPhCPh=CHPh) forms. When the same reaction is monitored under thermal conditions at 333 K the 2-diene complex is no longer detected but hydride containing Ru(CHPhCH2Ph)(H)(CO)2(dpae) and Ru(CO)2(dpae)(*trans*-stilbene) are seen. For **1**, the photochemical promotion of hydrogenation through 325 nm irradiation results in an approximate 5.5-fold increase in turnover at 333 K when compared to no irradiation. In contrast, **2** reacts thermally with H2 at 295 K through PPh3 and CO loss with both Ru(H)2(CO)(dpae)(solvent) and **3** being detected. Under irradiation, CO loss dominates and two isomers of Ru(H)2(CO)(dpae)(PPh3) form. While **2** forms the same 4 organic products at 295 K and a second isomer of Ru(CHPhCH2Ph)(H)(CO)2(dpae) alongside the diene complex no photochemical promotion of hydrogenation is observed.

**Introduction**

Transition metal complexes containing phosphine ligands have been widely employed as homogeneous catalysts1 for transformations such as alkene2-4 and alkyne5, 6 hydrogenation, hydroformylation, isomerisation and polymerisation. The use of multidentate phosphines as auxiliary ligands has attracted particular attention because of their ability to introduce both regio- and stereo-selectivity7-9 with longer catalyst lifetimes resulting from suppressed ligand dissociation as a result of the chelate effect.10

The properties of chelating ligands have been used extensively to improve catalytic control.11-16 Not surprisingly, they also impact on photochemical reactions such as those of ruthenium dihydride phosphine complexes. Thus Ru(H)2(P(CH2CH2PPh2)3) undergoes photochemical loss of dihydrogen and the resulting intermediate reacts rapidly with benzene to form an aryl hydride product.17 However, no evidence for C–H bond activation is seen when the ligand is changed to PPh2CH2CH2PPh218 despite the retention of the phenyl groups and the ethane ligand backbone. Additionally, when such complexes contain phosphines like PMe3­ they exhibit two distinct photochemical pathways, one involving H2 loss and the other, phosphine loss, with the reaction’s selectivity depending on the identity of the phosphine.11 Since the resulting Ru(II) intermediates can bind small molecules such as H2, C2H4, CO and HSiEt3, such systems can contribute usefully to catalysis.19-21 Berry *et al.* have shown how photochemical loss of PMe3 from Ru (H)(SiMe3)(PMe3)4 yields a 16 electron species, Ru(H)(SiMe3)(PMe3)3, that is capable of HH, SiH, CH and SiC bond activations, and established that alkyl hydride complexes can be detected in the reaction chemistry of such complexes.22 Replacing the phosphine in such ruthenium complexes by an N-heterocyclic carbene expands the range of reactions that complexes of this type can undergo.23-25 Photolysis of an NMR sample within an NMR spectrometer has become an established method to study photochemical reactions.26-33 We have reported a number of such investigations dealing with the photochemically induced addition of dihydrogen to complexes of the type Ru(CO)3(L)2, where L = PPh3, PMe3, PCy3, P(*p*-tolyl)3 and AsPh3, as well as studies on alkyne hydrogenation.34-36 The photochemical reaction of these tricarbonyl containing systems with hydrogen proceeds *via* the two competing pathways shown in Scheme 1 for L = PPh3. The first of these involves the loss of CO, followed by preferential H2 addition across the more π-accepting OC-Ru-CO axis of the resulting 16-electron intermediate to form the *cis*-*cis*-*trans*-L isomer of Ru(H)2(CO)2(L)2. In the second pathway, photochemical loss of both CO and L leads to the formation of an undetected 14-electron Ru(CO)2(PPh3) fragment which reacts further to form *cis*-*cis*-*cis* Ru(H)2(CO)2(L)2 or Ru(H)2(CO)2(L)(solvent) where toluene, THF or pyridine act as the solvent. In the case of L = PPh3, the *cis*-*cis*-*trans-*L product Ru(H)2(CO)2(L)2 has been shown to be an effective hydrogenation catalyst at elevated temperatures, with catalysis occurring *via* phosphine loss, although no reaction intermediates were seen.37

**Scheme 1** Reported photochemical and thermal reaction pathways for the reaction of Ru(CO)3(PPh3)2 with H2.37

These previous studies serve as a backdrop to the present work, which explores the effect that substitution of arsenic in place of phosphorus in the chelating ligand has on the activity of such complexes as alkyne hydrogenation catalysts. Previous comparisons of ruthenium phosphorus and arsine complexes have seen differences in catalytic activity.38-41 In the present work, we have employed *para*hydrogen induced polarization (PHIP)42,43, 44 in conjunction with NMR spectroscopy in a mechanistic study of thermal and *in-situ* photochemical alkyne hydrogenation in the related Ru(0) systems containing a bis-arsine ligand: Ru(CO)3(dpae) and Ru(CO)2(dpae)(PPh3) (where dpae = Ph2AsCH2CH2AsPh2) – see Scheme 2. The use of *para*hydrogen(*p*-H2) in PHIP is a relatively well-established tool in mechanistic chemistry,45 allowing low-concentration products, such as reaction intermediates, to be detected *via* enhanced NMR signals for nuclei that either originate in the *p*-H2 or can be detected *via* magnetization transfer. When combined with *in-situ* laser flash photolysis, product hydride resonances have been enhanced in intensity by a factor of nearly 30,000.46 *In-situ* photolysis47 has also been used to explore the evolution of NMR coherences that become accessible *via* *p*-H2 addition to a metal complex48, 49 with a view to harnessing these approaches to study fast reactions.49, 50 Thermally activated PHIP approaches have yielded information on the catalytic role of a number of mono-,51, 52 di-53, 54 and tri-nuclear55 transition metal species. Other achievements in this field include the sensitization of hydroformylation products56 as well as demonstrations that key species in cobalt- and iridium-catalysed hydroformylation processes can be detected.57 The transfer of polarization *via* a 13C nucleus to deuterium after the hydrogenation of a perdeuterated substrate,58 the investigation of *ortho*-*para* hydrogen interconversions and the study of hydrogen isotope scrambling have also been studied.59 Several palladium alkyl and vinyl complexes that play a direct role in alkyne hydrogenation have also been detected and studied using this approach.60, 61 Studies of heterogeneous reactions, hydrodesulphurisation and the signal amplification by reversible exchange process (SABRE) reflect further recent developments in this area.62-67

