A Parahydrogen Study of Catalytic Hydrogenation by Diphosphane-Substituted Triruthenium Clusters

Tom G. Prestwich,[a] Damir Blazina,[a] Simon B. Duckett,*[a] and Paul J. Dyson[b]

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The diphosphane-substituted clusters $[Ru_3(CO)_{10}(dppe)]$ and $[Ru_3(CO)_8(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane] are shown to catalytically hydrogenate diphenylacetylene. This process is highly solvent-dependent with fragmentation dominating in low-polarity solvents, which indicates that the dppe ligand does not stabilise the cluster under catalytic conditions. In solvents of higher polarity, the clusters are active hydrogenation catalysts of lower activity than their monodentate phosphane analogues $[Ru_3(CO)_{10}(L)_2]$ (L = PPh_3, PMe_2Ph, PMe_3, PCy_3).

Introduction

Catalysis by transition metal clusters is of considerable interest due to the ability of these species to act as homogeneous catalysts with properties that lie between those of mononuclear complexes and colloidal/nanoparticle catalysts, whilst also representing fragments of a metal surface.[1] The study of clusters is, however, complicated by the wide variety of reaction pathways available to them, and in particular their tendency to fragment to mononuclear metal complexes. One way to circumvent this problem might be to utilise clusters with supporting ligand scaffolds, such as bidentate phosphanes, which could potentially stabilise the cluster under catalytic conditions and hence minimise fragmentation.

Phosphane-substituted triruthenium clusters have been shown to exhibit significantly greater catalytic activity than their comparatively unreactive homoleptic parent $[Ru_3(CO)_{12}]$.[1] Compounds containing bidentate phosphane ligands have previously been studied in an effort to preclude cluster fragmentation. For example, it is well established that diphosphane-substituted triruthenium clusters react with unsaturated organic molecules,[2] yielding species that may correspond to intermediates in a catalytic cycle. It has also been shown that the 1,2-bis(diphenylphosphanyl)-methane (dppm) substituted species $[Ru_3(CO)_{10}(dppm)]$ and $[Ru_3(CO)_8(dppm)_2]$, as well as their arsanyl (dpam) analogues, react with hydrogen to form stable hydride clusters.[3] These phosphane-containing species were subsequently shown to be active catalysts for the isomerisation and hydrogenation of 1-hexene, with turnover frequencies being taken to be indicative of catalysis by an intact cluster.[4] Analogous species containing bulky cyclohexyl and pentafluorophenyl substituents on the bidentate phosphane ligand have been shown to catalyse hydroformylation reactions,[5] but exact mechanistic information about these processes remains elusive.

Consequently, we set out to explore the mechanism of catalysis by diphosphane-substituted triruthenium clusters by using the parahydrogen-induced polarisation (PHIP) effect.[6] This technique is applicable to mechanistic studies since it yields substantially enhanced resonances in ^1H NMR spectra. The extent of enhancement available has recently been shown to approach a factor of 28500,[7] making this technique ideal for the detection of transient species or those present in low concentration, such as reaction intermediates. PHIP has already been successfully used to study H_2 addition to,[8] and hydride migration on,[9] a number of triruthenium and triosmium clusters, as well as yielding unprecedented insights into catalytic hydrogenation by the tertiary phosphane (L) containing cluster family $[Ru_3(CO)_{12-x}(L)_x]$ (L = PPh_3, PMe_2Ph, PMe_3, PCy_3; x = 1−3).[10] It was discovered that isomers of $[Ru_3(H)(\mu\text{-}H)(CO)_9(L)_2]$ play a kinetically significant role in the hydrogenation of alkyne substrates such as diphenylacetylene. This catalytic transformation proceeds by initial CO loss, with each isomer exhibiting different rates for H_2 transfer to the hydrogenation product *cis*-stilbene. In addition, a less significant secondary reaction involving loss of L was detected, yielding a detectable product that contained both a pendant vinyl unit and a bridging hydrido ligand. Competing pathways involving fragmentation to form $[Ru(H)_2$-

[a] Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom, Fax: + 44-1904-432564
E-mail: sbd3@york.ac.uk
[b] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, 1015 Lausanne, Switzerland
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$(CO)_2(L)(alkene)$] were also observed and shown to be favoured by nonpolar solvents. Furthermore, it has very recently been reported that the presence of a stabilising phosphido group can stabilise the metal cluster framework under catalytic conditions, such that only cluster-based active species are observed with p-H_2, even in nonpolar solvents.[11]

In this paper, PHIP is utilised to investigate catalytic hydrogenation by the clusters $[Ru_3(CO)_{10}(dppe)]$ (**1**) and $[Ru_3(CO)_8(dppe)_2]$ (**2**) [dppe = 1,2-bis(diphenylphosphanyl)-ethane]. Our aim was to confirm mechanistically by the direct observation of key dihydride species whether the presence of the bidentate ligand exerts a stabilising influence on the cluster core whilst still allowing enough flexibility for catalytic transformations to take place, as well as to compare the stabilising effect of the diphosphane ligand to that of the phosphido ligand used in an earlier study.[11]

