Synthesis and Spectroscopic Characterization of Ruthenium(II) η^2-Dihydrogen Complexes of the Type $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO, $P(OCH_2)_3CEt$, PMe_2Ph; triphos = $PPh(CH_2CH_2PPh_2)_2$)

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The dihydride complexes $RuH_2(L)(triphos)$ (L = CO (**4**), $P(OCH_2)_3CEt$ (**5**), PMe_2Ph (**6**); triphos = $PPh(CH_2CH_2PPh_2)_2$) are prepared by reaction of $RuCl_2(L)(triphos)$ with $NaBH_4$ in refluxing ethanol. Protonation of **4–6** in CD_2Cl_2 at 193 K with $HBF_4{\cdot}OEt_2$ affords the η^2-dihydrogen complexes $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO (**7**), $P(OCH_2)_3CEt$ (**8**), PMe_2Ph (**9**)). Deprotonation of **7–9** with NEt_3 regenerates **4–6**. The monohydride complexes $[RuH(CH_3CN)(L)(triphos)]BF_4$ (L = $P(OCH_2)_3CEt$ (**10**), PMe_2Ph (**11**)) are prepared from **8** and **9**, respectively, by substitution of the η^2-dihydrogen ligand with CH_3CN. The η^2-dihydrogen coordination in **7–9** is established by variable-temperature ^1H NMR T_1 measurements and $^1J_{HD}$ coupling constants. Complex **7** is fluxional and gives a broad resonance in the hydride region of the ^1H NMR spectrum at all accessible temperatures, but the low T_1(min) value of 8 ms suggests the presence of one η^2-dihydrogen ligand. The hydride region of the ^1H NMR spectrum of each of complexes **8** and **9** consists of a broad resonance for the η^2-dihydrogen ligand and a binomial pseudoquintet for the terminal hydride ligand. The T_1(min) values of the η^2-dihydrogen resonance are 13 and 9 ms for **8** and **9**, respectively. The chemical shifts of the η^2-HD resonances for the isotopomers $[RuH(\eta^2\text{-}HD)(L)(triphos)]^+$ and $[RuD(\eta^2\text{-}HD)(L)(triphos)]^+$ are different by 0.080 ppm for L = $P(OCH_2)_3CEt$ and 0.067 ppm for L = PMe_2Ph due to the higher trans influence of deuteride compared to that of hydride. These two isotopomers show a $^1J_{HD}$ coupling constant of 32.8 Hz for L = $P(OCH_2)_3CEt$ and 32.2 Hz for L = PMe_2Ph.

Introduction

Since the discovery by Kubas of the first examples of nonclassical transition-metal η^2-dihydrogen complexes,[1] the area has been intensively investigated.[2] Despite an ever-increasing number of η^2-dihydrogen complexes containing monodentate or bidentate phosphines,[2,3] only a few examples containing chelating multidentate phosphines have appeared in the literature.[4-7] Such complexes can have unusual chemical and structural properties in comparison to their analogues containing monodentate or bidentate phosphines. For example, the complexes $[MH(\eta^2\text{-}H_2)\{P(CH_2CH_2PPh_2)_3\}]^+$ (M = Fe, Ru)[4b,c] exhibit much higher stability toward hydrogen loss compared with their diphosphine analogues $[MH(\eta^2\text{-}H_2)(PPh_2CH_2CH_2PPh_2)_2]^+$.[3e] The complexes $[ReH_6\{PPh(CH_2CH_2CH_2PCy_2)_2\}]^+$ [6a] and $[ReH_6\{PPh(CH_2CH_2PPh_2)_2\}]^+$ [7a] are shown by X-ray diffraction and ^1H NMR T_1 studies to contain an elongated η^2-dihydrogen ligand.

In our continuing study of hydride complexes in the classical/nonclassical borderline region,[2b-d,7-9] we have synthesized some ruthenium hydride complexes containing the chelating triphosphine ligand $PPh(CH_2CH_2PPh_2)_2$ (triphos). Of particular interest are η^2-dihydrogen complexes of the type $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$, where L is CO, $P(OCH_2)_3CEt$, or PMe_2Ph. These ligands with different electron-donating abilities are chosen to provide a range of π-back-bonding abilities of the ruthenium center, with the hope of varying the properties of the η^2-dihydrogen complexes. The cyclic phosphite $P(OCH_2)_3CEt$ is used because it tolerates treatment with the strongly reducing reagent $NaBH_4$, which is often used in the preparation of hydride complexes from their halide precursors.[10]

Results

The preparations and reactions of the compounds described in this paper are summarized in Scheme I. All the new compounds were identified from microanalytical and spectroscopic data, which are presented in the Experimental Section. The ^1H NMR spin–lattice relaxation times (T_1) for the η^2-dihydrogen and terminal hydride resonances of $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO (**7**), $P(OCH_2)_3CEt$ (**8**), PMe_2Ph (**9**)) are summarized in Table I.

