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On the Influence of "Arm-on, Arm-off" Processes on Alkene Hydrogenation Catalysed by a Rhodium Triphos Complex

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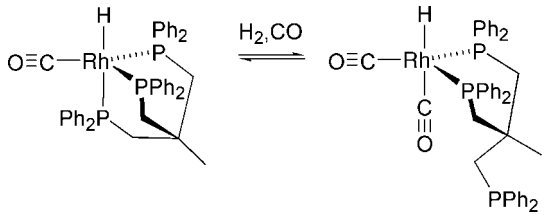
The influence of phosphane "arm-on, arm-off" association/dissociation in rhodium catalysed alkene hydrogenation using [Rh(COD)(κ^3-triphos)]PF_6 {**1**, COD = cyclooctadiene, triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane} has been investigated by comparison of the activity of **1** to mixtures of the related diphosphane complex, [Rh(COD)(κ^2-dppp)]PF_6 {**2**, dppp = 1,3-bis(diphenylphosphanyl)propane} and triphenylphosphane (THF, 50 °C, 1 bar H_2). These investigations are supplemented by a demonstration of the κ^2–κ^3 fluxionally of the triphos coordination in **1** by reversible reaction with $[RuCl_2(p\text{-cymene})]_2$ at room temperature in CH_2Cl_2. The product of this reaction, the bimetallic complex [(*p*-cymene)Cl_2Ru{(PPh_2CH_2)CMe(CH_2PPh_2)$_2$}Rh(COD)]PF_6, was isolated and fully characterized, including determination of the solid-state structure by X-ray diffraction analysis. Despite this evidence for facile arm-off dissociation of the triphos ligand in **1**, complex **2**, with or without triphenylphosphane, was found to be more efficient for the hydrogenation of styrene and cyclohexene. Notably, use of triphenylphosphane together with **2** was found to have beneficial effects – increasing the rate of styrene hydrogenation (in some cases) and helping to stabilise the metal center during cyclohexene hydrogenation. These observations are supported by mercury poisoning experiments and reactivity experiments with **2** in medium pressure sapphire NMR tubes.

Introduction

Tripodal triphosphane ligands have found widespread application in inorganic and organometallic chemistry.[1] Among these ligands, the C_3 symmetric 1,1,1-tris(diphenylphosphanylmethyl)ethane (triphos) and it's derivatives are among the most extensively investigated, forming a large variety of transition metal complexes, many of which have found applications in catalysis.[1,2] Bianchini and co-workers, in particular, have pioneered the use of this ligand in transition metal catalysis, using platinum group metals for a number of processes, including hydrogenation and hydroformylation of alkenes,[3] oxidation of catechols,[4] coupling reactions of alkynes,[5] and the hydrogenation, hydrogenolyis and hydrodesulfurisation of thiophenes.[6] Functionalisation of the triphos ligand by derivation of the bridgehead atom with appropriate moieties has allowed the formation of metallo-dendrimers[7] or immobilisation of metal complexes on silica[8] or into biphases;[9] facilitating catalyst reuse or modifying reactivity. Such immobilization is complemented by the tridentate nature of the ligand, stabilising the metal center during catalysis and reducing leaching.

Although commonly found in a tridentate (κ^3) coordination mode,[1] κ^2-coorindination of triphos is also observed in a number of transition metal complexes.[10] The interconversion between these κ^2 and κ^3 coordination modes by "arm-on, arm-off" association/dissociation of one of the phosphane arms has been implicated in the reactivity and catalytic activity of triphos complexes, particularly those of rhodium.[10c,11] Notably, Kiss and Hováth demonstrated a reversible arm-off dissociation in [Rh(CO)H(κ^3-triphos)], an active hydroformylation catalyst,[3a] and addition of CO under hydroformylation conditions at room temperature by high pressure IR and ^{31}P NMR spectroscopy (Scheme 1).[12] Caulton and co-workers have further affirmed the importance of this arm-off mechanism in hydroformylation catalysis by reactions of related hydride, alkyl and acetyl rhodium triphos complexes.[13] During their investigation of rhodium triphos, and related tripodal phosphane complexes, Huttner and co-workers suggested that the κ^3-coordination of the phosphane hinders hydrogenation,[14] and



Scheme 1.