Due to their very short lifetime, this *in-situ* photochemical approach will not detect the predicted 16-electron reaction intermediates Ru(CO)2(dpae) and Ru(CO)(dpae)(PPh3) themselves, but it should enable the detection of any longer-lived reaction products that form with *p*-H2. Furthermore, as the Only Parahydrogen Spectroscopy (OPSY) method distinguishes between hydrogen atoms originating from *p*-H2 and those from other sources, it might be expected that adding such a filter will enable the detection of these reaction intermediates even if the underlying signal intensities are comparable to those of the background response.68, 69 Additionally, the equipment used in the *in situ* irradiation study allows spatially resolved reaction mapping which we harness here to differentiate between thermal and photochemical reaction pathways.70 It is with these goals in mind that we now describe our results. The NMR-silent nature of arsine as one of the ligating centres presents some challenges in making unambiguous product assignments and to this end, the present work will be supported by density functional theory calculations. DFT-supported assignment is well-established in the field and has been shown to provide considerable additional insight in studies of metal complex reactivity.71-74

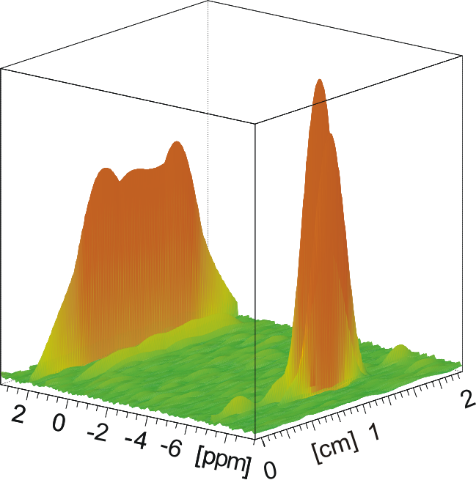
Results and Discussion

The compounds Ru(CO)3(dpae), **1,** and Ru(CO)2(dpae)(PPh3), **2**, used in this work were prepared and purified as described in the experimental section and Supporting Information.

**Reactivity of Ru(CO)3(dpae), 1, with *p*-H2**

**Thermal reactivity of 1 with *p*-H2**

Upon addition of *p-*H2 to a benzene-*d*6 solution of **1**, and warming to 308 K, the formation of **3** (Ru(H)2(CO)2(dpae))75 (Scheme 2) became evident through the observation of two *p*-H2 enhanced hydride resonances in the corresponding 1H NMR spectrum. These resonances appear as simple antiphase doublets at  –7.21 and –7.61, where JHH = –5 Hz. The  –7.21 signal arises from a hydride ligand that is *trans* to As while the  –7.61 signal arises from a hydride ligand that is *trans* to CO. Upon warming this sample to 348 K, the only hydride signals that are visible correspond to those of **3** and are now dramatically enhanced. The full characterization of **3** is described in the ESI and key NMR data is presented in Table S1.



**Scheme 2** Summary of the reaction pathways exhibited by **1** and **2** towards H2 based on data recorded between 298 K and 333 K. The species presented in the square brackets represent unseen reaction intermediates. The hydride chemical shifts for the products are indicated.

Repeating this experiment in the presence of CO and *p*-H2 led to a dramatic reduction in the size of the hydride signals for **3** thereby indicating its formation from **1** occursby CO loss, rather than through a more complex route involving the initial dissociation of one arm of the dpae ligand. The structure of **3** and route to its formation are illustrated pictorially in Scheme 2. The NMR signals for **3** are observable by normal NMR methods after the depletion of the *p*-H2 enhancement and/or venting of the H2 atmosphere, thereby confirming it to be a stable reaction product under these conditions.

**Photochemical reactivity 1 with *p*-H2**

It has previously been shown that low temperature irradiation of a solution of Ru(CO)3(PPh3)2 in toluene in the presence of *p*-H2 results not only in the formation of the CO loss product Ru(H)2(CO)2(PPh3)2 but also in the detection of Ru(H)2(CO)2(PPh3)(2-toluene).37 The generation of the latter species is quenched by addition of PPh3.

When a *p*-H2-containing sample of **1** in toluene-*d*8 is subject to concurrent UV laser irradiation at 325 nm and NMR monitoring at temperatures below 263 K no reaction products are detected. However, at temperatures of 263 K and higher, the photo-induced formation of **3** under 325 nm irradiation is indicated by the observation of enhanced hydride NMR signals relative to any baseline thermal reactivity at these temperatures.