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Scheme I

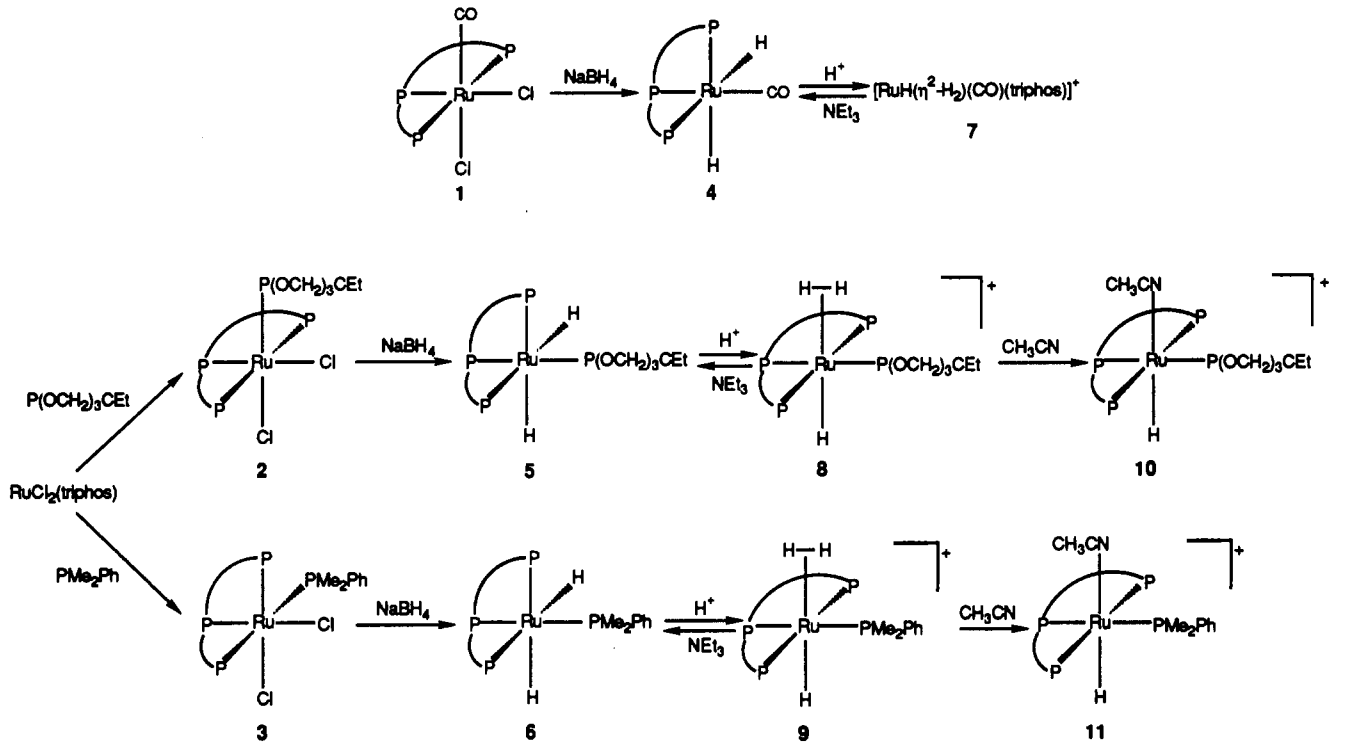

Table I. Variable-Temperature ^1H NMR T_1 Measurements on the η^2-Dihydrogen and Terminal Hydride Resonances of $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO (**7**), $P(OCH_2)_3CEt$ (**8**), PMe_2Ph (**9**)) in CD_2Cl_2 at 250 MHz

	7	8		9	
T, K	T_1,[a] ms	$T_1(H_2)$, ms	$T_1(H)$, ms	$T_1(H_2)$, ms	$T_1(H)$, ms
283				18	390
273				15	350
263		27	470	12	310
253		20	431	10	285
243		15	409	9	320
233	11	13	369	10	370
223	10	16	407	11	418
213	9	21	468	13	498
203	8	26	512		
193	11	31	633		
183	15				

[a] T_1 values for the averaged broad resonance due to rapidly exchanging dihydrogen and terminal hydride ligands.

Discussion

Preparation of $RuCl_2(L)(triphos)$ (L = CO (1), $P(OCH_2)_3CEt$ (2), PMe_2Ph (3)). Compound **1** is prepared from the reaction of $RuCl_3 \cdot xH_2O$ with triphos in refluxing dimethylformamide according to the literature procedure.[11] The new compounds **2** and **3** are synthesized in excellent yields (>90%) by the reaction of $RuCl_2(triphos)$[11] with $P(OCH_2)_3CEt$ or PMe_2Ph in refluxing toluene. They are isolated as air-stable yellow solids. Solutions of **2** and **3** slowly decompose when exposed to air.

The $^{31}P\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 shows an AMQ_2 splitting pattern. The lowest field resonance at δ 130.98 is assigned to $P(OCH_2)_3CEt$. This resonance appears as a pseudoquartet with a cis $^2J_{PP}$ coupling constant of 44.1 Hz. The $^{31}P\{^1H\}$ NMR data are consistent with an octahedral structure in which the triphos ligand occupies the three meridional sites and the $P(OCH_2)_3CEt$ ligand is cis to all three phosphorus atoms of triphos, as shown in Scheme I. It is known that triphos has no strong intrinsic preference for forming meridional or facial octahedral complexes.[12] The meridional configuration is adopted in **2** probably because this can place the π-accepting $P(OCH_2)_3CEt$ ligand trans to the π-donating chloride ligand.

The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits an AMQX splitting pattern in which the PMe_2Ph ligand shows a large trans $^2J_{PP}$ coupling constant of 322.6 Hz. The ^1H NMR spectrum shows two broad doublets ($^2J_{HP}$ = 8.9 Hz) for the two diastereotopic methyl groups of the PMe_2Ph ligand. The NMR spectroscopic data are consistent with an octahedral structure in which the triphos ligand occupies the three facial sites and the PMe_2Ph ligand is trans to one of the terminal phosphorus atoms of triphos (see Scheme I).

Preparation of $RuH_2(L)(triphos)$ (L = CO (4), $P(OCH_2)_3CEt$ (5), PMe_2Ph (6)). Treatment of **1**–**3** with an excess of $NaBH_4$ in refluxing ethanol affords the dihydride complexes $RuH_2(L)(triphos)$ (L = CO (**4**), $P(OCH_2)_3CEt$ (**5**), PMe_2Ph (**6**)) in good yields as air-stable beige or off-white solids. The corresponding dideuteride complexes $RuD_2(L)(triphos)$ (L = CO (**4**-d_2), $P(OCH_2)_3CEt$ (**5**-d_2), PMe_2Ph (**6**-d_2)) are similarly prepared by treatment of **1**–**3** with an excess of $NaBD_4$ in EtOD.