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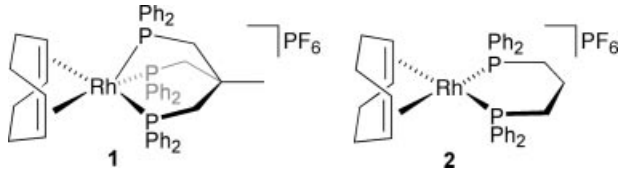
they demonstrated that related diphosphane complexes are significantly more active for the hydrogenation of (*Z*)-α-*N*-acetamidocinnamic acid.[15] Burk and co-workers have also reported similar behaviour for other rhodium tripodal phosphane systems.[16]

To further investigate the importance of phosphane arm-on, arm-off processes in the hydrogenation activity of rhodium triphos complexes, we report here a comparison of the activity of [Rh(COD)(κ^3-triphos)]PF_6 (**1**) with mixtures of the related diphosphane complex, [Rh(COD)(κ^2-dppp)]-PF_6 (**2**), and triphenylphosphane (Scheme 2).[14a,15] To complement these investigations, relevant in situ reactivity studies are also presented together with the demonstration of the κ^2–κ^3 interconversion in complex **1** using a ruthenium complex.

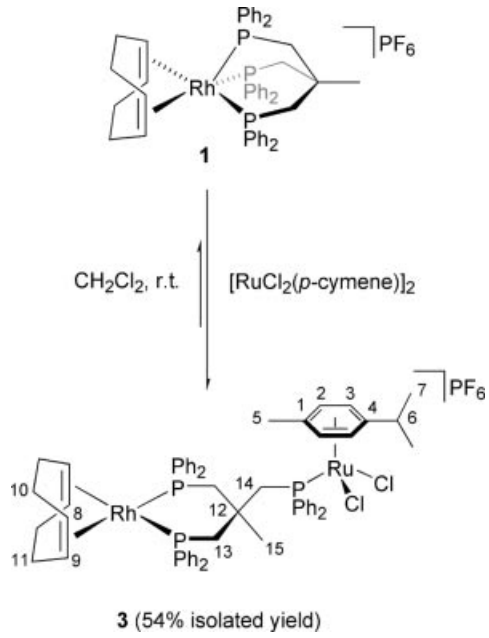


Scheme 2.

Results and Discussion

1. Reaction of 1 with [$RuCl_2$(*p*-cymene)]$_2$

To probe the presence of an arm-on, arm-off process, **1** was reacted at room temperature with the dinuclear ruthenium complex [$RuCl_2$(*p*-cymene)]$_2$, well known to react rapidly with phosphane ligands,[17] in an attempt to trap the κ^2-coordination mode of the triphos ligand. After 30 minutes, analysis of the reaction solution by ^{31}P NMR spectroscopy revealed the formation of the bimetallic complex, [(*p*-cymene)Cl_2Ru{(PPh_2CH_2)CMe(CH_2PPh_2)$_2$}-Rh(COD)]-PF_6 **3**, identified by the presence of characteristic singlet and doublet ($^1J_{RhP}$ = 141 Hz) resonances at δ = 16.6 and 13.1 ppm, respectively, in a 1:2 ratio together with a small quantity of **1** (Scheme 3). Subsequently, **3** was isolated, albeit in moderate yield (54%), following recrystallisation and the structure was further verified by ^{1}H and ^{13}C NMR spec-



Scheme 3. Formation and equilibrium of complex **3** (with NMR numbering scheme).