Results and Discussion

Hydrogen Addition to $[Ru_3(CO)_{10}(dppe)]$ (1)

The literature solid-state structure of **1**,[12] with the bidentate phosphane ligand located in the equatorial plane and bridging two metal centres, is consistent with the solution-state ^1H and ^{31}P NMR spectral features at 295 K (Table 1), which indicate the presence of only one ^{31}P environment. In addition, only one broad resonance is observed in the carbonyl region of the ^{13}C NMR spectrum at $\delta = 210.4$ ppm. This is indicative of rapid carbonyl exchange around the cluster framework under these conditions. Such effects have been reported in triiron clusters containing dppe ligands where evidence has been presented to support exchange by a merry-go-round mechanism[13] rather than the alternative mechanism of cluster core libration within the ligand polyhedron.[14]

On addition of p-H_2 to a $CDCl_3$ solution of **1** at 295 K, a new species, **3**, was formed, which yielded two mutually coupled enhanced hydride resonances at $\delta = -12.87$ and -14.74 ppm (Figure 1, Table 1). Based on previous work, it is suggested that the lower-field resonance corresponds to a terminal hydride (H_t), while the higher field resonance corresponds to a bridging hydride (H_b).[3,10] On careful examination, the resonance corresponding to H_b was found to appear as a doublet of doublets of antiphase doublets, indicative of coupling to two ^{31}P nuclei. The associated $^2J_{H,P}$ values of 9 Hz (to P_a signal at $\delta = 63.6$ ppm; by

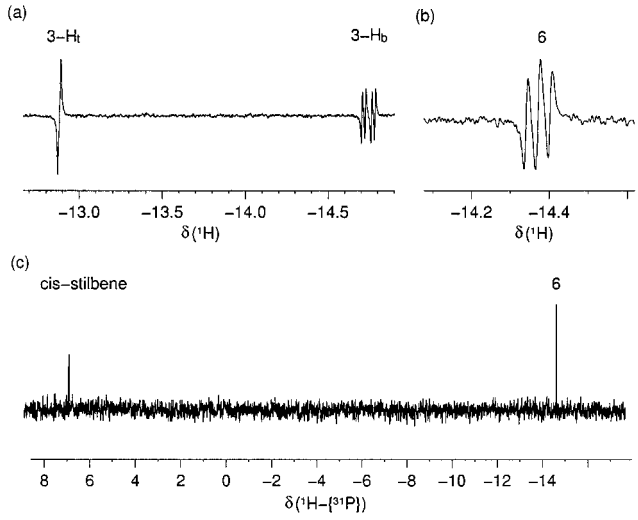


Figure 1. Selected regions of ^1H NMR spectra of **1** with p-H_2 in $CDCl_3$: (a) hydride region of **3** at 295 K; (b) in the presence of PhC≡CPh at 315 K, showing the bridging hydride resonance for **6**; (c) EXSY spectrum with a mixing time of 600 ms and selective irradiation of the hydride ligand yielding the $\delta = -14.36$ ppm signal, showing direct transfer of magnetisation from this site in **6** into *cis*-stilbene, the hydrogenation product

Table 1. NMR spectroscopic data for complexes **1**–**6** detected in $CDCl_3$ at 295 K unless otherwise indicated; H_t indicates terminal hydride and H_b bridging hydride, and the ^{31}P nuclei are labelled according to Figure 2

Compound	δ (^1H)	δ (^{31}P-{^1H})	δ (^{13}C-{^1H})
1	1.69 (d, $J_{H,P}$ = 12 Hz)	41.5 (s)	210.4 (br)
2	1.6–2.1 (m)	32.3 (m), 33.6 (m), 35.0 (m), 39.7 (m)	212 (br)
3	−12.87 [dd, $J_{H,P}$ = 3 Hz (P_b), $J_{H,H}$ = −7 Hz, H_t], −14.74 [ddd, $J_{H,P}$ = 9 Hz (P_a), 23 Hz (P_b), $J_{H,H}$ = −7 Hz (H_b)]	63.6 (s, P_a), 57.4 (s, P_b)	
4	−13.38 (t, $J_{H,P}$ = 12 Hz)	38.4 (s)	211.0 (br)
5a[a]	−4.93 [dd, $J_{H,P}$ = 12 Hz (P_a), $J_{H,H}$ = −7 Hz, H_t], −14.29 [tdd, $J_{H,P}$ = 30 Hz (P_a and P_b), 18 Hz (P_c), $J_{H,H}$ = −7 Hz, H_b]	51.08 (d, $J_{P,P}$ = 123 Hz, P_a), 51.12 (dd, $J_{P,P}$ = 123, 33 Hz, P_b), 49.03 (d, $J_{P,P}$ = 33 Hz, P_c)	
5b[a]	−5.02 (dd, $J_{H,P}$ = 14, $J_{H,H}$ = −7 Hz, H_t), −14.31 [tdd, $J_{H,P}$ = 31 Hz (P_a and P_b), 16 Hz (P_c), $J_{H,H}$ = −7 Hz, H_b]	49.16 (d, $J_{P,P}$ = 72 Hz, P_a), 48.58 (dd, J_{pp} = 72, 18 Hz, P_b), 50.30 (d, $J_{P,P}$ = 18 Hz, P_c)	
6[b]	−14.36 (td, $J_{H,P}$ = 12, $J_{H,H}$ = −4 Hz, H_b), +7.25 (d, $J_{H,H}$ = −4 Hz)	38.1 (s)	