The IR spectrum of **4** shows a strong ν(CO) band at 1923 cm^{-1} and two weak ν(Ru–H) bands at 1968 and 1800 cm^{-1}. The dideuteride complex **4**-d_2 shows a strong ν(CO) band at 1920 cm^{-1} and two weak ν(Ru–D) bands at 1376 and 1273 cm^{-1} (ν(H/D) = 1.40 and 1.41, respectively). The negligible change of the ν(CO) stretching frequency on going from **4** to **4**-d_2 suggests that the CO ligand is cis to both hydride ligands in **4**, because a trans disposition of the CO ligand and a hydride ligand should result in a significant shift of the ν(CO) band upon deuteration due to a resonance interaction between the vibration states of the ν(Ru–H) and ν(CO) stretching motions.[13] The $^{31}P\{^1H\}$ NMR spectrum of **4** shows an AM_2 splitting pattern. The hydride region

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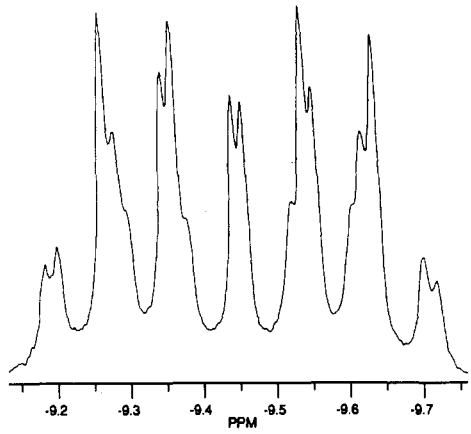


Figure 1. Hydride region of the ^1H NMR spectrum of $RuH_2\{P(OCH_2)_3CEt\}(triphos)$ (**5**) in CD_2Cl_2 at 250 MHz and 298 K.

of the ^1H NMR spectrum shows a symmetrical complex multiplet centered at δ −8.28. On the basis of its spectroscopic data, compound **4** is assigned an octahedral structure in which the triphosphine ligand occupies the three facial sites and the CO ligand is trans to the central phosphorus atom of triphos (see Scheme I).

The spectroscopic data for **5** and **6** are rather similar. In each case, the hydride resonance in the ^1H NMR spectrum appears as a symmetrical complex multiplet (Figure 1). The IR spectrum exhibits two weak ν(Ru–H) bands which are absent in the spectrum of the corresponding dideuteride complex. The $^{31}P\{^1H\}$ NMR spectrum shows an AM_2Q splitting pattern with a large trans $^2J_{PP}$ coupling between the L ligand and the central phosphorus atom of triphos. These spectroscopic data suggest that **5** and **6** adopt an octahedral structure similar to that of **4** (see Scheme I).

Formation of $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO (7), $P(OCH_2)_3CEt$ (8), PMe_2Ph (9)). Protonation of **4**–**6** with $HBF_4\cdot OEt_2$ in CD_2Cl_2 at 193 K affords the cationic η^2-dihydrogen complexes $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO (**7**), $P(OCH_2)_3CEt$ (**8**), PMe_2Ph (**9**)). The protonation is reversible because the addition of NEt_3 results in immediate deprotonation of **7**–**9** and quantitative regeneration of **4**–**6**. Compounds **7**–**9** are characterized spectroscopically, but attempts to isolate them have been unsuccessful due to facile and irreversible loss of dihydrogen at ambient temperature. The stability of $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ depends on the nature of the ligand L and increases in the order CO < $P(OCH_2)_3CEt$ < PMe_2Ph, which is the order of electron-donating ability of these ligands. Thus, the temperatures above which **7**–**9** decompose are 243, 263, and 283 K, respectively. A complicated mixture of decomposition products, which do not contain any hydride ligands, is formed, and these compounds have not been characterized. We do not understand the greater lability of **7**–**9** with respect to loss of the dihydrogen ligand compared with that of $[RuH(\eta^2\text{-}H_2)(PPh_2CH_2CH_2PPh_2)_2]^+$.[3e] No dinitrogen complexes can be obtained when solutions of **7**–**9** are allowed to decompose under an atmosphere of N_2.

The hydride region of the ^1H NMR spectrum of **7** exhibits a broad resonance at δ −6.13 ($\omega_{1/2} \approx 68$ Hz and 193 K) which is integrated as 3 ± 0.2 protons and assignable to the η^2-dihydrogen and terminal hydride ligands. This hydride resonance does not undergo decoalescence even at the lowest accessible temperature due to a rapid intramolecular exchange of hydrogen atoms between the η^2-dihydrogen and terminal hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum shows an AM_2 pattern. Support for the η^2-dihydrogen coordination in **7** is provided by the very low T_1(min) value observed for the averaged hydride resonance (vide infra), but the stereochemistry of **7** cannot be unequivocally assigned on the basis of the spectroscopic data.

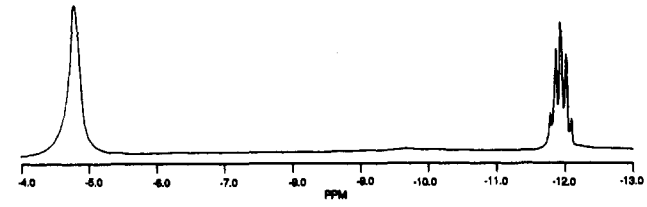
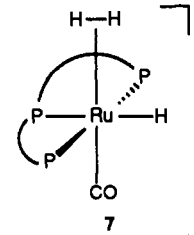


Figure 2. Hydride region of the ^1H NMR spectrum of $[RuH(\eta^2\text{-}H_2)\{P(OCH_2)_3CEt\}(triphos)]^+$ (**8**) in CD_2Cl_2 at 250 MHz and 213 K.