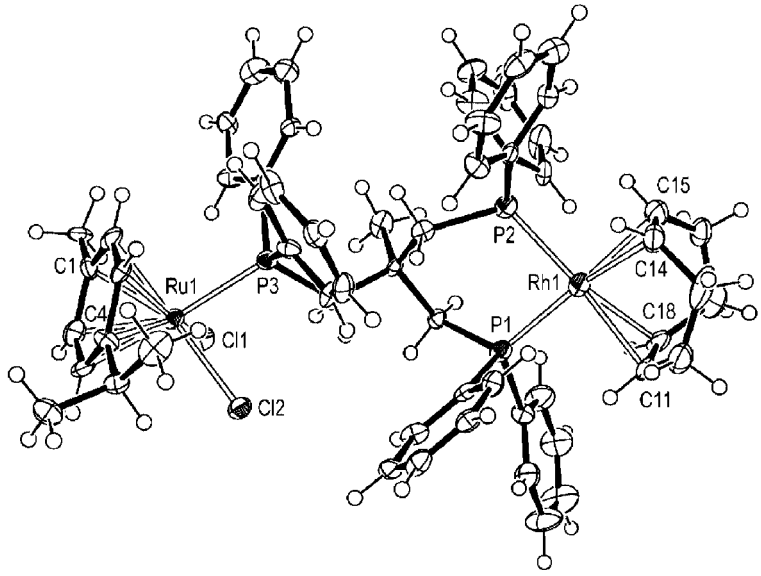


Figure 1.ORTEP representation of **3**; thermal ellipsoids drawn at 50%. Solvent molecules and counter anion omitted for clarity. Key bond lengths [Å] and angles [°]: Ru1–Cl1 2.420(3), Ru1–Cl2 2.421(2), Ru1–P3 2.356(3); Cl1–Ru1–Cl2 88.23(8), Cl1–Ru1–P3 88.37(9), Cl2–Ru1–P1 83.78(8); Ru1–C1 2.200(9), Ru1–C4 2.227(9), Ru1–C_{avg} 2.21(2), Rh1–P1 2.287(3), Rh1–P2 2.286(3); P2–Rh1–P3 88.06(10); Rh1–C11 2.274(8), Rh1–C18 2.263(9), Rh1–C14 2.217(10), Rh1–C15 2.226(10).

troscopy and electrospray ionization mass spectrometry (ESI-MS). Furthermore, the solid-state structure of **3** has been established by X-ray diffraction analysis – depicted in Figure 1. The bonding parameters about the Ru center are similar to related [$RuCl_2$(κ^1-phosphane)(*p*-cymene)] (Ru–P ≈ 2.4 Å)[18] complexes, while those about the Rh center are similar to [Rh(COD)(κ^2-dppp)]BF_4 {**1**·BF_4, Rh–P 2.311(2), 2.319(2) Å; P–Rh–P 90.81(4)°},[19] although the Rh–P bond length and P–Rh–P angle are slightly contracted in **3** in comparison to **1**·BF_4 {Rh1–P1, 2.287(3) Å; Rh1–P2, 2.286(3) Å; P1–Rh–P2, 88.06(10)°}. In CD_2Cl_2 solution at room temperature, **3** undergoes a slow equilibration reaction ($t_{1/2}$ = 22 ± 3 h) in which dissociation of the phosphane from the ruthenium-arene moiety results in an mixture of **1**, **3**, and [$RuCl_2$(*p*-cymene)]$_2$ with a equilibrium constant, *K*, of approximately 2, demonstrating the reversible nature of the triphos coordination.

2. Catalytic Activity

The catalytic activity of **1** and solutions of **2** containing various quantities of triphenylphosphane were first investigated for the hydrogenation of styrene. The hydrogenation experiments were carried out in THF, a weakly coordinating solvent,[20] at 50 °C under 1 bar of H_2 with a substrate to catalyst (S/C) ratio of 200:1; **2** was investigated with 0, 0.5, 1, 2, and 5 equiv. of triphenylphosphane. Conversion was monitored by GC during the reaction and results are listed in Table 1 with selected data depicted in Figure 2. Both complexes were found to exhibit incubation periods, consistent with previously reported kinetic studies on diphosphane rhodium complexes containing the COD ligand (attributed to hydrogenation of the diene).[21] From the hydrogenation curves (Figure 2) it is apparent that **1** is significantly less active than **2** under these conditions. Catalytic runs carried out with **2** in the presence of added triphenylphosphane showed enhanced rates of hydrogenation at 50% conversion in comparison to **2** alone – most pronounced with 1 equiv. of the phosphane. However, in the presence of excess triphenylphosphane significant reductions in the rate of hydrogenation with **2** are observed close to complete conversion (> 90%), resulting in longer reactions times than in the absence of triphenylphosphane (see insert in Figure 2). Addition of mercury, a selective poison for heterogeneous catalysis, did not inhibit catalytic activity for **2** + *n*PPh_3 (*n* = 0 or 1) significantly.[22]

Table 1. Hydrogenation of styrene using **1** and **2** + *n*PPh_3.[a]

	n	50% Conversion Time/h	TOF[b]/h^{-1}	> 99% Conversion Time/h
1		2.83	32	10
2	0	1.72	68	3.5
2[c]	0	1.81	62	4.5
2	0.5	1.63	74	3.5
2	1	1.50	80	3.0
2[c]	1	1.49	80	3.5
2	2	1.65	72	4.0
2	5	1.65	70	4.5

[a] Conditions: 2.6×10^{-5} mol pre-catalyst, S/C = 200:1, 20 mL of THF, 0.1 mL of octane (internal standard), 1 bar H_2. Conversion determined by GC analysis of reaction aliquots. [b] Calculated at 50% conversion from hydrogenation progress. [c] 0.1 mL of Hg added.

