Synthesis and Characterisation of Nonclassical Ruthenium Hydride Complexes Containing Chelating Bidentate and Tridentate Phosphine Ligands


Abstract: The synthesis and characterisation of nonclassical ruthenium hydride complexes containing bidentate PP and tridentate PCP and PNP pincer-type ligands are described. The mononuclear and dinuclear ruthenium complexes presented have been synthesised in moderate to high yields by the direct hydrogenation route (one-pot synthesis) or in a two-step procedure. In both cases [Ru(cod)-(metallyl)] served as a readily available precursor. The influences of the coordination geometry and the ligand framework on the structure, binding, and chemical properties of the M–H2 fragments were studied by X-ray crystal structure analysis, spectroscopic methods, and reactivity towards N2, D2, and deuterated solvents.

Keywords: chelates • dihydrogen complexes • hydrides • phosphine ligands • ruthenium

Introduction

The discovery of stable transition-metal complexes with molecular dihydrogen as a side-on bound ligand by Kubas et al. in 1983 was a breakthrough in the historical development of coordination chemistry.[1] Since then, dihydrogen complexes of transition metals have been the subject of considerable interest because they present models for the metal-induced activation of the hydrogen molecule,[2–4] either through oxidative addition or heterolytic cleavage.[2,3,5–8] In general, it is possible to obtain nonclassical metal–hydride complexes by direct reaction with hydrogen, by protonation of hydride complexes, or by reduction reactions.[3b] Stable coordination between the molecular dihydrogen and a metal centre is based on two contributions: the donation from the filled H2 s orbital to the empty d orbitals on the metal, and the back-bonding of the d electrons to the antibonding s* orbital of the hydrogen ligand. Thus, several factors, such as the ability of the metal to donate electrons and the nature of the ligand in the trans position, influence the stability and the reactivity of the M–H2 unit.[3,4,9] As recently highlighted by van Leeuwen et al., the structural demands of an ancillary chelating ligand can also play an important role in defining the properties of the η2-H2 ligand.[10] In the present paper, we report on the synthesis and characterisation of new nonclassical ruthenium hydride complexes with constrained ligand geometries, which substantiate the importance of well-defined structural features for the H2-binding mode and reactivity.[11]
[Ru(H₂)₂(PCy₃)₂] (1) (Cy = cyclohexyl, Figure 1). This species was proven to possess a unique structure with two classical hydrides and two molecular dihydrogen ligands in mutually cis positions as confirmed most recently by neutron diffraction for [Ru(H₂)(H)(PCyp₃)] (Cyp = cyclopentyl). Meanwhile, several ruthenium complexes containing nonclassical hydride ligands have been synthesised, allowing a better understanding of the stability, reactivity, and binding mode of the η⁻H₂ moiety. Complex 1 has found application as a starting material for a variety of ruthenium–dihydrogen complexes. Moreover, it has been used as a catalyst precursor for hydrogenation. The IR spectra of complexes 4a and 4b are readily obtained by hydrogenation of the allyl complexes 7a and 7b following a procedure previously developed in our group (Scheme 1). Under optimised conditions, 4a and 4b have been isolated in fair to excellent yields as orange microcrystalline solids directly from the reaction mixture upon cooling and filtration. Complex 4a shows high solubility in aromatic solvents and is remarkably stable in the solid state, even in the presence of air or under vacuum. Although the compounds are too thermally labile to detect the molecular ions directly, the fragmentation observed in mass spectroscopic analysis confirms a dinuclear structure for complex 4a.