[a] At 273 K. [b] At 315 K.

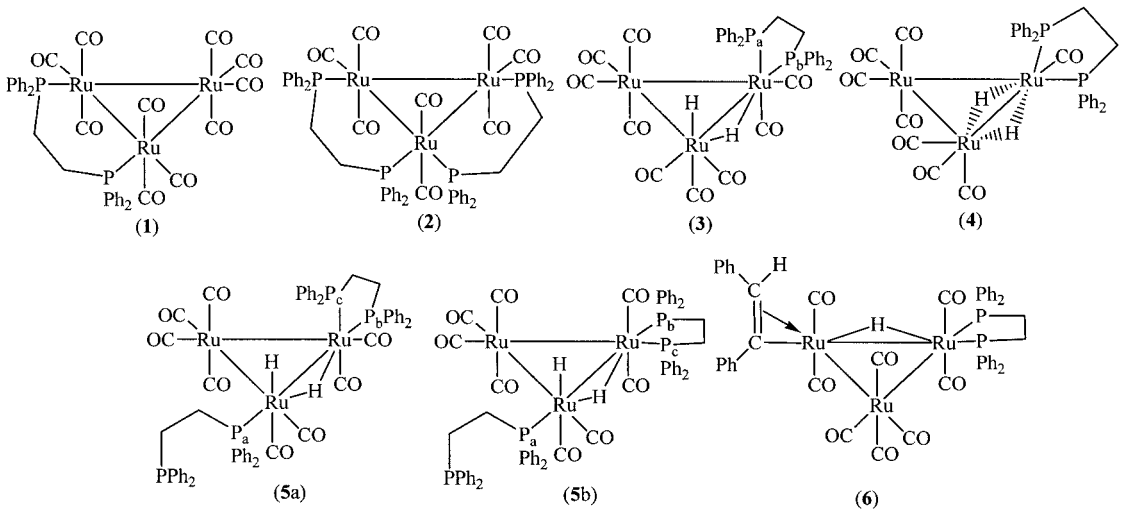


Figure 2. Structures of clusters **1**−**6**; **1** and **2** are from the literature,[12] the others were determined in this study

HMQC methods) and 23 Hz (to P_b signal at $\delta = 57.4$ ppm) indicate that H_b is *cis* to P_a and *trans* to P_b, as shown in Figure 2.[15] Both these ^{31}P centres were detected as simple singlets (vide infra). The resonance for H_t, meanwhile, appeared as a simple antiphase doublet. However, ^{31}P decoupling experiments revealed the presence of a small (3 Hz) coupling between H_t and P_b. In view of the very small size of the coupling between H_t and P_b, as well as the larger couplings from H_b to P_b and P_a, it is suggested that both the ^{31}P centres of the dppe ligand are located on the same Ru centre, which also coordinates the bridging hydride. The small phosphorus coupling between H_t and P_b therefore corresponds to a weak three-bond coupling, which is relayed through the Ru−Ru bond that is *trans* to P_b.

In view of the distinct *trans* and *cis* H_b-P coupling constants observed here, it is suggested that the dppe ligand occupies one axial and one equatorial centre on this metal centre. Previous reports indicate that ^{31}P centres in adjacent equatorial sites can exchange position rapidly on the NMR time scale.[10b] The observed singlet peak profile for the ^{31}P signals of the two sites could therefore be due to the occurrence of site exchange,[10,15] although it may arise because of mutual cancellation of the $^2J_{P,P}$ coupling through the metal centre and the $^3J_{P,P}$ coupling through the backbone of the dppe ligand. These two couplings would be expected to have opposite signs. Unfortunately, the need for *p*-H_2 amplification to detect **3** precluded the direct investigation of this process by ^{31}P EXSY methods, but the lack of any visible ^{13}C-^{31}P couplings in the associated NMR spectra of the precursor species **1** and **2** clearly demonstrates the presence of fluxionality in these systems. The proposed structure of **3** is shown in Figure 2.