In comparison to styrene, the initial rate of cyclohexene hydrogenation using **2** is significantly reduced by the addition of 1 equiv. of triphenylphosphane (Figure 3). However, mercury poisoning experiments suggest a significant degree of heterogeneous character to the active species for **2** alone, whereas, with 1 equiv. of triphenylphosphane there is no significant change in activity in the presence of mercury (Figure 3 and Table 2). This difference is also apparent to some degree by significant darkening of the reaction solution after ca. 90 min in the absence of triphenylphosphane, whereas with 1 equiv. of triphenylphosphane the solution remains yellow throughout the reaction. For **1**, the initial rate of hydrogenation is comparable to **2** with 1 equiv. of triphenylphosphane, although activity is gradually reduced and is accompanied by the reaction solution becoming green/brown – consistent with decomposition into inactive molecular species.

Together, these results are consistent with the ability of the triphos ligand to undergo reversible phosphane arm-off coordination during catalysis. While the catalytic activity of

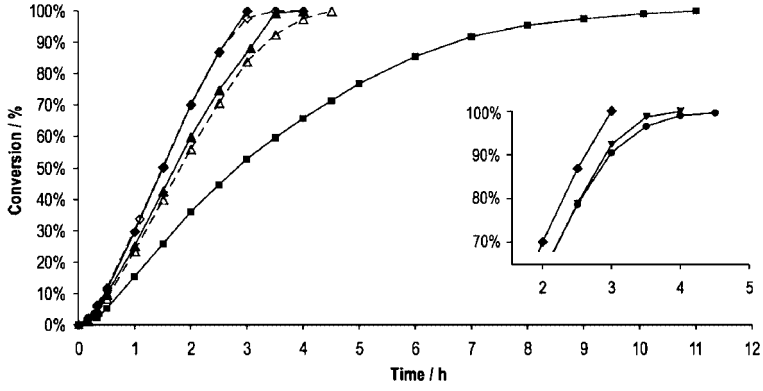


Figure 2. Hydrogenation of styrene using **1** (–■–) and **2** + *n*PPh_3 (*n* = 0, –▲–; 1, –♦–; 2, –▼– insert only; 5, –●– insert only). Mercury poisoning experiments for **2** + *n*PPh_3 (*n* = 0, --Δ--; 1, --◇--) are shown with dashed lines.

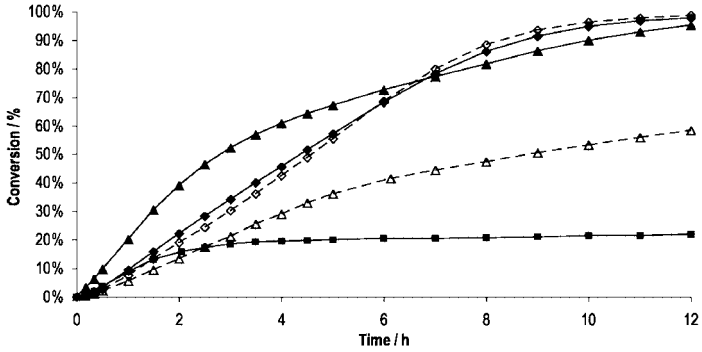


Figure 3. Hydrogenation of styrene using **1** (–■–) and **2** + *n*PPh_3 (*n* = 0, –▲–; 1, –♦–). Mercury poisoning experiments for **2** + *n*PPh_3 (*n* = 0, --Δ--; 1, --◇--) are shown with dashed lines.

Table 2. Hydrogenation of cyclohexene using **1** and **2** + *n*PPh_3.[a]

	n	50% Conversion Time/h	TOF[b]/h^{-1}
1		_[c]	_[c]
2	0	2.81	24
2[d]	0	8.78	6
2	1	4.36	22
2[d]	1	4.59	26

[a] Conditions: 2.6×10^{-5} mol pre-catalyst, S/C = 200:1, 20 mL of THF, 0.1 mL of octane (internal standard), 1 bar H_2. Conversion determined by GC analysis of reaction aliquots. [b] Calculated at 50% conversion from hydrogenation progress. [c] Conversion < 50%. [d] 0.1 mL of Hg added.