The hydride region of the ^1H NMR spectrum of **8** in CD_2Cl_2 at 213 K is shown in Figure 2. It consists of a broad resonance at δ −4.80 ($\omega_{1/2} \approx 75$ Hz), assigned to the η^2-dihydrogen ligand, and a well-resolved binomial pseudoquintet at δ −11.88 ($^2J_{PH}$ = 18.3 Hz), assigned to the terminal hydride ligand. The hydride region does not change significantly at all accessible temperatures, suggesting that the intramolecular exchange of hydrogen atoms between the η^2-dihydrogen and terminal hydride ligands is slow. The $^{31}P\{^1H\}$ NMR spectrum shows an AM_2Q splitting pattern with a large trans $^2J_{PP}$ coupling of 347.1 Hz between the $P(OCH_2)_3CEt$ ligand and the central phosphorus atom of the triphos ligand. The spectroscopic data of **8** indicate that the triphos ligand occupies three meridional positions of an octahedral polyhedron and that the η^2-dihydrogen and hydride ligands occupy two mutually trans positions, as shown in Scheme I. Thus, the binding mode of the triphos ligand changes from facial to meridional upon protonation of **5** to form **8**. In this way, the η^2-dihydrogen ligand is placed trans to the high-trans-effect terminal hydride ligand. This arrangement has been observed in many η^2-dihydrogen complexes and must be favorable.[3]

The ^1H and ^{31}P NMR spectra of **9** are similar to those of **8**. The hydride region of the ^1H NMR spectrum consists of a broad resonance at δ −4.61 ($\omega_{1/2} \approx 35$ Hz at 273 K), assigned to the η^2-dihydrogen ligand, and a binomial pseudoquintet at δ −11.39 ($^2J_{PH}$ = 19.5 Hz), assigned to the terminal hydride ligand. As in the case of **8**, the hydride region does not change significantly at all accessible temperatures. The $^{31}P\{^1H\}$ NMR spectrum shows an A_2MQ splitting pattern with a large trans $^2J_{PP}$ coupling of 222.0 Hz between the PMe_2Ph ligand and the central phosphorus atom of the triphos ligand. The spectroscopic data for **9** indicate an octahedral structure similar to that adopted by **8**, as shown in Scheme I.

The slow intramolecular exchange of hydrogen atoms between the η^2-dihydrogen and terminal hydride ligands in both **8** and **9** is in sharp contrast with the very rapid exchange observed for **7**. We postulate that the exchange in **7** is facilitated by a cis disposition of the η^2-dihydrogen and terminal hydride ligands as in the structure shown. This structure also places the η^2-



7

dihydrogen ligand trans to the high-trans-effect ligand CO. Another formulation for **7** that cannot be excluded is $[Ru(\eta^3\text{-}H_3)(CO)(triphos)]^+$, but such a species is as yet unprecedented as a stable ground-state structure.[9]

Formation of the Deuterated η^2-Dihydrogen Complexes. Reaction of $RuH_2(L)(triphos)$ (L = CO (**4**), $P(OCH_2)_3CEt$ (**5**), PMe_2Ph (**6**)) with $DBF_4\cdot OEt_2$ or reaction of **4**-d_2–**6**-d_2 with $HBF_4\cdot OEt_2$ at 193 K results in the formation of isotopomers of **7**–**9** with deuterium incorporation into both the η^2-dihydrogen and terminal hydride positions. In the case of **7**, neither the $^1J_{HD}$

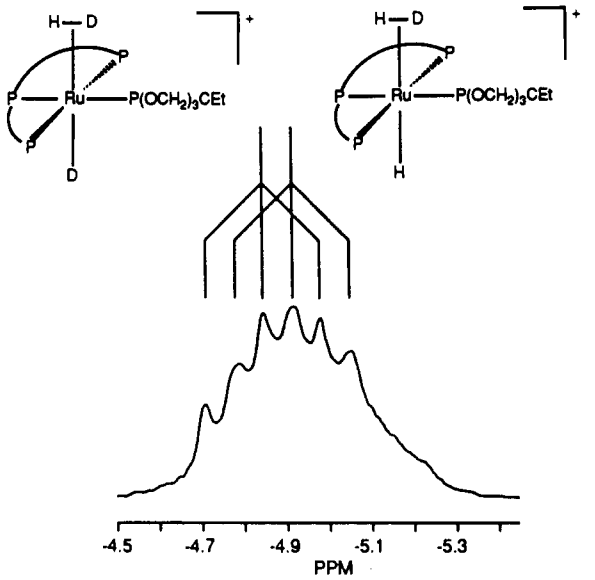


Figure 3. η^2-HD resonance in the ^{1}H NMR spectrum of the isotopomers [RuH(η^2-HD){P(OCH_2)$_3$CEt}(triphos)]$^+$ and [RuD(η^2-HD){P(OCH_2)$_3$CEt}(triphos)]$^+$ in CD_2Cl_2 at 250 MHz and 213 K.

coupling constant nor different isotopomers can be resolved, because the hydride region of the ^{1}H NMR spectrum shows only a very broad hydride resonance due to rapid fluxionality of the complex at all accessible temperatures.

In the case of **8** and **9**, the η^2-HD resonances for the isotopomers [RuH(η^2-HD)(L)(triphos)]$^+$ and [RuD(η^2-HD)(L)(triphos)]$^+$ are distinguishable (Figure 3) due to the higher trans influence of deuteride compared to hydride[14] on the chemical shift of the η^2-HD ligand. This phenomenon has been first reported by Morris et al.[3e-f,4a] The values of the trans isotope shift, defined as δ[(η^2-HD)–Ru–D] – δ[(η^2-HD)–Ru–H], are 0.080 ppm for L = P(OCH_2)$_3$CEt and 0.067 ppm for L = PMe_2Ph, which are in the expected downfield direction. Interestingly, the trans isotope effects are asymmetric; i.e., although deuteration of the terminal hydride ligand introduces a significant isotope shift for the trans η^2-HD resonance, the chemical shift of the terminal hydride ligand is not significantly affected by deuteration of the trans η^2-dihydrogen ligand. As shown in Figure 3, the two η^2-HD isotopomers show a $^1J_{HD}$ coupling constants of 32.8 Hz for L = P(OCH_2)$_3$CEt and 32.2 Hz for L = PMe_2Ph, providing unequivocal evidence for the η^2-dihydrogen coordination in complexes **8** and **9**. The isotopomers [RuH(η^2-H_2)(L)(triphos)]$^+$ and [RuD(η^2-H_2)(L)(triphos)]$^+$ are also present, but their broad η^2-dihydrogen resonances lie underneath the two η^2-HD resonances and thus are unresolvable.