The IR spectra of complexes 4a and 4b show characteristic bands that are readily assigned to terminal hydrides (Ru–H) and bridging hydrides (Ru-H-Ru), located for 4a at ŷ 1990 and 1552 cm⁻¹, respectively. As other parts of the IR...
The 1H NMR spectrum of 4a shows a single averaged signal for all hydridic ligands as a slightly broad singlet centred at $\delta = -11.8$ ppm, which integrates for six H atoms at various relaxation delays. The chemical shift value has also been confirmed by $^2$H NMR experiments with [D$_6$]-4a. When [D$_6$]-4a was generated in situ by charging a solution of 4a in [D$_8$]toluene with D$_2$ gas in a Young NMR tube, the deuteronium spectrum also revealed several signals between $\delta = 1.1$ and 1.9 ppm. These signals indicate H/D exchange by a C–H activation process at various positions of the dcpp ligands. The $^{31}$P NMR signal of 4a, which at room temperature is detected at $\delta = 69.5$ ppm, splits into two broad signals when the temperature is lowered to $\approx -80$°C. The high-field proton signal does not yet show significant decoherence at this temperature. Owing to the fast exchange between classical and nonclassical hydrides even at low temperature, it was not possible to determine separate resonance frequencies for the individual hydridic ligands or to measure P–H coupling constants.

In order to further evaluate the nature of the hydridic ligands in complex 4a, the minimum relaxation time $T_1$(min) was determined.$^{[26]}$ The values measured with a 400 MHz NMR spectrometer at various temperatures are graphically displayed in Figure 3. The $T_1$(min) for 4a was determined as 53 ms at 271 K. A comparison with the values reported for other similar complexes confirms the presence of a nonclassical structure, which is usually associated with $T_1$(min) $< 100$ ms. An H–H distance of 104 pm (±1 pm based on instrumental errors) can be calculated from the $T_1$(min) measurement. Owing to dynamic exchange with the other hydride signals, this value can be regarded only as the upper limit for the distance in the coordinated H$_2$ moiety, however.

Figure 3. Temperature-dependent evolution of the $T_1$ values measured for 4a. $T_1$/ms (A3 ms) [7/K (A2 K)]: 64 [300], 56 [283], 55 [263], 65 [243], 108 [223].

Additional evidence for the presence of a $\sigma$-coordinated hydrogen molecule is provided by the reaction of complex 4a with molecular nitrogen to form the complex [H-(dcpp)Ru($\mu$-H)_2Ru(dcpp)(N$_2$)] (8).$^{[1,3,4]}$ After exposure of a [D$_8$]toluene solution of 4a to a nitrogen stream in a Young valve NMR tube, the high-field region of the 1H NMR spectrum shows, together with a small signal for the starting complex, one apparent doublet at $\delta = -9.2$ ppm ($\Delta\nu = 53$ Hz), one broad signal at $\delta = -15.5$ ppm and one triplet at $\delta = -19.4$ ppm (t. $^2$(H,P) = 33 Hz). The $^{31}$P NMR shows two signals of equal intensity at $\delta = 75.1$ ppm (s) and $\delta = 47.1$ ppm (s) and reveals 9% of the starting material at $\delta = 68$ ppm (s). The reaction is reversible and compound 4a is quantitatively restored when the same solution is exposed to hydrogen gas. Interestingly, 4a can also easily be converted to 8 in the solid state under 14 bar nitrogen pressure, indicating that the coordination sphere in both solution and solid state is identical.

The solid-state structure of the ruthenium hydride 4a was determined by single-crystal X-ray structure analysis. Crystals of 4a, suitable for X-ray investigation, were obtained by slow evaporation of a hexane solution under hydrogen atmosphere. Figure 4 depicts a graphical representation of the molecular structure and Table 1 summarises selected bond lengths and angles.$^{[25]}$ Notably, all hydrogen atoms in the coordination sphere of the ruthenium centres could be located and fully refined.

Figure 4. ORTEP diagram of the molecular structure of 4a as determined by single X-ray diffraction.