1 is attributed to the ability of the triphos ligand to undergo an arm-off dissociation process, leading to active species containing the κ^2-coordinated ligand and a vacant coordination site (i.e. becoming directly analogous to **2**), the adoption of the κ^3-mode during catalysts is suggested to complete with substrate significantly during catalysis resulting in significantly lower activity than **2**. This suggestion is supported by similar reductions in activity observed for the hydrogenation of styrene with **2** and excess triphenylphosphane, but only near reaction completion, when substrate concentration is low. The reduced effect of triphenylphosphane coordination in comparison to the arm-on, arm-off process in **1** is presumably due to the absence of the chelate effect and the bulky nature of triphenylphosphane. (*Note:* no reaction with **2** and triphenylphosphane can be detected in THF cf. κ^3-coordination of the triphos ligand in **1**.) The failure of **1** to hydrogenate cyclohexene to completion may also be rationalised by the tendency of the triphos ligand in **1** to adopt a κ^3-coordination mode. This feature together with the more hindered nature of cyclohexene could be responsible for the decomposition observed with this substrate in comparison with styrene.

While the arm-on coordination appears to be detrimental the catalytic activity of **1**, the addition of triphenylphosphane, in an attempt to mimic this behaviour,[23] during catalysis with **2** had a number of beneficial outcomes. For example, in the hydrogenation of cyclohexene with **2**, addition of triphenylphosphane appeared to stabilise the metal center, i.e. by reversible coordination, preventing decomposition with only a minor decrease in activity. For styrene, addition of, for example, one equivalent of triphenylphosphane noticeably increased the rate of hydrogenation. As Osborn-type rhodium and iridium complexes are known to react with arenes under hydrogenation conditions to form inactive species of the type, $[M(\eta^6\text{-arene})L_2]^+$,[20] reversible coordination of triphenylphosphane may help prevent the formation of species of this nature and thus enhance the rate of hydrogenation. This possibility was thus investigated further (see below).

3. Effect of Triphenylphosphane on the Formation of $[Rh(\eta^6\text{-toluene})(\kappa^2\text{-dppp})]^+$

To further investigate the enhancement of catalytic activity of **2** with triphenylphosphane for styrene hydrogenation, reactions of **2** with hydrogen (ca. 12 bar) in the presence of toluene (ca. 80 equiv.) and triphenylphosphane were carried out in medium pressure sapphire NMR tubes.[24,25] In the absence of triphenylphosphane, following COD hydrogenation, $[Rh(\eta^6\text{-toluene})(\kappa^2\text{-dppp})]^+$ **4** is formed quantitatively.[26] However, in the presence of 5 equiv. of triphenylphosphane **4** cannot be detected and instead a species assigned to *cis*-$[RhH_2(PPh_3)_2(\kappa^2\text{-dppp})]^+$ **5** is observed in ca. 94% yield.[27] The identity and geometry of this species is deduced primarily from the $^{31}P\{^1H\}$ NMR spectrum, which exhibits four distinct phosphorus resonances with characteristic multiplicity and coupling constants (Figure 4). Notably, those centred at δ = 31.3 and 18.3 ppm exhibit large $^2J_{PP}$ coupling constants of 318 Hz, suggesting a *trans* arrangement of two of the phosphane moieties,[28] and $^1J_{RhP}$ coupling constants of ca. 100 Hz. The other phosphorus resonances, centred at 21.6 and –3.6 ppm, have smaller $^1J_{RhP}$ coupling constants (82 and 85 Hz) consistent with phosphane moieties *trans* to hydride ligands.[29] The remaining $^2J_{PP}$ coupling constants, ca. 20 Hz, are typical for *cis*-coordinated phosphane ligands.[28] Furthermore, the ^1H NMR spectrum exhibits two broad doublets at –10.55 and –11.33 ppm with $^2J_{PH}$ coupling constants of 132 and 136 Hz, respectively. A similar species, containing instead a tetradentate phosphane, has been reported by Bianchini and co-workers.[30]