Upon addition of 1 atm of CO to the sample, the hydride resonances for **3** were no longer visible at 315 K. This observation confirms that **3** is formed by loss of CO rather than the dissociation of an arm of the dppe ligand, a result which is not unexpected for a μ_2-phosphane, and further supports the proposed structure of **3**.

We have previously reported that oxidative addition of H_2 to clusters of the type $[Ru_3(CO)_{10}(L)_2]$, where L is a monodentate tertiary phosphane such as PPh_3, leads to three isomeric products of $[Ru_3(H)(\mu\text{-}H)(CO)_9(L)_2]$. One of these isomers matches the structure of **3** where both phosphane ligands are on the same metal centre but it is the least preferred of the three. The major isomer with L = PPh_3 has both phosphane ligands in equatorial locations on separate ruthenium centres spanned by the bridging hydride. Such an arrangement is not observed in the case of **3**, but would require both the dppe ligand and a hydride to bridge the same Ru−Ru bond, a situation that might be sterically unfavoured due to the elongated nature of the Ru−H−Ru bond.[16]

The hydrido ligands of $[Ru_3(H)(\mu\text{-}H)(CO)_9(L)_2]$ proved to be highly fluxional, undergoing both site exchange, interisomer exchange and reductive coupling to form H_2.[10b] The fluxional behaviour of the hydrido ligands in **3** was probed by the same EXSY methodology (Supporting Information). At 295 K, exchange between the two hydrido ligands proceeded at a rate of 3.4 s^{-1}; exchange with free H_2, which must be occurring in view of the enhanced hydride resonances exhibited by **3**, was not evident on this time scale. This behaviour is similar to that reported for $[Ru_3(H)(\mu\text{-}H)(CO)_9(L)_2]$, although it should be noted that with monodentate phosphane species, the rate of hydride interchange in the analogous isomer was slower under identical reaction conditions.

Over prolonged reaction times, the hydride resonances for **3** disappeared as the *p*-H_2 enhancement was depleted, and a stable resonance, assigned to species **4**, built up slowly at $\delta = -13.38$ ppm. This signal was split into a triplet by a 12 Hz coupling to two equivalent ^{31}P nuclei resonating at $\delta = 38.4$ ppm in the corresponding ^{31}P NMR spectrum. Since *p*-H_2 enhancement in these spectra would be quenched by a species with unpaired electrons, this resonance must correspond to two chemically equivalent hydrides, while its chemical shift is indicative of bridging hy-

dride coordination. In the view of the configuration of the dppe ligand in **3** and of the apparent equivalence of the ^{31}P nuclei in **4**, the structure of **4** shown in Figure 2 is proposed. ^{31}P NMR investigations revealed that **4** is still a very minor product; after 18 h under H_2, the ratio of **1**/**4** was determined to be 20:1. ^{13}C NMR revealed that the carbonyl ligands in this product are highly fluxional at room temperature, with only one broad carbonyl signal being observed. According to the proposed structure, cluster **4** is an unsaturated, 46-electron species. This is not completely unexpected, since stable 46-electron dihydride clusters of the iron group, such as the osmium cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, are known.[17] It should, however, be noted that the ruthenium analogue $[Ru_3(\mu\text{-}H)_2(CO)_{10}]$ is unstable and can only be prepared by prolonged photolysis[18] in contrast to **4** which is stable and thermally accessible, albeit in small amounts. We further note that the hydride resonance for **4** disappears on venting the H_2.

Surprisingly, on changing the solvent to $[D_8]$toluene and warming with *p*-H_2, no cluster-containing hydrides were observed, and the only species evident was the known mononuclear complex $[Ru(CO)_2(dppe)(H)_2]$, characterised by enhanced hydride resonances at $\delta = -6.32$ and -7.55 ppm.[19] This contrasts with the situation observed with the $[Ru_3(CO)_{12-x}(L)_x]$ systems ($x = 1-3$), where the corresponding cluster-based dihydrides are observed under these conditions[10] and indicates that the dppe ligand makes the triruthenium cluster more susceptible to solvent effects than is the case with monodentate phosphanes.