The dimeric structure of 4a is made of two slightly distorted octahedra, whose centres are occupied by the two ruthenium atoms. The phosphine groups exhibit an anticline arrangement, which minimises the steric effect of the cyclohexyl groups in the backbones. The bite angle measured for the two dcpp ligands in 4a ($\simeq 95^\circ$) is slightly larger than previously reported for 7a ($\simeq 91.3^\circ$).$^{[25]}$ The distances between the bridging hydrides and the ruthenium centres are significantly longer than those measured for the remaining hydro-
gen atoms. Most significantly, two hydrogen atoms were located in an arrangement characteristic of a coordinated H₂ molecule at Ru1 with an H–H distance of 0.83 Å. Considering the dynamic behaviour of 4a in solution, this value is in full agreement with the upper limit derived from T1 measurements. The H₂ moiety is almost fully aligned with the plane described by the phosphorus atom P2, the ruthenium centre Ru1, and the bridging hydride H2. This arrangement may be explained in terms of a favourable overlap between the σ*- on H₂ and a filled d orbital on the metal, which allows most efficient backbonding.

Comparison of the structure of complex 4a with the known dimeric ruthenium hydride complexes 9 and 10, containing nonchelating phosphine ligands (Figure 5)[29] contributes to a better understanding of how the electronic and structural environment around the metal centre affects the hydrogen coordination. It has been shown that complex 9, with its PPh₃ ligand, must be formulated as a nonclassical dihydrogen complex,[29a] whereas complex 10, with the PPr₃ ligand adopts the form of a classical dihydride.[29b] Following classical arguments, this difference arises because the stronger basicity of the PPr₃ ligand favours back donation into the antibonding orbital of the coordinated σ-H₂ ligand, which leads finally to rupture of the H–H bond. However, based on the basicity of the phosphine ligands, a classical dihydride structure would also be expected for complex 4a (dppe: pKᵢ⁻≈10; PPr₃: pKᵢ⁻≈8; PPh₃: pKᵢ⁻ = 2.7).[29] which is obviously not in agreement with the experimentally determined structure in the solid state and in solution.

A closer inspection of the molecular structures of the three complexes reveals that the coordination geometry in the P-Ru-P unit plays a more important role in defining the bonding situation of the Ru–H₂ moiety than does the ligands basicity.[10] It is well known that changes in P-M-P coordination geometry can influence the electronic properties at the metal centre more strongly than purely electronic factors through changes in the hybridisation[30a] or by changing the overlap of the lone pair of the donor with the M²⁺ trajectory.[30b] In the present case, the -(CH₂)₃- backbone in dppe fixes the two donor units in a cis arrangement with a bite angle of 95.3 (P1-Ru1-P2) and 95.9° (P3-Ru2-P4), very similar to the one observed in 9b (≈95°). The bulky PPr₃ ligands in 10 maximise their distance freely, thus widening the P-Ru-P angles to 113.10° (P1-Ru1-P2) and 106.75° (P3-Ru2-P4). Thus, the nonclassical structure in the dimeric complexes can be associated with the smaller bite angle, whereas the dihydride structure is adopted for larger bite angles. If the angle opens up fully to adjust a trans arrangement of the two donor ligands, the dimeric structures break up to form the monomeric complexes of type 1-3 in the presence of excess hydrogen. Naturally, this is not possible if the cis arrangement is permanently fixed as in the complexes with bidentate ligands.

In an attempt to generate monomeric nonclassical ruthenium hydride complexes with a chelating ligand framework, we turned our attention toward pincer-type ligands that allow a trans arrangement of two electron-rich and bulky phosphorous donor groups. In a one pot procedure, [Ru2(cod)(metal)],) 11 was hydrogenated (7 bar) at 50°C in the presence of phosphine 12. A reddish-brown solid precipitated from MeOH solution and was isolated by filtration of the reaction mixture at room temperature.