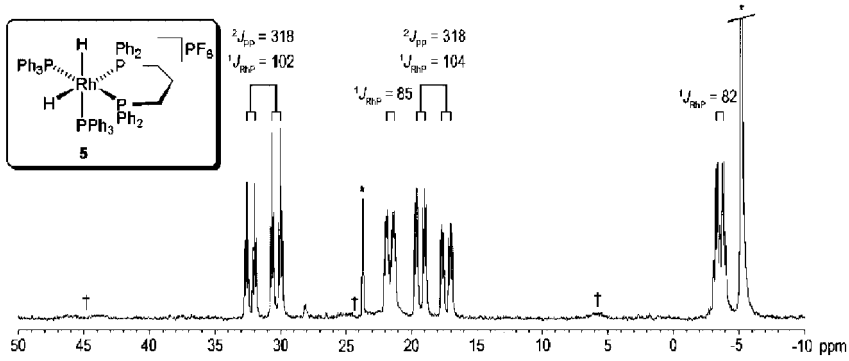
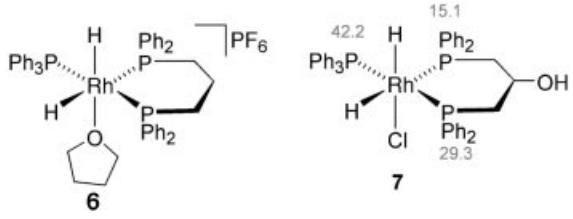


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of **5**. * PPh_3 ($\delta \approx 5$ ppm) and $OPPh_3$ ($\delta \approx 24$ ppm), † denotes complex **6**.

In the presence of 1 equiv. of triphenylphosphane **4** is formed, although only in modest yield (ca. 24%), together with a new species, exhibiting two broad doublets of doublets at 45.0 ($^2J_{PP}$ = 340 Hz, $^1J_{RhP}$ = 112 Hz) and 24.0 ppm ($^2J_{PP}$ = 340 Hz, $^1J_{RhP}$ = 112 Hz) and a broad resonance at 5.8 ppm (ca. 54%), and a small amount of **5** (ca. 12%). This new species is tentatively assigned as *cis*-$[RhH_2(THF)(PPh_3)(\kappa^2\text{-dppp})]^+$ (**6**, Scheme 4) on the basis of these data and their good agreement with that of the known complex *cis*-$[RhH_2Cl(PPh_3)(\kappa^2\text{-}\{PPh_2CH_2\}_2CHOH)]$ **7** (Scheme 4).[27,31] A small quantity of this complex is also observed during the reaction with 5 equiv. (ca. 4%).



Scheme 4. Proposed structure of **6** and the known compound **7** {annotated with ^{31}P NMR spectroscopic data ([D_8]toluene / ppm)}.[31]

Combined these data are consistent with the ability of triphenylphosphane to hinder the coordination of arene substrates or products under catalytic conditions, supporting the observation of enhanced activity on addition of triphenylphosphane during hydrogenation of styrene with complex **2**.

Concluding Remarks

The influence of the phosphane arm-on, arm-off process in rhodium triphos complexes for hydrogenation catalysis has been further established by comparison to related dppp systems with added triphenylphosphane. Despite further evidence for facile dissociation of one of the triphos arms in these systems, by the reaction of **1** with $[RuCl_2(p\text{-cymene})]_2$, the tendency of this ligand to adopt a κ^3-coordination appears to significantly encumber catalytic activity by competing with the substrate for vacant coordination sites on the metal. In comparison, in an attempt to mimic the κ^3-coordination motif in the triphos complex, added triphenylphosphane results in the enhancement of the rate of catalytic activity during the hydrogenation of styrene with **2**, although with excess triphenylphosphane, reduction in the hydrogenation rate close to completion is observed – upholding the proposed reduction of activity by κ^3-coordination of the triphos ligand in **1**. The enhanced rate of styrene hydrogenation is attributed to the ability of triphenylphosphane to prevent the coordination of the substrate or product (by weak and reversible coordination) during catalysis, and this hypothesis is supported by medium pressure in situ reactions of **2** with H_2, toluene and different quantities of triphenylphosphane. The use of triphenylphosphane with **2** also has the beneficial effect of stabilizing the metal center towards decomposition during catalysis as demonstrated in the hydrogenation of cyclohexene.