The photochemical nature of this reaction was confirmed from the spatially resolved hydride signal intensity *versus* chemical shift plot recorded during the *in-situ* monitoring of this reaction. The irradiation cross-sectional volume, as defined by the laser beam profile, is much smaller than the total volume of sample present in the tube. As a result of this, the hydride resonances that are seen for **3** onlyappear with substantial intensity in the region of the NMR tube that is centred on the point of laser irradiation. This is illustrated in Figure 1 where the reference peak, at  1.9, is due to the protons of the ethane backbone of the dpae ligand of **1**. The length scale illustrated in this plot corresponds to displacement from the bottom of the NMR tube and the signal intensity profile mimics that of the NMR coil response. This control signal provides a roughly constant response across the active NMR sample length. However, when the hydride signals of **3** are examined, peaks can be seen along this axis at the intersection with their chemical shift that are centred on the irradiation point. Given that there are no analogous hydride peaks present outside this region, the result demonstrates the photochemical nature of this reaction.

**Figure 1** Spatially resolved 1H chemical shift image (ppm and cm from bottom of sample) for a sample of **1** in C6D6 in the presence of *p*-H2 with concurrent 325 nm laser irradiation orthogonal to the axis of the NMR tube at 295 K showing the enhanced hydride resonances that are seen for **3**. The ethane bridge protons of dominant **1** are also shown to illustrate the signal response that results across the whole length of the NMR tube. It is clear that the hydride signals for **3** appearonlyin the irradiated region of the sample at 298 K.

When this reaction is monitored at 333 K instead of 298 K, thermal reaction of **1** contributes additionally to the formation of **3**. This change is seen in the corresponding thermal control and irradiation images which detail the sum of the signal intensities for the two hydride peaks of **3** as a function of displacement from the bottom of the NMR coil. There is a difference in NMR signal intensity with vertical displacement between the two data sets that confirms **3** forms through both thermal and photochemical steps at this temperature. Assuming that the relative intensities of these peaks scale linearly with the amount of **3**, the photochemical pathway is deduced to be favoured by a factor of 3.4 over the thermal contribution.

**Probing the dynamic behaviour of the hydride ligands in 3**

A series of exchange spectroscopy measurements (EXSY) were made to probe the hydride ligand dynamics exhibited by **3** at temperatures between 305 and 350 K. At 305 K, a visible nOe connection between the two hydride resonances confirms a *cis* arrangement and suggests little if any thermal exchange. However, at higher temperatures, the two hydride peaks connect by a positive signal that indicates hydride ligand site interchange. Fitting yielded the rates listed in Table S3. No evidence for the reductive elimination of H2 from **3** was seen in these experiments,although repeating them at 320 K in the presence of 0.5 atm of CO, saw a reduction in the hydride site interchange rate from 1.64 s–1 to 0.65 s–1. This suggests that thermally-initiated hydride site interchange proceeds *via* CO dissociation, and thereby reveals a route by which **3** could become involved in catalysis. The activation parameters, H‡ and S‡, for this process are 94 ± 6 kJ mol–1 and 55 ± 20 J K–1 mol–1, respectively. The thermal reaction leading to the PHIP-enhanced detection of **3** is shown in Scheme 2 as the result of CO loss from **1**.

**Reactivity of Ru(CO)2(dpae)(PPh3), 2, with *p*-H2**

**Thermal reactivity of 2 with *p*-H2**

The analogous thermally-initiated reaction of **2** with *p*-H2 was first studied in C6D6 solution. This reaction also yielded the phosphine loss product **3** as the major product, but does so *via* a quite different route than **1**. At 295 K, weakly polarized NMR signals for the hydride ligands of what we propose are solvent-stabilised *cis-cis*-Ru(H)2(2-benzene)(CO)(dpae), **4a**, are observed at  –3.48 and –5.39 (with a mutual JHH coupling of –3.5 Hz). We have reported previously that Ru(H)2(CO)2(PPh3)(2-toluene) exhibits hydride resonances, at  –2.95 and –4.91, while those for Ru(H)2(CO)2(PPh3)(THF) appear at  –3.66 and –5.26.37 As expected, repeating this reaction with *p*-H2 in THF-*d*8, **2** yields hydride ligand signals which now appear at  –3.90 and –6.21 and that can be assigned to THF adduct *cis-cis*-Ru(H)2(CO)(dpae)(THF), **4b**. These assignments are based on the chemical shift similarities between these species. **4** therefore represents the preferred low-temperature H2-addition product, produced by phosphine and CO loss from **2**. **3**, which is readily detected at higher temperature, forms from **4** *via* the replacement of the weakly binding solvent by CO.

When the analogous reaction is completed in toluene at 353 K, the minor complexes, *cis-cis*-Ru(H)2(CO)2(1-dpae)(PPh3) **5** andRu(H)2(CO)(1-dpae)2(PPh3) **6** form as evidenced by the observation of their weak hydride ligand signals. The former product signals appear at  –7.0 while the hydride signals for **6** appear at –6.55 (JPH = 26 Hz) and  –8.47 (JPH = 30 Hz, see Supporting Information). These species are not discussed further.