Hydrogen Addition to $[Ru_3(CO)_8(dppe)_2]$ (2)

The ^{31}P NMR spectroscopic data for **2** (Table 1) indicate the presence of multiple isomers in solution, a feature already established for clusters containing multiple bidentate phosphanes;[3,5] the proposed structure of **2** is illustrated in Figure 2. When a sample of **2** was treated with *p*-H_2 in $CDCl_3$ at 295 K, two enhanced hydride signals were detected in the corresponding ^1H NMR spectrum at $\delta = -4.93$ and -5.02 ppm, due to terminal hydrides, and further two at $\delta = -14.29$ and -14.31 ppm, assigned to bridging hydrides. COSY investigations revealed that the resonances at $\delta = -4.93$ and -14.29 ppm correspond to one product (due to protons **5a**-H_t and **5a**-H_b, respectively) while those at $\delta = -5.02$ and -14.31 ppm correspond to another (due to protons **5b**-H_t and **5b**-H_b, respectively); the similarity between this situation and that previously observed for $[Ru_3(H)(\mu\text{-}H)(CO)_9(L)_2]$ (L = monodentate phosphane)[10] suggests that **5a** and **5b** correspond to two isomeric dihydride products. Characterisation of these species was complicated by hydride signal overlap, but the terminal hydride resonances could be resolved by cooling the sample to 273 K (Figure 3). The resonance for **5a**-H_t showed one coupling of 12 Hz to a single *cis*-^{31}P centre that was located at $\delta = 51.08$ ppm (P_a; Figure 2) by HMQC methods in addition to a -7 Hz H-H coupling. The analogous signal for **5b**-H_t also showed an interaction with a single ^{31}P nucleus, resonating at $\delta = 49.16$ ppm ($J_{H,P}$ = 14 Hz, P_a). It can therefore be concluded that the ruthenium centre to which the terminal hydride is coordinated also binds one phosphorus atom in both products.

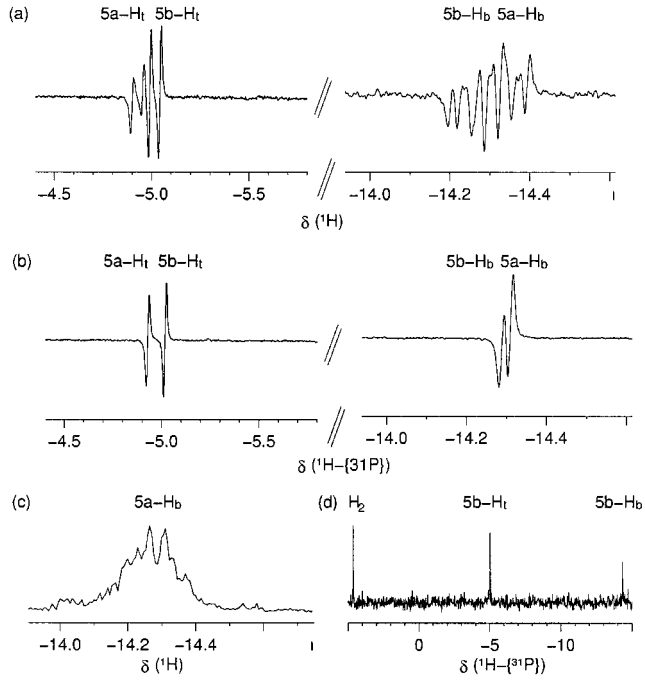


Figure 3. Selected regions of NMR spectra of **2** obtained with *p*-H_2 in $CDCl_3$ at 273 K: (a) ^1H spectrum showing the hydride resonances for **5a** and **5b**; (b) ^1H spectrum with $\{^{31}P\}$ decoupling; (c) cross-section of a 2D ^1H-^{31}P HMQC spectrum with retention of ^{31}P couplings, showing that the signal for **5a**-H_b is a triplet of doublets due to $^2J_{H,P}$ couplings; (d) cross-section of a 2D EXSY spectrum recorded at 285 K with a mixing time of 500 ms, showing exchange from **5b**-H_t into the bridging position on the same isomer and into free H_2, while exchange into **5a** is absent

As already stated, the bridging hydride signals for **5a** and **5b** show extensive overlap due to the presence of multiple ^1H-^{31}P couplings. However, they were successfully analysed by comparison of multiple high-resolution ^1H-^{31}P HMQC experiments where the ^{31}P couplings were either retained or decoupled (Figure 3). Careful examination of the two resonances in the ^1H dimension, revealed that **5a**-H_b appeared as a doublet of triplets due to two $^2J_{H,P}$ couplings of 30 Hz (to P_a at $\delta = 51.08$ ppm and to P_b at $\delta = 51.12$ ppm) and an 18 Hz coupling to P_c ($\delta = 49.03$ ppm). This suggests that P_a and P_b are *trans* to the bridging hydride, while P_c is *cis* to it. Furthermore, P_a and P_b showed a mutual ^{31}P coupling of 123 Hz, which is attributed to their *trans* arrangement across a metal−metal vector.[5,20]

P_b and P_c also coupled to each other, but with a smaller constant of 33 Hz. It can therefore be deduced that P_b and P_c are *cis* to each other and bound to the same metal centre. Since P_a is located on the Ru centre that binds the terminal hydride, the observed coupling patterns signify that the other two phosphorus nuclei must bind to the metal atom that coordinates the bridging hydride, as shown in Figure 2. In addition, since the structures of **3** and **4** suggest that the dppe ligand and the hydride do not bridge the same metal centre, P_b and P_c can be deduced to originate from the same phosphane ligand. It should also be noted that no "arti-

facts'' arising from double and triple quantum coherences were detected in these HMQC spectra,[21] and it was therefore concluded that only single quantum transitions were being observed.