Experimental Section

General: All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents (CH_2Cl_2, THF, toluene) were dried catalytically under dinitrogen using a solvent purification system, manufactured by Innovative Technology Inc. All other solvents were p.a. quality and saturated with nitrogen prior to use. Styrene and cyclohexene were saturated with nitrogen and stored over activated molecular sieves. $[Rh(COD)(\kappa^3\text{-triphos})]PF_6$ (**1**),[15] $[Rh(COD)(\kappa^2\text{-dppp})]PF_6$ (**2**),[14a] and $[RuCl_2(p\text{-cymene})]_2$[32] were prepared as described elsewhere. All other chemicals are commercial products and were used as received. NMR spectra were recorded with a Bruker Avance 400 spectrometer at room temperature, unless otherwise stated. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. The NMR labelling for complex **3** is given in Scheme 3. ESI-MS were recorded on a Thermo Finnigan LCQ DecaXP Plus quadrupole ion trap instrument according to a literature protocol;[33] CH_2Cl_2 was used as the solvent for all experiments with a capillary temperature of 80 °C and spray voltage of 5.0 kV.

Preparation of $[(p\text{-Cymene})Cl_2Ru\{(PPh_2CH_2)CMe(CH_2PPh_2)_2\}Rh(COD)]PF_6$ (3): A solution of $[Rh(COD)(\kappa^3\text{-triphos})]PF_6$ (0.070 g, 0.071 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.022 g, 0.036 mmol) in CH_2Cl_2 (10 mL) was stirred at room temp. for 30 min. The solution was then concentrated to ca. 5 mL and hexane (ca. 10 mL) added precipitating out a small amount of a un-

identified brown impurity, which was removed by filtration. The product was obtained as a microcrystalline orange solid from the filtrate upon standing at –20 °C. Yield 0.049 g (54%). Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2/hexane solution of the complex at –20 °C. ^{1}H NMR (CD_2Cl_2): δ = 7.26–7.92 (m, 30 H), 5.12 (d, $^3J_{HH}$ = 6.1, 2 H, H^3), 5.07 (d, $^3J_{HH}$ = 5.7, 2 H, H^2), 4.74–4.84 (m, 2 H, H^8), 4.01–4.11 (m, 2 H H^9), 3.00–3.10 (m, 2 H, H^{13}), 2.70–2.78 (m, 2 H, H^{14}), 2.59 (sept, $^3J_{HH}$ = 6.9, 1 H, H^6), 2.41–2.50 (m, 2 H, H^{10}), 2.30–2.41 (m, 2 H, H$^{10'}$), 2.06–2.21 (m, 4 H, H^{11}), 1.83–1.96 (m, 2 H, H$^{13'}$), 1.78 (s, 3 H, H^5), 1.05 (d, $^3J_{HH}$ = 7.0, 6 H, H^7), –0.09 (s, 3 H, H^{15}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 127–135 (m), 109.6 (s, C^4), 104.4–104.9 (m, C^9), 98.8–99.3 (m, C^8), 95.3 (s, C^1), 89.9 (d, $^2J_{PC}$ = 3, C^2), 86.3 (d, $^2J_{PC}$ = 6, C^3), 45.0–45.7 (m, C^{14}), 39.7 (d, $^2J_{PC}$ = 6, C^{12}), 36.2–36.9 (m, C^{13}), 31.4 (s, C^{15}), 30.3 (s, C^6), 30.0 (s, C^{10}), 29.9 (s, C^{11}), 21.4 (s, C^7), 17.1 (s, C^5) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 16.6 (s, 1 P, Ru*P*Ph$_2$), 13.1 (d, $^1J_{RhP}$ = 141, 2 P, Rh*P*Ph$_2$), –144.4 (sept, $^1J_{PF}$ = 711, 1 P, *P*F$_6$) ppm. ESI-MS (CH_2Cl_2, 80 °C, 5 kV) positive ion: *m*/*z*, 834 (30%) [M –RuCymeneCl$_2$]$^+$, 1141 [M]$^+$. ESI-MS^2 (+1141): *m*/*z*, 834 [M – RuCymeneCl$_2$]$^+$. $C_{59}H_{65}Cl_2F_6P_4RhRu$ (1286.94 g mol^{-1}): calcd. C 55.07, H 5.09; found C 55.14, H 5.11.