It is worth noting that, regardless of the choice of solvent, the addition of PPh3 to the corresponding solution results in the detection of Ru(H)2(CO)2(PPh3)2 and **3**, with the signals for **4, 5** and **6** being suppressed.This confirms thatdisplacement of the dpae ligand in **2** is possible at elevated temperatures when the reaction with H2 is completed in the presence of a suitable 2-electron donor.

**Photochemical reactivity of 2 with *p*-H2**

The reaction of **2** with *p*-H2 was then monitored by NMR spectroscopy with concurrent 325 nm irradiation. At temperatures above 263 K four enhanced hydride ligand signals appear as shown in Figure 2 which are attributed to isomers **7a** and **7b** ofScheme 2. Thetwo sets of antiphase doublets of doublets at  –7.52 and –8.22 exhibit *cis* phosphorus couplings (21 and 24 Hz, respectively) to a nucleus that resonates at  66.2 in the corresponding HMQC experiment thereby confirming that the species responsible for these resonances contains a PPh3 group. Minor product, **7b** gives rise to the weaker hydride resonances at  –7.74 and –9.13 and now the phosphorus centre resonates at  49.8. The magnitudes of the 2JHP couplings for **7b** were, 17 and 66 Hz, respectively, and indicate that the higher field hydride resonance arises from a ligand *trans* to 31P. As the production of both **7a** and **7b** are quenched by the addition of CO, it is likely that CO loss rather than arsine dechelation leads to these photoproducts (see Table S3).

**Figure 2** Hydride region of a 1H NMR spectrum of **2** in C6D6 recorded in the presence of *p*-H2 with concurrent UV laser photolysis at 295 K. Enhanced hydride resonances for **7a** and **7b** are indicated.

The products **7a**:**7b** form in an 11:1 ratio if the NMR signals of both are assumed to exhibit identical overall PHIP signal enhancement levels. This ratio proved invariant to reaction time, sample concentration and the temperature at which photolysis took place. These data indicate that both form directly from **2** *via* the common 16-electron fragment Ru(CO)(dpae)(PPh3). While **7a** can be seen by normal NMR methods after the depletion of the *p*-H2 enhancement and/or venting of the H2 atmosphere, **7b** was no longer detected.We therefore conclude that **7a** is both the kinetic and thermodynamic product of H2-addition to Ru(CO)(dpae)(PPh3). This agrees with the predicted preference for H2 addition across the most -accepting axis of Ru(CO)(dpae)(PPh3) of Scheme 2 (see the Supporting Information for DFT-derived stability data).

Hence photochemically, CO loss dominates from **2**.In fact,no additional hydride signals were detected when the photolysis was performed at temperatures up to 315 K. However, hydride signals for **3** were, readily detected at temperatures above this due to competitive thermal loss of PPh3 from **2**. The NMR hydride signal intensity profiles for **3** and **7a** resulting from the reaction of a sample starting as **2** with hydrogen, with and without irradiation at 333 K were determined. The ratio of thermal to photochemical signal intensities of **3** under these conditions is 1:51. These data reveal therefore that **2** is far more photochemically active under 325 nm irradiation than **1**.

**Probing the dynamic behaviour of the hydride ligands in 7a**

The only dynamic process that could be observed in EXSY experiments that targeted **7a** over the temperature range 280-350 K proved to be H2 reductive elimination for which H‡ and S‡ were determined to be 109 ± 12 kJ mol–1 and 65 ± 34 J K–1 mol–1, as listed in Table S3. These values are consistent with a dissociative reaction pathway.

**Catalytic Activity to Alkyne Hydrogenation**

**Thermally initiated alkyne hydrogenation by 1**

In order to investigate the alkyne hydrogenation activity of these systems, samples of **1** were prepared in toluene-*d*8 containing a 100-fold excess of Ph-C≡C-Ph under a 3 bar atmosphere of *p*-H2. This substrate was used to remove the possibility of terminal-internal alkene isomerisation. These samples were then slowly heated to 363 K while being monitored by NMR spectroscopy. Polarized hydride resonances for **3** begin to appear at 315 K with further weak PHIP-enhanced resonances attributable to the hydrogenation product *cis*-stilbene emerging at 335 K. GCMS analysis of the reaction mixture at this point revealed the formation of both *cis-* and *trans-*stilbene as well as 1,2-diphenylethane, the double hydrogenation product. As a result, it was decided to monitor this reaction using the OPSY protocol which employs magnetic field gradients to distinguish hydrogen atoms originally in *p*-H2 from those in other species. These OPSY measurements contained signals for *cis-* and *trans-*stilbene as well as 1,2-diphenylethane in agreement with the results of the GCMS analysis.

Repeating these OPSY measurements at 343 K increased the intensity of the hydrogenation product signals, with two additional signals appearing at  2.88 and  2.64. These PHIP-enhanced resonances appear as doublets that share a common splitting of +15.3 Hz. Additionally, when Ph-13C≡C-Ph is employed as the substrate, the  2.64 signal connects with a 13C resonance at  37.1 while that at  2.88 connects to a second 13C signal at  38.5. These chemical shifts are characteristic of those in a Ru(alkene) complex,76 and the associated JHH value suggests that the two inequivalent alkene protons are arranged in a *trans* fashion. EXSY methods confirmed that these two proton sites interconvert on the NMR timescale which indicates fluxional behaviour in the species Ru(CO)2(dpae)(*trans*-stilbene) (**8**) that interconverts the protons responsible for the two inequivalent resonances.The JHC value of 132 Hz that was determined for the  2.64 1H signal is smaller than that for free alkene (154 Hz) and suggests a degree of sp3 character in the bonding which requires a metal centre capable of substantial transfer of electron density into the bound alkene \* orbital. Product **8** isillustrated in Scheme 3.