1H NMR and 31P NMR analysis in [D₈]THF solution confirmed the presence of the new nonclassical polyhydride complex [Ru(dtbpbm)(H₂)₂] 5 (dtbpbm = 1,3-bis(di-tert-butylphosphino)methylen) as major reaction product, together with small amounts (<10%) of unidentified side products. In solution the nonclassical trihydride 13 is generated owing to loss of H₂ (38%). The two dihydrogen complexes 5 and 13 result from coordination of the ligand and intramolecular C–H activation at the 2-position in the aromatic ring (Scheme 2).[31] At room temperature the five hydrogen atoms in the coordination sphere of the ruthenium centre of complex 5 give rise to an average broad signal centred at δ = –9.21 ppm, while the equivalent phosphorous atoms lead to a singlet at δ = +107.8 ppm in the 31P NMR spectrum. 1H NMR experiments performed at low tempera-

Table 1. Selected distances and angles of complex 4a.

<table>
<thead>
<tr>
<th>Distances [Å]</th>
<th>Angles [°]</th>
</tr>
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<tr>
<td>Ru1–H1</td>
<td>1.83 (4) H1-Ru1-H2</td>
</tr>
<tr>
<td>Ru1–H2</td>
<td>1.78 (3) H2-Ru1-H3</td>
</tr>
<tr>
<td>Ru1–H3</td>
<td>1.73 (3) H5-Ru1-H3</td>
</tr>
<tr>
<td>Ru1–H5</td>
<td>1.68 (4) H5-Ru1-H3</td>
</tr>
<tr>
<td>Ru1–H6</td>
<td>1.63 (6) H6-Ru1-H3</td>
</tr>
<tr>
<td>Ru2–H1</td>
<td>1.84 (4) P1-Ru1-Ru2</td>
</tr>
<tr>
<td>Ru2–H2</td>
<td>1.91 (3) H4-Ru1-H2</td>
</tr>
</tbody>
</table>

Figure 5. Dinuclear ruthenium hydride complexes 9a (R = Cy), 9b (R = Ph), and 10 (R = iPr) containing nonchelating phosphine ligands.

Ruthenium Hydrides

CDCl$_3$ at room temperature gave the known ruthenium complex [Ru(dtbpmb)HCl] 16 according to $^1$H and $^{31}$P NMR (Scheme 3,[23a,31])

$[\text{Ru}(\text{cod})(\text{metallyl})]_2$ 11 reacts cleanly under similar conditions with the direct hydrogenation route and the PNP pincer ligand dtbpmb 17 to give the complex [Ru(dtbpmb)H$_2$] 6 (Scheme 4). Complex 6 is isolated directly from the reaction mixture by filtration at room temperature; it is a light-brown, microcrystalline powder obtained good yields under optimised conditions. In contrast to the situation in complex 5, the neutral two-electron donor group of the pyridine moiety in 17 results in the coordination of two classical hydrides and one molecular hydrogen ligand. At room temperature, the $^1$H NMR spectrum has a signal at $\delta = -7.3$ ppm (t, 4H, $^2J(H,P) = 13.2$ Hz) and upon cooling the sample to $-80^\circ$C the triplet changes to a broad signal. $T_1$ was measured to be $77$ ms at $\theta_{\text{trans}} = 228$ K (Figure 6), resulting in an upper limit of $111$ ppm ($\pm 1$ pm, based on instrumental error) for the H–H distance in the H$_2$ moiety.

In the $^3$P NMR spectrum, the signal was found at $\delta = 104.3$ ppm. The pentahydride complex is generated in solution by H$_2$ loss. The dihydrogen ligand in complex 6 can be replaced by N$_2$, but the reactivity of 6 differs significantly from that of complexes 1–4 (Scheme 5). Firstly, the ligand exchange is relatively slow (66% conversion after 90 min) and small amounts of unreacted 6 can be detected by $^1$H NMR spectroscopy even after bubbling a stream of nitrogen through a solution of 6 in [D$_8$]toluene overnight. Furthermore, the complex [Ru(dtbpmb)H$_2$(N$_2$)] 18 (we assume it to be monomeric but a dinitrogen-bridged dimer cannot be excluded of course) $^{31}$P NMR: $\delta =$ +99.6 ppm; $^1$H NMR: $\delta = -4.6$ (t, $^2J(H,P) = 16.81$ Hz) and $-12.8$ ppm) appears to be unstable and converts to a dynamic system of presumably polynuclear complexes as indicated by two sets of broad signals at $\delta = +81$–74 and $+70$–65 ppm (see Supporting Information for details). This process is fully reversible and complex 6 is restored quantitatively (by NMR) under hydrogen atmosphere.