The resonance for proton **5b**-H_b was analysed in a similar way (Table 1, Figure 2). In brief, this resonance contains a 31 Hz *trans* triplet splitting to two phosphanes [$\delta = 49.16$ (P_a) and $\delta = 48.58$ (P_b) ppm] as well as a 16 Hz *cis* splitting due to P_c ($\delta = 50.30$ ppm). Nuclei P_a and P_b now exhibit a 72 Hz coupling, while P_b and P_c couple with a $^2J_{P,P}$ value of 18 Hz. Therefore, once again, P_b and P_c originate from the same dppe ligand and bind to the same ruthenium centre, which also coordinates the bridging hydride.

The structural difference between **5a** and **5b** thus stems from the orientation of the dppe ligand that contains P_b and P_c. In view of previous reports in related triosmium systems, which found that the coupling between an axial and an equatorial ligand is larger than that between two equatorial ligands,[15] it is suggested that in **5a**, P_b is an equatorial site and P_c is axial, whereas in **5b** both the phosphorus atoms are in equatorial locations. The small difference in chemical shift between axial and equatorial ^{31}P centres is in agreement with previous observations.[15] It should be noted that although the proposed structures for **3** and **5a** contain identical ligand arrangements on one ruthenium centre (a dppe ligand bridging between an axial and equatorial sites), P-P couplings are only observed in the spectra of **5a**. This indicates that the presence of the second dppe ligand on this species slows down dppe site interchange.

When these experiments were repeated in the presence of 1 atm of CO, there was no decrease in the signal intensities observed for **5a** and **5b**. It is therefore reasonable to assume that H_2 addition to **2** proceeds by a change in the coordination mode of one of the dppe ligands (in both cases, the one that contains P_a) from η^2 to η^1 (Figure 2). H_2 addition to triruthenium clusters by initial de-coordination of chelating phosphane ligands has been reported previously.[22] This mechanism also parallels the situation observed with related $[Ru_3(CO)_9(L)_3]$ systems, which undergo H_2 addition by loss of phosphane.[10d] Because of the need for p-H_2 amplification, the uncoordinated ^{31}P centres in these species could not be detected directly. Magnetisation transfer experiments have been used here to detect signals for key heteronuclei that couple directly to the hydrides, but this is not the case for the hydrides and the uncoordinated phosphorus centres of **5a** and **5b**. Attempts to detect the uncoordinated ^{31}P centres therefore proved unsuccessful but there can be no doubt of their presence.

When **5a** and **5b** were investigated by EXSY methods at 285 K, intra-isomer hydride exchange and H_2 elimination were detected in both cases (Figure 3 and Supporting Information). The rate constant for hydride self-exchange was determined to be 4.8 s^{-1} for **5a** and 4.6 s^{-1} for **5b**, while the rates for H_2 elimination were 1.5 s^{-1} for both isomers. The similarity of the intra-isomer hydride ligand exchange rates agrees with the very similar structures and relative abundances of the two isomers. Interestingly, inter-isomer exchange is not observed. These observations contrast those made on related $[Ru_3(H)_2(CO)_9(L)_2]$ systems, which exhibit both intra- and inter-isomer exchange under similar conditions.[10] Intra-isomer hydride exchange in $[Ru_3(H)_2(CO)_9(PPh_3)_2]$, under these conditions, occurs at the slower rate of 1.6 s^{-1}, and elimination of H_2 is also slow on the NMR time-scale.[10] The bidentate phosphane therefore facilitates hydride site exchange and H_2 elimination in these clusters.

At prolonged reaction times, the enhanced hydride signals corresponding to **5a** and **5b** disappeared as the extent of p-H_2 enrichment fell. However, no new stable dihydride species were detected at this point with only **2** being evident in the corresponding ^1H and ^{31}P NMR spectra. This indicates that the η^1-dppe ligand is able to re-coordinate with concurrent H_2 elimination. Repeating the investigation in [D_8]toluene once again yielded enhanced hydride resonances for the known mononuclear species $[Ru(CO)_2(dppe)(H)_2]$,[19] and no cluster based hydride products were observed.