**Scheme 3** Reaction intermediates detected when **1** reacts thermally with H2 and PhC≡CPh, with key 1H resonances indicated.

When the same sample is warmed still further to 353 K, four additional PHIP-enhanced proton signals appear at

 –6.26 (position temperature sensitive), 3.98, 4.04 and 4.26 as shown in Figure 3a, alongside those of **8**. The resulting COSY measurement confirms that all of these signals arise from the same species, which we identify as the alkyl-hydride Ru(CHPhCH2Ph)H(CO)2(dpae) (**9a**) of Scheme 3. Notably, the  4.04 signal of **9a** couples to the hydride ligand resonance through a +2.8 Hz splitting in accord with a three bond connection.77 This contrasts with the hydride signals seen for the dihydride complexes that have been already described which appear in emission-absorption because of their negative two-bond HH spin-spin couplings.The presence of the alkyl arm in **9a** was further confirmed through the use of the 13C labelled substrate, which allowed the  4.04 resonance to be connected to a carbon resonance at  26.8, while the  3.98 and 4.26 signals connect to a common carbon signal at  52.6. On the basis of a comparison of the hydride chemical shift of **9a** with those of **3**-**7** and the later DFT data we conclude that its hydride ligand is *trans* to arsenic and thereby suggest the structure shown in Scheme 3**.** The PHIP enhanced nature of these four signals requires reversible hydrogen exchange to take place in the alkyl intermediate in order for the hydride to appear as a weak antiphase signal; the RuCHPh proton and the hydride must come from the same molecule of *p*-H2. The hydride signal appears weakly in the corresponding OPSY measurement, while the alkyl signals themselves are readily visible and hence the level of associated exchange is low.

Magnetization transfer from **9a** into free *cis*-stilbene was observed in the corresponding EXSY spectra at 358 K thereby confirming that this complex plays a direct role in alkyne hydrogenation (Figure 3b) in a process that presumably requires CO loss. In support of this, we note the related complexes Ru(R)(H)(CO)2(L)2 (where L = PMe2Ph or PMe3 and R = Ph or Et) slowly eliminate ethane and benzene at 295 K.78,79,80

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**Figure 3.**  Selected regions of a series of PHIP enhanced 1H NMR spectra obtained for reactions undertaken in the presence of Ph-C≡C-Ph-d10 and *p*-H2 in toluene-d8. (a) for **1** at 353 K using the OPSY filtering method (b) Selective excitation EXSY measurement at 353 K to establish that **9a**,formed from **1**,leads to *cis*-stilbene. (c) analogous OPSY spectrum for **2** nowat 308 K (signals for 3 not in this region)

**Thermally initiated alkyne hydrogenation by 2**

When a sample of **2** in toluene-*d*8 containing a 100-fold excess of Ph-C≡C-Ph under a 3 bar atmosphere of *p*-H2 was monitored at 295 K by 1H NMR spectroscopy, a quite different reactivity to that observed under thermal conditions, was observed as five polarized resonances for two new inorganic products were evident in the 0 and 10 ppm region of the corresponding 1H NMR spectrum, in addition to a simple antiphase doublet at  -11.34 which did not couple to 31P.

The most significant of these signals appear at  6.26 and 1.38 exhibit a mutual JHH coupling of 8 Hz. These resonances were subsequently attributed to due to Ha and Hb of **c**omplex **10** (Ru(CO)2(dpae)(2-CHPh=CPhCPh=CHPh)) (Scheme 4) following analogous study of the alkyne hydrogenation under photolysis by **1**, described in section 2.3.3.

The three remaining alkyl-type signals appear at  4.19, 4.06 and 3.18 and couple together. Furthermore, the hydride resonance at  -11.34 couples to the  3.18 signal according to COSY spectroscopy (JHH = + 5.6 Hz) and hence they logically arise from a second isomer of **9a**. The alkyl ligand of this isomer is predicted to lie *trans* to arsenic rather than CO (**9b**), with the hydride *trans* to CO as illustrated in Scheme 4 (see DFT section). This difference is consistent with the change in hydride ligand chemical shift.



**Scheme 4** Reaction intermediates detected when **2** reacts thermally with H2 and PhC≡CPh at 295 K; key 1H resonances are indicated.

When the temperature was raised to 308 K, the 1H NMR signals for both **9b** and **10** increased in intensity but additional signals for **3** appear. These signals were again most readily detected in the corresponding OPSY 1H NMR spectrum as shown in Figure 3c. However, upon warming further to 318 K the signals for **10** and **9b** become significantly weaker while those for **3** drastically increase in size with signals for Ru(H)2(CO)2(PPh3)2, **5** and **7a** also become visible. At 328 K, the signals for **3** and Ru(H)2(CO)2(PPh3)2 now dominate the hydride region of the resulting NMR spectra with *cis*-stilbene signals dominating the organic region. When the temperature reaches 338 K, signals for **8** appear at  2.88 and 2.64,with those of *cis* and *trans-*stilbene becoming clearly visible in the corresponding OPSY NMR experiment. At 368 K signals for metal complexes **8** and **9a** are again seen but those for **3** stilldominate. Hence, we conclude that warming changes the rate of hydrogen turnover, thereby providing insight into the mechanism of this process. Further justification for these deductions will be given below.