^{1}H NMR T_1 Measurements for 7–9 and Estimation of the H···H Distances of the η^2-H_2 Ligands. ^{1}H NMR spin–lattice relaxation times (T_1) of hydride resonances have been proved useful in the structural assignment of transition-metal hydride complexes, specifically in determining whether they contain one or more η^2-dihydrogen ligands.[3,15] The variable-temperature ^{1}H NMR T_1 measurements on the η^2-dihydrogen and terminal hydride resonances of **7–9** in CD_2Cl_2 at 250 MHz are given in Table I.

The very low T_1(min) value of 8 ms for the averaged hydride resonance of **7** at 213 K and 250 MHz suggests the presence of one η^2-dihydrogen ligand and the formulation of **7** as [RuH(η^2-H_2)(CO)(triphos)]$^+$. Assuming that the T_1(min) value for the terminal hydride is 369 ms, as observed for **8** (see below), a T_1(min) value of 5 ms for the η^2-dihydrogen ligand can be estimated from the observed T_1(min) value of **7**.[16] This translates to an H···H distance of 0.77 Å,[17] assuming rapid rotation of the η^2-dihydrogen ligand around the Ru–H_2 bond.[3c,e] This distance is only slightly longer than that (0.74 Å) of free dihydrogen. This result must be taken with caution, however, because of the possible large error in the estimation of the T_1(min) value for the η^2-dihydrogen ligand.

The T_1(min) values for the η^2-dihydrogen ligand are 13 and 9 ms for **8** and **9**, respectively, whereas those for the terminal hydride ligand are much higher, 369 ms for **8** and 285 ms for **9**. Again assuming rapid rotation of the η^2-dihydrogen ligand,[3c,e] the H···H distances can be estimated to be 0.89 Å for **8** and 0.84 Å for **9**.[17]

In the preceding calculations, we have assumed that the dipole–dipole interaction between the two protons in the η^2-dihydrogen ligand is the only contributor to the relaxation of this ligand. We have not yet taken account of the contributions to the relaxation from the terminal hydride ligand, the protons of the phosphine ligands, the phosphorus nuclei, and the ruthenium isotopes (^{99}Ru, $I = {}^5/_2$, abundance 12.72%; ^{101}Ru, $I = {}^5/_2$, abundance 17.07%). These contributions can be approximated by use of the T_1(min) value of the terminal hydride ligand.[3e,f] Nevertheless, the true T_1(min) value for the isolated η^2-dihydrogen ligand is insignificantly different from the uncorrected value due to the large difference between the T_1(min) values of the η^2-dihydrogen and terminal hydride ligands.[18] As a result, the H···H distance of the η^2-dihydrogen ligand in **7–9** is essentially unaffected when the correction is applied.

It is noteworthy that complexes **8** and **9** show similar H···H distances and $^1J_{HD}$ coupling constants for the η^2-dihydrogen ligand, which suggests that the H–H bond order is roughly the same in both complexes. This is surprising because the decreased electron-donating ability of the phosphite ligand[19] in **8** should decrease the Ru(d_π) to H_2(σ^*) back-donation, leading to a higher H–H bond order. A rationalization of our results is that these complexes lie at the early stage of the oxidative addition of dihydrogen at the metal center, and thus the H_2(σ) to M(d_σ) donation is the predominant component of the M–H_2 interaction.[20] As a result, there is relatively small variation in the H–H bond order on changing the electron-donating ability of the coligands. On the other hand, for those complexes which lie at the late stage of the oxidative addition of dihydrogen and accordingly contain a significantly elongated η^2-dihydrogen ligand, the M(d_π) to H_2(σ^*) back-donation becomes important.[20] Thus, the H–H bond order depends strongly on the electron-donating ability of the coligands. This has been observed in a series of ReH_7{P(C_6H_4-*p*-X)$_3$}$_2$ complexes that contain isosteric phosphine ligands with different electron-donating abilities.[8b]

Preparation of [RuH(CH_3CN)(L)(triphos)]BF_4 (L = P(OCH_2)$_3$CEt (10), PMe_2Ph (11)). When solutions of **8** and **9**, generated at low temperature, are allowed to warm slowly to room temperature in the presence of an excess of acetonitrile, the monohydride complexes [RuH(CH_3CN)(L)(triphos)]BF_4 (L = P(OCH_2)$_3$CEt (**10**), PMe_2Ph (**11**)) are formed by displacement of the η^2-dihydrogen ligand with acetonitrile. Complexes **10** and **11** can be isolated as pale-yellow solids, and they form very air-

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(16) For two types of rapidly exchanging protons (H_a and H_b), the observed T_1 for the average resonance, T_1(obs), is determined by the equation ($n_a + n_b$)/T_1(obs) = n_a/T_1(a) + n_b/T_1(b), where n_a and n_b are the numbers of H_a and H_b and T_1(a) and T_1(b) are the T_1 values for H_a and H_b.
(17) For a rapidly rotating η^2-H_2 ligand, the H···H distance, r_{HH}, is calculated from the equation $r_{HH} = 4.611(T_1(\text{min})/\nu)^{1/6}$, where T_1(min) is in seconds and ν is in megahertz.[3c,e]
(18) The corrected T_1(min) value for the η^2-dihydrogen ligand, T_1(H_2,true), is calculated from the equation $1/T_1(H_2,\text{true}) = 1/T_1(H_2,\text{obs}) - 1/T_1(H,\text{obs})$, where T_1(H_2,obs) and T_1(H,obs) are the observed T_1(min) values for the η^2-dihydrogen and terminal hydride ligands, respectively.[3e,f]
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sensitive solutions. The displacement reaction is irreversible; i.e., the starting η^2-dihydrogen complexes **8** and **9** cannot be regenerated by reactions of **10** and **11** with H_2.