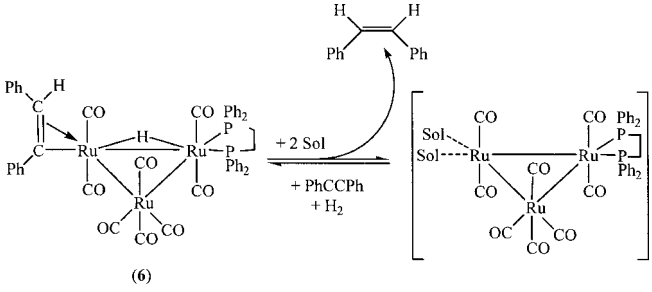
Catalytic Hydrogenation of Diphenylacetylene

In order to examine the catalytic activity of these systems towards the hydrogenation of diphenylacetylene, samples of **1** and **2** were monitored in $CDCl_3$ in the presence of p-H_2 and a 100-fold excess of the substrate. When **1** was examined in this way, the formation of **3** was totally suppressed and a new species, **6**, was detected at 315 K and above (NMR spectroscopic data: Table 1). This species yielded two enhanced ^1H resonances at $\delta = -14.36$ and $+7.25$ ppm in the corresponding ^1H NMR spectrum, which were shown to couple by COSY experiments. The hydride resonance appeared as a triplet of antiphase doublets (Figure 1), due to coupling to two identical phosphorus centres (J_{PH} = 12 Hz) and the vinyl proton ($J_{H,H} = -4$ Hz). On the basis of similarity of these spectral features to those reported previously,[10,11] **6** is suggested to correspond to a vinyl hydride cluster, where the sign of the $J_{H,H}$ coupling indicates that the vinyl group occupies the two equatorial locations on a single ruthenium centre (Figure 2). In order for the ^{31}P centres to appear equivalent at these elevated temperatures, the dppe ligand must be located on the opposite metal centre to the vinyl group, occupying the two equatorial sites (cf. **4** and **5b**). Phosphane ligands in such arrangements are able to undergo rapid exchange, which would make them appear equivalent to the bridging hydride.[10b]

These spectra also contained an enhanced resonance for *cis*-stilbene, the hydrogenation product of diphenylacetylene. EXSY investigations revealed direct magnetisation transfer from **6** into *cis*-stilbene was occurring (Figure 1) and thereby confirmed that **6** is an active intermediate involved in catalytic hydrogenation by **1**. The hydrogenation process was then investigated in a quantitative manner in $CDCl_3$ at 320 K and the resulting data were analysed by simulation (Supporting Information).[10,23] The rate of elimination of *cis*-stilbene from **6** was determined to be 0.06 s^{-1}; this is slower than the rates exhibited by mononuclear phosphane analogues {for instance, species derived from

$[Ru_3(CO)_{10}(PPh_3)_2]$ and $[Ru_3(CO)_{10}(PMe_2Ph)_2]$ exhibit pseudo-first-order hydrogenation rates between 0.07 and 0.18 s^{-1} at the lower temperature of 301 K} and hence the dppe-containing species is a less active hydrogenation catalyst.

Since **3** was not detected in these catalytic experiments, it can be concluded that either **6** is formed from **1** at the expense of **3**, or that **3** converts rapidly into **6** in the presence of diphenylacetylene. When the experiment was repeated in the presence of only a fivefold excess of substrate, **6** was still the only species detected. As **6** still contains the dppe ligand, its formation must proceed by loss of CO. This was confirmed by the addition of 1 atm of CO to the system, which quenched both the formation of **6** and the catalytic hydrogenation. Further experiments were then completed where the $[H_2]$ was varied from 1 to 4 atm. It was discovered that the rate of stilbene elimination is independent of $[H_2]$, which indicates that although H_2 is required to generate **6**, it is not required for stilbene elimination. Elimination of stilbene from **6** will therefore afford an unsaturated species, viz. $[Ru_3(CO)_8(dppe)]$, which may be stabilised by the solvent. The existence of such a stabilising influence has already been proposed by Fontal et al. for the analogous dppm systems.[4] The unsaturated species will subsequently be able to re-coordinate both H_2 and substrate in order to repeat the catalytic process, as illustrated in Scheme 1.



(6)

Scheme 1. Catalytic hydrogenation of diphenylacetylene by **6**

When **2** was employed as the catalytic precursor, **5a** and **5b** were observed at the same relative intensity as in the absence of substrate. No new hydride-containing species were observed, but a gradual build-up of normal ^1H resonances corresponding to *cis*-stilbene was evident at temperatures above 315 K. Since no *p*-H_2 activity is observed in the stilbene product, the rate of its formation must be sufficiently slow for normal signals to be observed; **2** is thus a poorer catalytic precursor than **1** in this reaction.