**Photochemically-initiated alkyne hydrogenation by 1**

When samples containing **1** and a 100-fold excess of diphenylacetylene were first photolysed at 295 K in the presence of *p*-H2 the two hydride resonances for **3** were readily detected alongside signals for **10** at  6.40 (Ha) and 1.56 (Hb). Both of these signals appear as simple antiphase doublets whose absorption/emission profile reflects mutual JHH couplings of +8 Hz. This behaviour suggests there is an odd number of bonds between the two coupled resonances. These resonances are also visible in the corresponding double quantum filtered OPSY experiment. Hence they must arise from two hydrogen atoms previously located in a single *p*-H2 molecule. These resonances appear with different intensities due to their line widths of 3.3 Hz and 6.3 Hz which result in different degrees of cancellation due to their antiphase signal profile.

When Ph-13C≡C-Ph-d10 is used as the substrate, these enhanced proton resonances proved to couple to two different 13C centres. Specifically, HMQC spectroscopy shows that proton **10**-Ha couples directly to a 13C atom which resonates at  64.2 that exhibits a JHC coupling of 178 Hz while proton **10**-Hb couples directly to a 13C centre that appears at  45.0 with a JHC coupling of 144 Hz. A typical NMR spectrum is presented in Figure S1.

GCMS analysis of the solution at this stage reveals the formation of 1,2,3,4-tetraphenylbutadiene in addition to *cis* and *trans* stilbene and 1,2-diphenylethane. On this basis, the identity of **10** is deduced to be the 18-electron coupling product Ru(CO)2(dpae)(2-CHPh=CPhCPh=CHPh). The measured CH couplings support bound and free alkene moieties as their values are indicative of sp2 and sp3 character, respectively.

Chemical shift imaging at 333 K shows a 5.5-fold increase in hydrogenation turnover under irradiation (Figure 4). The analogous ratio of the relative strengths of the hydride signals for **3** under photochemical and thermal conditions was however reduced to 0.8:1 from the 3.4:1 value found in the absence of substrate. We interpret this as confirmation that photolysis of **1** leads to productive catalysis as **3** no longer forms as efficiently, with H2 instead being transferred into these organic products.

**Figure 4** Normalised spatially resolved profile showing the total intensity of the 1H NMR signals seen for *cis* and *trans* stilbene as a function of relative distance from the bottom of the NMR tube during their formation at 333 K through hydrogenation catalysed by precatalyst **1** in the presence and absence of 325 nm irradiation. This plot illustrates the higher hydrogenation efficiency of **1** under irradiation.

It should be noted that the tetraphenylbutadiene product only forms at low temperatures. This suggests that the 16-electron product Ru(CPh=CPhH)(H)(CO)(dpae) formed by hydride insertion into Ru(H)2(CPh≡CPh)(CO)(dpae) is only then effectively trapped by Ph-C≡C-Ph; an increased intermediate lifetime could enable the binding of Ph-C≡C-Ph to compete with C-H bond formation. This requirement is consistent with the photochemical and thermal pathways yielding different products. Furthermore, in the corresponding OPSY experiments, the formation of *cis*-stilbene is shown to be favoured over *trans*-stilbene in the early stages of the reaction, at which point the 1,2-diphenylethane signals are weak but they then strengthen as the proportion of free alkene in solution increases during the reaction.

A series of NMR experiments were completed to identify the reaction pathway leading to **10**. Firstly, a sample of **1** that had been exposed to UV irradiation for 1 hr to preform **3** was examined. OPSY monitoring of this sample revealed very limited photochemical activity under 325 nm irradiation, which suggests that there is limited, if any, contribution of **3** to the formation of **10** under 325 nm irradiation. In addition, irradiation of **1** in the presence of the alkyne, CO and *p*-H2 yielded enhanced signals for **3** only, thereby revealing that CO readily out-competes the alkyne for binding thereby suppressing the detection of **10**. When the same experiment was conducted with a 50-fold excess of PPh3 instead of CO, enhanced hydride signals for **7a** and **7b** were seen in addition to those of **3** with relative intensity ratios of 11:1:110 alongside the suppression of the signals for **10**. These data suggest therefore that binding PPh3 now out competes that of the alkyne, again preventing the observation of **10**.

**7** (Ru(H)2(CO)(dpae)(PPh3)) is a double ligand loss product of **2**, and the fact it constitutes ~10% of the photoproducts confirms the existence of a suitable reaction pathway to both initiate hydrogenation and form **10** wherein both H2 and the alkyne can bind to Ru. A further experiment where a sample of **1** and *p*-H2 were irradiated at 298 K, which contained authentic *cis*-stilbene, failed to result in the detection of any PHIP-enhanced organic products. Hence, the alkyne, and the associated semi-alkyne hydrogenation step, is needed to enable the PHIP detection of these organic and ruthenium based reaction products.