As can be deduced from their spectroscopic data, complexes **10** and **11** retain the stereochemistry of the parent complexes **8** and **9** except that the η^2-dihydrogen ligand is replaced by acetonitrile. In the IR spectrum, the acetonitrile ligand gives ν(CN) bands at 2261 cm^{-1} for **10** and 2245 cm^{-1} for **11**.[12a,21] The hydride ligand and the methyl group of the acetonitrile ligand each appear as binomial pseudoquintets in the ^1H NMR spectrum. The multiplicity arises from cis coupling to the four coplanar phosphorus atoms (see Scheme I). The $^5J_{HP}$ coupling constants (6.8 Hz for **10** and 7.3 Hz for **11**) for the acetonitrile ligand are unusually large compared with the range of 2–3 Hz previously observed.[4c,12a,21b]

Conclusion

We have synthesized and characterized a number of new ruthenium hydride complexes containing the chelating triphosphine ligand $PPh(CH_2CH_2PPh_2)_2$ (triphos). The neutral dihydride complexes $RuH_2(L)$(triphos) (L = CO (**4**), $P(OCH_2)_3CEt$ (**5**), PMe_2Ph (**6**)) adopt an octahedral structure in which the triphosphine ligand occupies the three facial sites. Protonation of **4–6** affords the cationic η^2-dihydrogen complexes $[RuH(\eta^2\text{-}H_2)(L)(triphos)]^+$ (L = CO (**7**), $P(OCH_2)_3CEt$ (**8**), PMe_2Ph (**9**)). At least in the case of **8** and **9**, the binding mode of the triphos ligand changes from facial to meridional upon the protonation, which makes it possible to place the η^2-dihydrogen ligand trans to the high-trans-influence terminal hydride ligand. This disposition results in an isotope effect of the terminal hydride ligand on the chemical shift of the η^2-HD resonances of the isotopomers of **8** and **9** due to the higher trans influence of deuteride than of hydride. Our finding of similar H···H distances and $^1J_{HD}$ coupling constants for the η^2-dihydrogen ligand in **8** and **9** suggests that the increased electron-donating ability of the ligand L ($P(OCH_2)_3CEt < PMe_2Ph$) has surprisingly little effect on the H–H bond order. These complexes thus model the early stage in the oxidative addition of H_2 to transition-metal complexes, where the $H_2(\sigma)$ to $M(d_\sigma)$ donation rather than the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation is predominant.

Experimental Section

General Procedures. All manipulations were performed under a dry N_2 atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, heptane, and tetrahydrofuran were distilled from Na/Ph_2CO; dichloromethane was distilled from CaH_2. All solvents were stored under N_2 over 4-Å molecular sieves. All chemicals were purchased from Alrich and used without further purification. $DBF_4{\cdot}OEt_2$ was prepared by reaction of $[Et_3O]BF_4$ with EtOD. $RuCl_2(CO)$(triphos) and $RuCl_2$(triphos) were prepared according to the literature method.[11]

^1H and ^{31}P NMR spectra were recorded on Bruker WM 250 and WM 500 spectrometers, respectively. ^1H chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H_3PO_4 as reference. ^1H NMR T_1 measurements were carried out at 250 MHz by the inversion–recovery method using a standard 180°–τ–90° pulse sequence. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Microanalyses were carried out by Desert Analytics.

$RuCl_2${$P(OCH_2)_3CEt$}(triphos) (2). To a suspension of $RuCl_2$(triphos) (200 mg, 0.28 mmol) in toluene (20 mL) was added $P(OCH_2)_3CEt$ (51 mg, 0.31 mmol). The mixture was refluxed for 2 h, and then the solvent was removed in vacuo. A small amount (ca. 0.1 mL) of CH_2Cl_2 was added to the residue, giving a clear yellow solution. Addition of Et_2O (4 mL) and hexane (20 mL) gave a yellowish solid. After the mixture was cooled to 0 °C, the solid was filtered off, washed with heptane (2 × 5 mL) and hexane (2 × 5 mL), and dried in vacuo. Yield: 226 mg (92%). Anal. Calcd for $C_{40}H_{44}Cl_2O_3P_4Ru$: C, 55.30; H, 5.11. Found: C, 55.46; H, 5.23. ^1H NMR (CD_2Cl_2, 298 K): δ 7.7–6.9 (c, 25 H, Ph), 3.42 (c, 2 H, CH_2), 3.28 (c, 2 H, CH_2), 2.98 (br d, $^3J_{HP}$ = 5.1 Hz, 6 H, OCH_2), 2.80 (c, 2 H, CH_2), 2.50 (c, 2 H, CH_2), 0.62 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2CH_3), 0.38 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 130.98 (q, $^2J_{PP}$ = 44.1 Hz, 1 P, $P(OCH_2)_3CEt$), 101.19 (br q, $^2J_{PP}$ = 20.2 Hz, 1 P, PPh), 37.31 (br d, $^2J_{PP}$ = 44.5 Hz, 2 P, PPh_2).

$RuCl_2(PMe_2Ph)$(triphos) (3). This complex was prepared analogously to **2** by using $RuCl_2$(triphos) (200 mg, 0.28 mmol) and PMe_2Ph (78 mg, 0.57 mmol) and refluxing for 2.5 h and was isolated as a yellow solid. Yield: 227 mg (95%). Anal. Calcd for $C_{42}H_{44}Cl_2P_4Ru$: C, 59.71; H, 5.25. Found: C, 59.86; H, 5.34. ^1H NMR (CD_2Cl_2, 298 K): δ 8.0–6.7 (c, 30 H, Ph), 2.77 (c, 2 H, CH_2), 2.48 (c, 2 H, CH_2), 1.98 (c, 4 H, CH_2), 1.31 (br d, $^2J_{HP}$ = 8.9 Hz, 3 H, CH_3), 1.08 (br d, $^2J_{HP}$ = 8.9 Hz, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 88.06 (q, $^2J_{PP}$ = 19.5 Hz, 1 P, PPh), 61.44 (q, $^2J_{PP}$ = 24.4 Hz, 1 P, PPh_2), 38.41 (ddd, $^2J_{PP}$ = 322.6 Hz, $^2J_{PP}$ = 23.8 Hz, $^2J_{PP}$ = 17.1 Hz, 1 P, PPh_2), –3.57 (ddd, $^2J_{PP}$ = 322.6 Hz, $^2J_{PP}$ = 31.7 Hz, $^2J_{PP}$ = 24.4 Hz, 1 P, PMe_2Ph).