The lower catalytic activity of the dppe-containing clusters when compared with monodentate phosphane analogues of the type $[Ru_3(CO)_{10}(L)_2]$ indicates that the dppe ligand impedes substrate binding and hence slows down catalytic hydrogenation. This is supported by the significantly lower catalytic activity of **2** when compared to **1**. The same trend was observed by Fontal et al. for dppm-substituted analogues, based on reaction yields and catalytic turnover.[4]

When the catalytic investigations on **1** and **2** were repeated using $[D_8]$toluene as the solvent, no cluster-based hydrides could be observed and the only detected hydride product was the known mononuclear species $[Ru(CO)_2(dppe)(H)_2]$.[19] Hydrogenation was evident by the observation of a very slow build-up of normal signals corresponding to *cis*-stilbene at temperatures above 335 K. This again indicates that the dppe-substituted triruthenium clusters are highly susceptible to solvent effects, in agreement with literature observations for dppm analogues,[4] and demonstrates directly that they undergo significant fragmentation to less active mononuclear species in low-polarity solvents. Thus, the bidentate ligand is unable to stabilise the cluster framework under catalytic conditions.

Finally, it is interesting to compare the influence of the dppe ligand on the cluster core with that exerted by the phosphido group.[11] In solvents of moderate polarity, such as $CDCl_3$, the dppe-substituted cluster **1** is a superior catalyst compared to the phosphido-containing cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$; at 315 K, **1** leads to catalytic hydrogenation at a rate of 0.06 s^{-1}, whereas $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$ becomes active only at 340 K. However, in low-polarity solvents such as toluene, the phosphido group is able to exert a stabilising influence on the cluster, such that only cluster-based species are observed under catalytic conditions; in contrast, fragmentation dominates in the case of dppe-substituted clusters **1** and **2**. These results also indicate that stabilising the cluster framework can result in lower catalytic activity. Therefore, the exact nature of the stabilising group, as well as the exact reaction conditions, are clearly of crucial importance if cluster fragmentation under catalytic conditions is to be precluded.

Conclusion

The clusters $[Ru_3(CO)_{10}(dppe)]$ (**1**) and $[Ru_3(CO)_8(dppe)_2]$ (**2**) have been shown to lead to catalytic hydrogenation of diphenylacetylene. This process is solvent-dependent, with fragmentation dominating in low-polarity solvents, indicating that the dppe ligand does not stabilise the cluster under catalytic conditions; this is in contrast to $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$, where only cluster-based active species are observed under such conditions. In solvents of higher polarity, clusters **1** and **2** are active catalysts, but exhibit lower activity than their monodentate phosphane analogues $[Ru_3(CO)_{10}(L)_2]$ (L = PPh_3, PMe_2Ph, PMe_3, PCy_3), which is indicative of the dppe ligand impeding substrate binding. The exact nature of the phosphane ligand is thus of great importance in the effort to preclude cluster fragmentation during catalytic transformations.

Experimental Section

General: All synthetic manipulations were carried out under dry nitrogen using standard Schlenk or glove-box techniques. Subsequent purifications were carried out without precautions to exclude air. THF was dried and distilled prior to use, whilst all other

solvents were used as received. $[Ru_3(CO)_{12}]$ (Strem), dppe, benzophenone (Aldrich) and sodium (Fluka) were also used as received. The clusters $[Ru_3(CO)_{10}(dppe)]$ (**1**) and $[Ru_3(CO)_8(dppe)_2]$ (**2**) were prepared using a literature method[12] and purified by recrystallisation from hexane/dichloromethane. Characterisation was achieved by comparison of characteristic solution IR (ν_{CO}) and FAB MS with the literature data. NMR measurements were made using NMR tubes fitted with J. Young Teflon valves and solvents (dried and degassed) were added by vacuum transfer in a high-vacuum line. For the PHIP experiments, hydrogen enriched in the *para* spin state was prepared by cooling H_2 to 18 K over activated charcoal. The studies were carried out with sample concentrations of approximately 1 μM and spectra were recorded with a Bruker DRX-400 spectrometer with ^1H at 400.1 MHz, ^{13}C at 100.1 MHz and ^{31}P at 162.0 MHz, respectively. ^1H NMR chemical shifts are reported in ppm relative to residual ^1H signals in the deuterated solvents ([D_7]toluene: δ = 2.13 ppm; $CHCl_3$: δ = 7.27 ppm), ^{13}C NMR in ppm relative to $CDCl_3$ (δ = 77.05 ppm), and ^{31}P NMR in ppm downfield of an external 85% solution of phosphoric acid. Modified COSY, HMQC and EXSY pulse sequences were used as described previously.[24] In the exchange and hydrogenation studies, EXSY spectra were acquired immediately after exposing the sample to *p*-H_2 and introducing it into the NMR probe. The results were modelled for hydride exchange and hydride transfer into free H_2, or for hydride transfer into the hydrogenation product, applying published procedures.[10,23] The rate constants obtained in this way were multiplied by two to take into account the analysis method.[25]

Supporting Information: Lists of raw and simulation data and details of the analysis method are available for hydride exchange and H_2 elimination in species **3**, **5a** and **5b**, as well as for catalytic hydrogenation by **6** (footnote on first page of this article).

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