**Photochemically initiated hydrogenation of 2**

When a sample of **2** and a 100-fold excess of diphenylacetylene is photolysed at 295 K in the presence of *p*-H2, polarised hydride resonances for both isomers of **7** againappear, with the same relative intensities as was the case in the absence of the alkyne substrate. In the corresponding high-sensitivity OPSY experiment, recorded at 308 K, signals for the three hydrogenation products, *cis* and *trans* stilbene and 1,2-diphenylethane,are detected. The corresponding imaging experiments reveal, however, that in this case the hydrogenation reaction is not accelerated by photolysis and hence **2** is deduced to be a poor photo-hydrogenation catalyst when compared to **1**.

**Theoretical calculations**

DFT calculations at the PBE0/LANL2TZ(f) level were undertaken in support of this work and the proposed product assignments. Specifically, complexes **7** (Ru(H)2(CO)(dpae)(PPh3)), **8** (Ru(CO)2(dpae)(*cis*-stilbene)), **9** (Ru(H)(CHPhCH2Ph)(CO)2(dpae)) and **10** (Ru(H)2(CO)(dpae)(η2-CHPh=CPh-CPh=CHPh)) were all found to correspond to stable minima as described in the Supporting Information, and their detection in these experiments is therefore further rationalised

In the case of Ru(H)2(CO)(dpae)(PPh3), **7**,the isomer with hydride ligands *trans* to arsenic and CO (**7a**) was found to be 16.8 kJ mol-1 more stable than the arrangement where the hydrides are *trans* to arsenic and phosphine (**7b**) whilst being 33.3 kJ mol-1 less stable than **3**. This supports therefore the detection of **7** and predominance of isomer **7a**. Furthermore, the alkene complex Ru(CO)2(dpae)(*trans*-stilbene) proved to be 6.4 kJ mol-1 less stable than the corresponding Ru(CO)2(dpae)(*cis*-stilbene) complex in contrast with our detection of **8**.The 13C-H couplings seen experimentally are consistent with the degree of back bonding predicted by the DFT results. The stability difference between these isomers is a consequence of the phenyl ring alignment in the bound stilbene complex which for the *cis* form can orient itself away from the rings of the dpae ligand. The detection of **10** is again fully consistent with its computed stability.

In the case of **9**, the most stable alkyl hydride isomers of Ru(H)(CHPhCH2Ph)(CO)2(dpae) were found to have their hydride ligands *trans* to CO and arsenic respectively. In both cases, the alkyl arm lies *trans* to arsenic (Scheme S1). We conclude therefore that the significant difference that is observed between the hydride chemical shifts of **9a** and **9b** reflects the difference in *trans* ligand.

**Conclusions**

In this paper we have described how the two ruthenium complexes Ru(CO)3(dpae) (**1**) and Ru(CO)2(PPh3)(dpae) (**2**) of Scheme 2 react with dihydrogen, and how each is a precatalyst for alkyne hydrogenation. Compound **1** was found to undergo both thermal and photochemical H2 addition *via* CO loss to yield Ru(H)2(CO)2(dpae) (**3**). The hydride ligands of **3** were found to undergo positional interchange in a process whose rate is reduced by added CO which suggests Ru(H)2(CO)(dpae) is thermally accessible in agreement with the observed hydrogenation activity. The activation parameters for this process, H‡ and S‡, were determined as 94 ± 6 kJ mol–1 and 55 ± 20 J K–1 mol–1, respectively.

In contrast, compound **2** reacts with H2 to form solvated *cis-cis*-Ru(H)2(CO)(dpae)(sol) (**4**)(sol = benzene, toluene and THF) at low temperatures, with **3** dominating at higher temperatures. Upon 325 nm irradiation, however, two isomers of Ru(H)2(CO)(dpae)(PPh3)(**7a** and **7b**, Scheme 2)are readily detected, although again, at higher temperatures **3** dominates. While no evidence for their interconversion was observed via EXSY, the loss of H2 from **7a** occurs withthe activation parameters H‡ = 109 ± 12 kJ mol–1 and S‡ = 65 ± 34 J K–1 mol–1. These values are consistent with a dissociative reaction process. We note that Ball and Mann observed hydride interchange in the related complex Ru(H)2(CO)(PPh3)3 and proposed that it occurs *via* a trigonal twist mechanism.81 It therefore appears that the chelating arsine ligand in **7** suppresses such a process.

Both **1** and **2** were observed to thermally convert diphenylacetylene into *cis*-stilbene, *trans*-stilbene and 1,2-diphenylethane. A range of reaction intermediates were detected (Scheme 5) with turnover for **2** starting at 295 K in agreement with the detection of **4** without alkyne. **1** required photolysis to operate at this temperature and 1,2,3,4-tetraphenylbutadiene and **10** (Scheme 4) could be seen under these conditions with Ru(CO)2(dpae)(*trans*-stilbene) (**8**) readily seen at higher temperatures.

The detection of Ru(CO)2(dpae)(2-CHPh=CPhCPh=CHPh) (**10**) at 295 K during the thermal studies with **2** and photochemical studies with **1** indicates that these precursors provide a route to the common intermediate Ru(H)2(CO)(dpae) which, upon alkyne binding, forms Ru(CPh=CHPh)H(CO)(dpae). At these low temperatures, the binding of a second molecule of alkyne, leading to **10**,competes with reductive C-H bond coupling, or H2 addition, migration and CO binding, which leads to Ru(CHPhCH2Ph)H(CO)2(dpae) (**9**). The formation of the double ligand loss product Ru(CO)(dpae), a precursor toRu(H)2(CO)(dpae), has precedent based on the photochemistry of Fe(CO)5.82

We have used spatially resolved chemical shift imaging methods to distinguish between photochemical and thermally promoted reactions in this study. The most striking result from this approach was the observation that hydrogenation by **1** upon 325 nm irradiation is faster by a factor of 5.5.