$RuH_2(CO)$(triphos) (4). To a suspension of $RuCl_2(CO)$(triphos) (250 mg, 0.34 mmol) in absolute ethanol (20 mL) was added $NaBH_4$ (257 mg, 6.81 mmol). The mixture was refluxed for 1 h, and then the solvent was removed in vacuo. The residue was extracted with benzene (2 × 15 mL), and the extract was filtered through Celite. The volume of the filtrate was reduced to ca. 0.2 mL. Addition of Et_2O (10 mL) resulted in the precipitation of an off-white solid. The precipitation was completed with the addition of hexane (15 mL). The solid was filtered off, washed with hexane (2 × 4 mL), and dried in vacuo. Yield: 184 mg (81%). Anal. Calcd for $C_{35}H_{35}OP_3Ru$: C, 63.14; H, 5.30. Found: C, 63.01; H, 5.11. IR (Nujol): ν(CO) 1923 cm^{-1}; ν(Ru–H) 1968, 1800 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.6–6.9 (c, 25 H, Ph), 2.6–2.2 (c, 4 H, CH_2), 2.1–1.9 (c, 2 H, CH_2), 1.8–1.6 (c, 2 H, CH_2), –8.28 (c, 2 H, Ru–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 104.42 (t, $^2J_{PP}$ = 22.9 Hz, 1 P, PPh), 69.15 (d, $^2J_{PP}$ = 22.9 Hz, 2 P, PPh_2).

RuH_2{$P(OCH_2)_3CEt$}(triphos) (5). To a suspension of $RuCl_2(P(OCH_2)_3CEt)$(triphos) (200 mg, 0.23 mmol) in absolute ethanol (20 mL) was added $NaBH_4$ (174 mg, 4.60 mmol). The mixture was refluxed for 30 min, and then the solvent was removed in vacuo. The residue was extracted with benzene (2 × 15 mL), and the extract was filtered through Celite. The volume of the filtrate was reduced to ca. 0.2 mL. Addition of Et_2O (4 mL) and hexane (15 mL) resulted in the precipitation of an off-white solid. The precipitation was completed with the addition of heptane (10 mL). The solid was filtered off, washed with heptane (2 × 5 mL), and dried in vacuo. Yield: 143 mg (78%). Anal. Calcd for $C_{40}H_{46}O_3P_4Ru$: C, 60.06; H, 5.80. Found: C, 59.86; H, 5.34. IR (Nujol): ν(Ru–H) 1849, 1642 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 8.2–7.0 (c, 25 H, Ph), 4.13 (br d, $^3J_{HP}$ = 4.3 Hz, 6 H, OCH_2), 2.2 (c, 4 H, CH_2), 1.80 (c, 2 H, CH_2), 1.60 (c, 2 H, CH_2), 1.15 (q, J = 7.7 Hz, 2 H, CH_2CH_3), 0.79 (t, J = 7.7 Hz, 3 H, CH_2CH_3), –9.45 (c, 2 H, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 144.59 (dt, $^2J_{PP}$ = 402.0 Hz, $^2J_{PP}$ = 30.5 Hz, 1 P, $P(OCH_2)_3CEt$), 111.62 (d of br s, $^2J_{PP}$ = 402.0 Hz, 1 P, PPh), 69.69 (br s, 2 P, PPh_2).

$RuH_2(PMe_2Ph)$(triphos) (6). This complex was prepared analogously to **5** by using $RuCl_2(PMe_2Ph)$(triphos) (200 mg, 0.24 mmol) and $NaBH_4$ (179 mg, 4.74 mmol) and was isolated as a beige solid. Yield: 128 mg (70%). Anal. Calcd for $C_{42}H_{46}P_4Ru$: C, 65.01; H, 5.98. Found: C, 64.88; H, 5.86. IR (Nujol): ν(Ru–H) 1843, 1700 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 8.3–6.8 (c, 30 H, Ph), 3.73 (c, 2 H, CH_2), 2.20 (c, 2 H, CH_2), 1.52 (c, 4 H, CH_2), 1.48 (t, $^2J_{HP}$ = 7.3 Hz, 6 H, CH_3), –9.12 (c, 2 H, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 114.59 (dt, $^2J_{PP}$ = 255.0 Hz, $^2J_{PP}$ = 10.8 Hz, 1 P, PPh), 99.51 (dt, $^2J_{PP}$ = 255.0 Hz, $^2J_{PP}$ = 26.1 Hz, 1 P, PMe_2Ph), 69.5 (br d, $^2J_{PP}$ = 21.7 Hz, 2 P, PPh_2).

The dideuteride complexes $RuD_2(L)$(triphos) (L = CO (**4**-d_2), $P(OCH_2)_3CEt$ (**5**-d_2), PMe_2Ph (**6**-d_2)) were prepared analogously to the corresponding dihydride complexes **4–6** by using an excess of $NaBD_4$ in EtOD.

$[RuH(\eta^2\text{-}H_2)(CO)$(triphos)$]^+$ (7). $RuH_2(CO)$(triphos) (30 mg, 0.045 mmol) was dissolved in CD_2Cl_2 (0.4 mL) in a 5-mm NMR tube. The solution was cooled to –78 °C (dry ice/acetone), and $HBF_4{\cdot}OEt_2$ (85%, 6.1 μL, 0.045 mmol) was added via a microsyringe. The sample was shaken and then quickly introduced into a precooled NMR probe. ^1H and ^{31}P NMR spectra show quantitative protonation of **4** to give **7**. ^1H NMR (CD_2Cl_2, 223 K): δ 7.7–6.9 (c, 25 H, Ph), 2.9–2.5 (c, 4 H, CH_2), 2.4–2.2 (c, 2 H, CH_2), 2.2–1.9 (c, 2 H, CH_2), –6.13 (br s, $\omega_{1/2} \approx 68$ Hz, 3 H, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 220 K): δ 93.89 (br s, 1 P, PPh), 63.55 (br s, 2 P, PPh_2).