$^1$H NMR studies of the long term stability of complex 6 in aromatic solvents reveal an interesting H/D exchange pro-

cess in [D₆]toluene or C₆D₆, whereby complex 6 incorporates deuterium from the solvents into the PNP pincer backbone ([D₆]-6, Scheme 6). Preferably, the C4 position of the pyridyl system (δ = 6.5 ppm; ≥ 95% D) and the benzylic positions (δ = 3.1 ppm; ∼ 25% D) are deuterated within 72 h at room temperature. Interestingly, the hydride area of the ¹H NMR still shows hydridic signal at this stage. This indicates that a slow H/D exchange between 6 and the solvent is followed by a rapid exchange at the pincer backbone from the intermediate ruthenium deuteride. After three weeks, the sealed NMR sample also shows a decrease of from the intermediate ruthenium deuteride. After three

The expected bands between 1488 and 1202 cm⁻¹ for ruthenium deuterides could not be detected in the indicated area. These results show that a synthesis of [D₆]-6 seems impossible because during the synthesis under D₂ gas rapid H/D scrambling occurs and finally a partly deuterated pincer backbone is obtained and the expected ruthenium deuterides are exchanged to ruthenium hydrides.

**Conclusion**

In summary, we have presented the synthesis and characterisation of two types of nonclassical ruthenium hydride complexes containing chelating ligands with defined coordination geometries. The straightforward preparation is achieved by hydrogenation of readily available bis-methallyl complexes. Dimeric complexes of type 4 are obtained with bidentate cis chelating phosphine ligands, whereas monomeric complexes 5 and 6 can be generated with tridentate PCP and PNP pincer ligands. The presence of coordinated dihydrogen molecules was confirmed by X-ray structure analysis and IR and NMR spectroscopic techniques. The stable coordination of the H₂ molecule in the binuclear polyhydride complexes is strongly influenced by the coordination geometry, which appears to play a more decisive role than the basicity of the P donor groups.

The monomeric complex 6 with a PNP pincer ligand shows an interesting reactivity in particular relating to C–H bond activation processes. Whereas it is typically the acidic benzylic position that is activated in other ruthenium complexes of this ligand class,[32] complex 6 shows a strong preference for the activation of aromatic C–H bonds. The implication of this reactivity for catalysis is currently under investigation in our laboratories and will be reported separately.

**Experimental Section**

**General:** All reactions were performed under Ar, H₂, D₂, or N₂ atmospheres using Schlenk or glove-box techniques. Solvents and substrates were purchased from Aldrich, Acros, and Strem and were purified according to standard procedures.[23] The PNP ligand dtbpmp 17 was synthesised according to the procedure by Milstein et al.[24] and Hartwig and Kawatsura.[25] The allyl complexes 7a and 7b were prepared according to a previously reported synthesis.[26] The syntheses of the ruthenium hydrides were carried out in a modified thick-walled glass reactor (Büchi Glas Uster Miniclave), comparable with a Fischer–Porter bottle.

**SAFETY WARNING:** The use of pressurised gases can be hazardous and must only be carried out with suitable equipment and under appropriate safety precautions.