The related complexes Ru(H)2(CO)(AsPh3)(dpae) and Ru(H)2(CO)(AsPh3)(dppe), where one arm of the chelating ligand is *trans* to hydride and the other t*rans* to AsPh3, have been reported by Jun *et al*.39 These materials catalyse the conversion of propionaldehyde to propan-1-ol at 403 K and 30 atm H2 pressure. The suggested mechanism for these transformations involves the loss of the monodentate AsPh3 ligand and therefore the involvement of the same key intermediate Ru(H)2(CO)(dpae) as revealed here. Consequently, catalysis by such a pathway has precedent.

These results highlight the importance of the ligand sphere in controlling the efficiency of such transformations and suggest that comparisons of arsine and phosphine ligand systems may be useful if new catalytic pathways are to be found. We are currently studying related Ru(II) dppe complexes using these methods and have seen analogous signals whose full assignment is on-going.



**Scheme 5** Catalytic cycle (blue) showing the lowest energy route for the hydrogenation of diphenylacetylene by **1** or **2** with brown species detected. Note: the appearance of the PHIP signals in the NMR spectra suggest that hydride transfer to the alkene is reversible.

Experimental Section

Ru(CO)3(PPh3)2 was prepared and purified using a literature procedure.83

**Preparation of Ru(CO)3(dpae) (1)**

The compound Ru(CO)3(dpae) was prepared by adapting the literature procedure for the preparation of Ru(CO)3(dppe).84 In a typical experiment, Ru3(CO)12 (100 mg, 0.16 mmol), dpae (230 mg, 0.47 mmol) and benzene (25 mL) were place in a stainless steel autoclave. The autoclave was flushed with CO three times before being pressurised to 80 atm with CO and heated to 373 K for 16 hours. After cooling to room temperature, the excess pressure was released and the pale yellow solution reduced to half volume before cooling to 273 K for 4 hours; this gave Ru(CO)3(dpae) as a yellow microcrystalline material. The complex was washed with benzene and light petroleum and dried in vacuo. Yield: 420 mg (95%). Analysis C: 52.51% (51.88% Theoretical) and H 3.50% (3.60% Theoretical). The characterization data for this complex are given in Table S1.

**Preparation of Ru(CO)2(PPh3)(dpae) (2)**

To prepare this complex, Ru(CO)3(PPh3)2 (100 mg, 0.14 mmol) and dpae (69 mg, 0.14 mmol) were refluxed in toluene (10 mL) under a continuous flow of N2 for 4 hours. The sample was then left to stand at room temperature for 12 hours, yielding a yellow microcrystalline precipitate of Ru(CO)2(PPh3)(dpae), which was then recrystallized from THF/pentane (1 : 2). Yield: 87 mg (68%). Analysis C: 68.10% (67.6% Theoretical) and H 4.93% (4.81% Theoretical). The characterization data for this compound are given in Table S1.

**NMR methods**

All NMR solvents (Apollo Scientific) were dried and degassed prior to use. NMR measurements were made using NMR tubes fitted with J. Young valves and solvents were added by vacuum transfer. For the PHIP experiments, enrichment in *para*hydrogen was achieved by cooling H2 to 18 K over a paramagnetic catalyst (activated charcoal) as described previously.85 All the NMR studies were carried out with sample concentrations of approximately 1 mM and NMR spectra were recorded on either a Bruker DMX-400 or DRX-400 spectrometer with 1H at 400.1, 31P at 161.9 and 13C at 100.0 MHz, respectively. 1H NMR chemical shifts are reported in ppm relative to residual 1H signals in the deuterated solvents (toluene-d7,  2.13 and C6D6, 7.16), 13C NMR shifts are relative to toluene-d8,  21.3 and C6D6,  128.4 with 31P NMR shifts in ppm downfield of an external 85% solution of phosphoric acid. Modified COSY, HMQC and EXSY pulse sequences were used as previously described.86, 87 1H EXSY spectra used to obtain kinetic data were processed using literature methods88 and analysed as described.89 The chemical shift imaging methods employed here are described in the supporting information.

**In-situ photolysis**

This was achieved using a modified NMR probe, as described previously.90 A Kimmon IK3202R-D 325 nm He–Cd 27 mW continuous wave (CW) laser was used as the light source.

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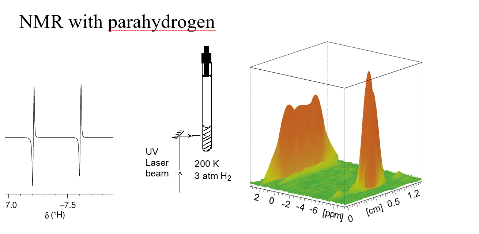
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**Entry for the Table of Contents**



The thermal and photochemical reactivity of Ru(CO)3(dpae) (**1**) and Ru(CO)2(dpae)(PPh3) (**2**) towards diphenylacetylene is probed by NMR with parahydrogen. Several reactive species including Ru(CO)2(dpae)(2-CHPh=CPhCPh=CHPh), Ru(CHPhCH2Ph)(H)(CO)2(dpae) and Ru(CO)2(dpae)(*trans*-stilbene) are seen.

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