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[RuH(η^2-H_2){P(OCH_2)$_3$CEt}(triphos)]$^+$ (8). This complex was prepared analogously to **7** by using **5** (30 mg, 0.038 mmol) and HBF_4·OEt_2 (85%, 5.1 μL, 0.038 mmol). ^{1}H NMR (CD_2Cl_2, 213 K): δ 8.0–7.0 (m, 25 H, Ph), 3.70 (br s, 6 H, OCH_2), 3.0 (m, 4 H, CH_2), 2.3 (m, 2 H, CH_2), 1.90 (m, 2 H, CH_2), 0.98 (br s, 2 H, CH_2CH_3), 0.60 (br s, 3 H, CH_2CH_3), –4.80 (br s, $\omega_{1/2} \approx 75$ Hz, 2 H, Ru(η^2-H_2)), –11.88 (quintet, $^2J_{HP}$ = 18.3 Hz, 1 H, RuH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 220 K): δ 134.64 (dt, $^2J_{PP}$ = 347.1 Hz, $^2J_{PP}$ = 40.1 Hz, 1 P, P(OCH_2)$_3$CEt), 107.60 (dt, $^2J_{PP}$ = 347.1 Hz, $^2J_{PP}$ = 37.0 Hz, 1 P, PPh), 63.71 (br d, $^2J_{PP}$ = 22.9 Hz, 2 P, PPh_2).

[RuH(η^2-H_2)(PMe_2Ph)(triphos)]$^+$ (9). This complex was prepared analogously to **7** by using **6** (30 mg, 0.039) and HBF_4·OEt_2 (85%, 5.3 μL, 0.039 mmol). ^{1}H NMR (CD_2Cl_2, 273 K): δ 7.8–6.5 (c, 30 H, Ph), 3.56 (c, 4 H, CH_2), 2.80 (c, 2 H, CH_2), 2.5 (c, 2 H, CH_2), 0.72 (br s, 6 H, CH_3), –4.61 (br s, $\omega_{1/2} \approx 35$ Hz, 2 H, Ru(η^2-H_2)), –11.39 (quintet, $^2J_{HP}$ = 19.5 Hz, 1 H, RuH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 263 K): δ 97.36 (br s, 2 P, PPh_2), 7.12 (dt, $^2J_{PP}$ = 222.0 Hz, $^2J_{PP}$ = 20.4 Hz, 1 P, PPh), 2.41 (dt, $^2J_{PP}$ = 222.0 Hz, $^2J_{PP}$ = 14.3 Hz, 1 P, PMe_2Ph).

[RuH(CH_3CN){P(OCH_2)$_3$CEt}(triphos)]BF_4 (10). To a solution of **5** (0.30 g, 0.37 mmol) in CH_2Cl_2 (20 mL) cooled in a dry ice/acetone bath was added HBF_4·OEt_2 (85%, 56 μL, 0.41 mmol) via a microsyringe. After 5 min, CH_3CN (0.50 mL, 9.38 mmol) was added. The solution was allowed to warm slowly to room temperature and then was concentrated in vacuo to ca. 0.1 mL. Addition of Et_2O (25 mL) resulted in the precipitation of a pale-yellow solid, which was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo. Yield: 0.31 g (90%). Anal. Calcd for $C_{42}H_{48}BF_4NO_3P_4Ru$: C, 54.43; H, 5.22; N, 1.51. Found: C, 54.23; H, 5.29; N, 1.67. IR (Nujol): ν(Ru–H) 1966 cm^{-1}; ν(CN) 2261 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.7–6.8 (c, 25 H, Ph), 3.68 (d, $^3J_{HP}$ = 4.9 Hz, 6 H, OCH_2), 2.93–2.55 (c, 8 H, CH_2), 2.13 (quintet, $^5J_{HP}$ = 6.8 Hz, 3 H, CH_3CN), 0.96 (q, J = 7.9 Hz, 2 H, CH_2CH_3), 0.63 (t, J = 7.9 Hz, 3 H, CH_2CH_3), –17.19 (quintet, $^2J_{HP}$ = 19.6 Hz, 1 H, RuH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 133.63 (dt, $^2J_{PP}$ = 361.5 Hz, $^2J_{PP}$ = 41.1 Hz, 1 P, P(OCH_2)$_3$CEt), 102.39 (dt, $^2J_{PP}$ = 361.5 Hz, $^2J_{PP}$ = 38.0 Hz, 1 P, PPh), 65.05 (br s, 2 P, PPh_2).

[RuH(CH_3CN)(PMe_2Ph)(triphos)]BF_4 (11). This complex was prepared analogously to **10** by using **6** (0.30 g, 0.39 mmol), HBF_4·OEt_2 (58 μL, 0.43 mmol), and CH_3CN (0.51 mL, 9.67 mmol) and was isolated as a pale yellow solid. Yield: 0.31 g (91%). Anal. Calcd for $C_{44}H_{48}BF_4NP_4Ru$: C, 58.54; H, 5.36; N, 1.55. Found: C, 58.68; H, 5.30; N, 1.66. IR (Nujol): ν(Ru–H) 1971 cm^{-1}; ν(CN) 2245 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.9–6.8 (c, 25 H, Ph), 3.17–2.77 (c, 4 H, CH_2), 2.70–2.57 (c, 2 H, CH_2), 2.43–2.26 (c, 2 H, CH_2), 2.15 (quintet, $^5J_{HP}$ = 7.3 Hz, 3 H, CH_3CN), 1.00 (t, J_{HP} = 8.7 Hz, 6 H, PMe_2), –17.31 (quintet, $^2J_{HP}$ = 23.0 Hz, 1 H, RuH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 92.37 (br s, 2 P, PPh_2), –1.32 (dt, $^2J_{PP}$ = 257.9 Hz, $^2J_{PP}$ = 30.5 Hz, 1 P, PPh), –4.19 (dt, $^2J_{PP}$ = 257.9 Hz, $^2J_{PP}$ = 27.5 Hz, 1 P, PMe_2Ph).

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