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[H(dppe)Ru(p-H)(dppe)] (4a): Allylic complex 7a (259 mg, 0.4 mmol) and hexane (5 mL) were introduced in a thick-walled glass reactor, which was subsequently charged with H₂ (7 bar). The light grey
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![Figure 7. Comparison of the IR spectra of [Ru(dtbpmp)H₂(H₂)] (6) (black), [D₆]-Ru(dtbpmp)H₂(H₂) [D₆]-6 (grey) and the free ligand dtbpmp 17 (light grey).](image)
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suspension was heated under stirring to 55°C for 18 h. After cooling to room temperature, the autoclave was vented and the solution was filtered by cannula. Complex 4a was obtained as a dark orange powder (216 mg, 0.2 mmol; >99% yield) after drying under H₂ atmosphere. Suitable crystals for X-ray analysis were obtained by slow evaporation of a solution from the mother liquor. For these data, see also Supporting Information. M.p. 230°C (decomp); ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 2.4–1.1 (m, 106H, δe); –11.8 ppm (br, 6H, Ru-H); ¹³C NMR (75 MHz, [D₆]toluene, 25°C): δ = 39.8 (8.5; PCH of Cy), 29.3 (δ, 16C, o-CH₃ of Cy), 28.0 (16C, m-CH₃ of Cy), 27.4 (8C, p-CH₃ of Cy), 24.5 (3C, CH₂; CH₂(CH₃)₂P); ²³P NMR (122 MHz, CD₂Cl₂, 25°C): δ = 6.95 ppm (s); IR (KBr): 1927 ppm (s, ν(C-H)); 1592 (m, ν(P-H)); 1517 (s, ν(P-C)); 1458 (s, ν(=C-)); 1351 (s, δ(C-H)).

Reagent of [Ru(μ-H)₂(H₂)(dppm)] (4a) with deuterium gas to [D₆]-4a: A Young NMR tube containing a [D₆]toluene solution of 4a was cooled with liquid nitrogen. After evacuation the tube was slowly filled with [D₆]-4a. The reaction was stirred for 18 h, cooled to room temperature, and the C₆D₆ solution was removed by cannula under a red solution filtered through a cannula under an H₂ stream and the remaining solid was washed under an H₂ stream with n-pentane (12 mL). The autoclave was flamed with 2 bar H₂ gas (or D₂ gas) at room temperature, then the pressure was increased to 55°C (oil bath), and the H₂ pressure was stabilised at 7 bar. The reaction was stirred for 18 h, cooled to room temperature, and the C₆D₆ solution was removed by cannula under a red solution filtered through a cannula under an H₂ stream and the remaining solid was washed under an H₂ stream with n-pentane to give a yellow-brown solid, which was primarily stored under 1 bar hydrogen in the autoclave. The product was transferred into a dry Schlenk tube using a glove box and further dried under an H₂ stream. Finally it was stored under 1 bar hydrogen in an additionally sealed (paraform) Schlenk tube at –20°C (323 mg, 74%). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 6.8 (t, 1H, νH); 7.7 ppm (t, 4H, ν(H-P)); 7.3 ppm (s, 2H, ν(H-H)); 7.0 ppm (s, 2H, ν(H-H)); 6.8 ppm (t, 2H, ν(H-H)); 2.3 ppm (t, 2H, ν(H-H)); 1.9 ppm (t, 2H, ν(H-H)); 1.7 ppm (s, 2H, ν(H-H)); 1.6 ppm (t, 2H, ν(H-H)); 1.3 ppm (s, 2H, ν(H-H)); 1.2 ppm (t, 2H, ν(H-H)); 1.0 ppm (t, 2H, ν(H-H)).

Reaction of [D₆]-4a with H₂ to give a yellow-brown solid (118 mg, 54%). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 6.5 (t, 1H, νH); 7.3 ppm (t, 4H, ν(H-P)); 7.0 ppm (s, 2H, ν(H-H)); 6.7 ppm (s, 2H, ν(H-H)); 6.7 ppm (s, 2H, ν(H-H)); 2.2 ppm (t, 2H, ν(H-H)); 1.9 ppm (t, 2H, ν(H-H)); 1.6 ppm (t, 2H, ν(H-H)); 1.3 ppm (s, 2H, ν(H-H)); 1.2 ppm (t, 2H, ν(H-H)); 1.0 ppm (t, 2H, ν(H-H)); 1.0 ppm (t, 2H, ν(H-H)).