Medium Pressure NMR Experiments: Reactions of **2** (9 mg) with H_2 (12 bar) and toluene (0.1 mL, ca. 80 equiv.) were carried out in 10 mm sapphire NMR tubes in THF (2.5 mL) with the appropriate quantity of triphenylphosphane. All samples were prepared under nitrogen. Reaction progress was followed by ^{31}P NMR spectroscopy until complete consumption of **2** was observed, typically < 5 h (no further change in product distributions were observed). Selected ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data for **5** and **6** follow; referenced externally to TMS and 85% H_3PO_4, respectively. ^{1}H NMR (**5**, THF, hydride region): δ = –10.55 (br. d, $^2J_{PH}$ = 132, 1 H), –11.33 (br. d, $^2J_{PH}$ = 136, 1 H) ppm. ^{31}P{^{1}H} NMR (**5**, THF): δ = 31.3 (ddt, $^2J_{PP}$ = 318, $^1J_{RhP}$ = 102, $^2J_{PP}$ = 21, 1 P), 21.6 (dq, $^1J_{RhP}$ = 85, $^2J_{PP}$ = 20, 1 P), 18.3 (dddd, $^2J_{PP}$ = 318, $^1J_{RhP}$ = 104, $^2J_{PP}$ = 26, $^2J_{PP}$ = 16, 1 P), 3.6 (dq, $^1J_{RhP}$ = 82, $^2J_{PP}$ = 23, 1 P) ppm. ^{31}P{^{1}H} NMR (**6**, THF): δ = 45.0 (br. d, $^2J_{PP}$ = 340, $^1J_{RhP}$ = 112, 1 P), 24.0 (br. d, $^2J_{PP}$ = 340, $^1J_{RhP}$ = 112, 1 P) 5.8 (br., 1 P) ppm. The hydride region of the ^{1}H NMR spectrum of **6** was broad and uninformative.

Catalytic Evaluations: Catalytic experiments were conducted in a 50 mL three-necked round-bottomed flask equipped with a 2.0 L latex balloon (Dräger/2165694) connected via a 6 cm reflux condenser and gas tap, a septum cap and gas adaptor. Following pressurisation of the balloon with hydrogen (1 bar), via successive vacuum hydrogen cycles, the flask was charged with pre-catalyst (2.6×10^{-5} mol) and magnetic stirring bar and placed under an inert atmosphere. THF (20 mL), octane (0.1 mL), substrate (5.2×10^{-3} mol) and, for the poisoning experiments, mercury (0.1 mL) were then added via syringe through the septum cap. The system was then placed under H_2 by three vacuum/H_2 cycles and then heated at 50 °C. The hydrogenation was followed by sampling the reaction solution at *t* = 10, 20, 30, 60, 90, 120, 180, 210, 240, 270, 300 min and every successive hour up to *t* = 12 h by GC (Varian chrompack CP-3380 gas chromatograph) or until reaction completion. Full hydrogenation data is given in the supplementary material.

Crystallography: Relevant details for the structure refinement are given in Table 3 and selected geometrical parameters for **3** are found in caption of Figure 1. Data collection for the X-ray structure determination was performed on a KUMA CCD diffractometer system using graphite monochromated Mo-K_α radiation (0.71073 Å) and a low-temperature device [140(2) K]. Data reduction was performed using CrysAlis RED.[34] The structure was solved using SIR97,[35] and refined (full-matrix least-squares on F^2) using SHELXTL.[36] An absorption correction was applied to the data set (empirical, DELABS).[37] All non-hydrogen atoms were refined anisotropically, with hydrogen atoms placed in calculated positions using the riding model. The occupancy of one of the CH_2Cl_2 molcules was refined to 66% and it was necessary to retrain the displacement parameters of some atoms. The graphical representation of **3** was made with ORTEP3.[38]

Table 3. Crystal data and details of the structure determinations of **3**.

Formula	$C_{59}H_{65}Cl_2F_6P_4RhRu\cdot4.66\,CH_2Cl_2$
M	1682.81
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	11.8544(10)
b /Å	16.506(2)
c /Å	19.485(2)
α /°	105.563(10)
β /°	90.054(8)
δ /°	100.954(9)
V /Å^3	3600.5(7)
Z	2
Density /g cm^{-3}	1.552
μ /mm^{-1}	1.002
θ range /°	$3.09 < \theta < 25.25$
Measured reflections	21093
Unique reflections	11146 [R_{int} = 0.0832]
Number of data/restraints/parameters	11146/126/798
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	*R*1 = 0.0622, *wR*2 = 0.1122
Largest diff. peak and hole /e Å^{-3}	1.377 and –0.975 [rms = 0.112]
GoF[b]	0.819

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [b] $GoF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

CCDC-645738 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Full hydrogenation profiles for catalysis with **1** and **2**.

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