Reagent of [Ru(μ-H)₂(H₂)(dppm)] (4a) with nitrogen gas to [D₆]-4a: A Young NMR tube containing a [D₆]toluene solution of 4a was cooled with liquid nitrogen. After evacuation the tube was slowly charged with N₂ (0.5 bar) and warmed up to room temperature. ¹H NMR spectrum was measured over 10 min. ¹H NMR (300 MHz, [D₆]toluene, 25°C): δ = 1.11–2.36 ppm (dcepp), (no hydride signal observed in the hydride region); ¹³C NMR (122 MHz, [D₆]toluene, 25°C): δ = 6.81 ppm (s).

[(dppm)Ru(p-H₂)(dppm)] (4b): Starting from the allyl precursor 7b the same procedure used for 4a was followed. Conversion: 36%, ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 0.8–2.3 ppm (dcepp), –11.3 ppm (br, 6H, Ru-H); ²P NMR (122 MHz, CD₂Cl₂, 25°C): δ = 114.3 ppm (s); IR (KBr): ν = 2943 (w, Ru-H); 1653 cm⁻¹ (w, Ru-H).

[Ru(dpbmp)[H₂(H₂)] (5): A mixture of [Ru(cod)(metal)] [11] (0.118 g, 0.369 mmol) and 1,3-bis(d-tert-butylphosphinomethyl)benzene (12) (0.146 g, 0.370 mmol) in methanol (5 mol%) was introduced in a thick-walled glass autoclave, which was subsequently charged with H₂ (7 bar) and stirred for 66 h at 50°C. After cooling to room temperature, the autoclave was vented and the solution was filtered by cannula and washed twice with small amounts of methanol. Complex 5 was obtained as a reddish brown powder (80 mg, 45%) after drying under H₂ atmosphere at 50°C.

[(dppm)Ru(H₂)(dppm)] (6): A Büchi glass autoclave, equipped with a stirring bar, was filled with [Ru(cod)(metal)] [11] (281 mg, 0.88 mmol; 1 equiv), dbbmp (17) (364 mg, 0.92 mmol; 1.05 equiv) and degassed n-pentane (12 mL). The autoclave was flushed with 2 bar H₂ gas (or D₂ gas) at room temperature, then the temperature was increased to 55°C (oil bath), and the H₂ pressure was stabilised at 7 bar. The reaction was stirred for 18 h, cooled to room temperature, and the C₆D₆ solution was removed by cannula under a red solution filtered through a cannula under an H₂ stream and the remaining solid was washed under an H₂ stream with n-pentane to give a yellow-brown solid, which was primarily stored under 1 bar hydrogen in the autoclave. The product was transferred into a dry Schlenk tube using a glove box and further dried under an H₂ stream. Finally it was stored under 1 bar hydrogen in an additionally sealed (paraform) Schlenk tube at –20°C (323 mg, 74%). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 6.8 (t, 1H, νH); 7.7 ppm (t, 4H, ν(H-P)); 7.0 ppm (s, 2H, ν(H-H)); 6.7 ppm (s, 2H, ν(H-H)); 2.4 ppm (t, 2H, ν(H-H)); 1.9 ppm (t, 2H, ν(H-H)); 1.6 ppm (t, 2H, ν(H-H)); 1.3 ppm (s, 2H, ν(H-H)); 1.2 ppm (t, 2H, ν(H-H)); 1.0 ppm (t, 2H, ν(H-H)).
25°C: δ = 99.6 ppm (brs). For further tabulated values see Supporting Information.

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