

Study of the Interaction of [Ru(C₅H₅)Cl(dippe)] and [Ru(C₅Me₅)Cl(dippe)] with Dihydrogen, Dinitrogen, and Other Small Molecules. X-ray Crystal Structures of [Ru(C₅Me₅)H₂(dippe)][BPh₄], [Ru(C₅H₅)(CNBu^t)(dippe)][BPh₄], and [Ru(C₅H₅)(η²-C₂H₄)(dippe)][BPh₄]

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The complexes [CpRuCl(dippe)] and [Cp^{*}RuCl(dippe)] (Cp = C₅H₅; Cp^{*} = C₅Me₅; dippe = 1,2-bis(diisopropylphosphino)ethane) react with H₂ and Na[BPh₄] in EtOH or MeOH to furnish the dihydrides [CpRuH₂(dippe)][BPh₄] (**1**) and [Cp^{*}RuH₂(dippe)][BPh₄] (**2**). These compounds are deprotonated by KOBu^t to yield the monohydrides [CpRuH(dippe)] (**3**) and [Cp^{*}RuH(dippe)] (**4**), which can be protonated back by HBF₄·OEt₂ at low temperatures to give the dihydrogen adducts [CpRu(H₂)(dippe)][BF₄] (**5**) and [Cp^{*}Ru(H₂)(dippe)][BF₄] (**6**). These compounds rearrange irreversibly to the dihydride form as the temperature is raised. A kinetic study of these rearrangement processes suggests that the isomerization mechanism is different in each case. The dinitrogen complex [CpRu(N₂)(dippe)][BPh₄] (**7**) and the acetone adduct [CpRu(Me₂CO)(dippe)][BPh₄] (**8**) were obtained by reaction of [CpRuCl(dippe)] with Ag⁺ in acetone under dinitrogen or argon, respectively, followed by NaBPh₄/EtOH. Both compounds react with atmospheric oxygen yielding [CpRu(η⁶-C₆H₅BPh₃)] (**9**) and ¹Pr₂P(O)CH₂-CH₂P(O)¹Pr₂. The dinitrogen adduct [Cp^{*}Ru(N₂)(dippe)][BPh₄] (**10**) was also obtained, but it reacts irreversibly with traces of O₂ to give the dioxygen complex [Cp^{*}Ru(O₂)(dippe)][BPh₄], previously known. A range of neutral donors L also react with [CpRuCl(dippe)] or [Cp^{*}RuCl(dippe)] and NaBPh₄ furnishing the corresponding complexes [CpRu(L)(dippe)][BPh₄] (L = CO (**11**), CNBu^t (**12**), C₂H₄ (**13**), or [Cp^{*}Ru(L)(dippe)][BPh₄] (L = CO (**14**), CNBu^t (**15**), C₂H₄ (**16**)). The ethylene adduct **16** is only stable under an ethylene atmosphere, whereas **13** is a stable species. The X-ray crystal structures of compounds **2**, **12**, and **13** are also reported.

Introduction

Since the discovery by Kubas of dihydrogen coordination to a metal center without dissociation,¹ several criteria for determining the stability of the metal dihydrogen bond have been proposed.² One of them predicts the stability of adducts of the type [M(η²-H₂)-L_n] based upon the stretching frequency ν(N₂) for the associated dinitrogen complexes [M(N₂)L_n], which is an indirect measure of the electron density at the metal center.³ Thus, if ν(N₂) falls in the range 2060–2160 cm⁻¹, the corresponding dihydrogen complex is expected to be a stable species. This criterion has proved to be specially effective in predicting relative stabilities for d⁶ transition metal dihydrogen complexes.⁴ However, there are many cases in which, for a given dihydride or dihydrogen complex, the associated dinitrogen complex is not known. This is what happens for half-sandwich

ruthenium derivatives of the type [(C₅R₅)Ru(H₂)P₂]⁺ (R = H, Me; P₂ = two monodentate phosphine ligands or one bidentate phosphine ligand), which constitute one of the most important classes of known dihydride/dihydrogen complexes,^{2,5} since they offer a unique opportunity to study the physical and chemical properties of coordinated H₂ as a function of the ligand environment. As far as we are aware, no half-sandwich dinitrogen complex of the type [(C₅R₅)Ru(N₂)P₂]⁺ has been reported, despite the well-known capabilities of the cyclopentadienyl- and pentamethylcyclopentadienyl-ruthenium bis(phosphine) auxiliaries for binding and activating a wide range of small molecules.⁶ One possible reason for this could be the instability of the ruthenium–dinitrogen bond.⁷ Continuing our work on small molecule activation by transition metal complexes containing the bulky, strong electron releasing diphosphine 1,2-bis(diisopropylphosphino)ethane, we have now shown that the [CpRu(dippe)]⁺ and [Cp^{*}Ru(dippe)]⁺

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Table 1. Summary of Relevant IR (Nujol) and NMR Data for Compounds Prepared in This work^a

compound	no.	IR data (cm ⁻¹)	relevant NMR data	
			³¹ P{ ¹ H}	¹ H
[CpRuH ₂ (dippe)][BPh ₄]	1		101.3	-10.370 (t, J(H,P) = 26 Hz, RuH ₂)
[Cp*RuH ₂ (dippe)][BPh ₄]	2		93.3	-9.840 (t, J(H,P) = 27.3 Hz, RuH ₂)
[CpRuH(dippe)]	3	1971, ν(RuH)	118.5 ^b	-15.231 (t, J(H,P) = 16.7 Hz, RuH)
[Cp*RuH(dippe)]	4	1973, ν(RuH)	108.3 ^b	-14.810 (t, J(H,P) = 17.7 Hz, RuH)
[CpRu(H ₂)(dippe)][BF ₄]	5		109.8 ^c	-10.440 (s br, Ru(H ₂)) ^e
[Cp*Ru(H ₂)(dippe)][BF ₄]	6		102.1 ^d	-10.640 (s br, Ru(H ₂)) ^e
[CpRu(N ₂)(dippe)][BPh ₄]	7	2145, ν(N ₂)	91.7 ^d	
[CpRu(Me ₂ CO)(dippe)][BPh ₄]	8	1650, ν(C=O)	92.9 ^c	
[Cp*Ru(N ₂)(dippe)][BPh ₄]	10	2120, ν(N ₂)	79.3 ^d	
[CpRu(CO)(dippe)][BPh ₄]	11	1959, ν(CO)	95.9	
[CpRu(CNBu ^t)(dippe)][BPh ₄]	12	2104, ν(CN)	98.5 ^c	1.450 (s, CNC(CH ₃) ₃)
[CpRu(C ₂ H ₄)(dippe)][BPh ₄]	13		88.7 ^c	2.498 (t, J(H,P) = 2.6 Hz, Ru(C ₂ H ₄))
[Cp*Ru(CO)(dippe)][BPh ₄]	14	1926, ν(CO)	83.4	
[Cp*Ru(CNBu ^t)(dippe)][BPh ₄]	15	2105, ν(CN)	86.1	1.410 (s, CNC(CH ₃) ₃)
[Cp*Ru(C ₂ H ₄)(dippe)][BPh ₄]	16		75.1 ^c	1.968 (t, J(H,P) = 2.8 Hz, Ru(C ₂ H ₄))

^a CDCl₃ is used as solvent, unless otherwise stated. ^b C₆D₆. ^c CD₃COCD₃. ^d CD₂Cl₂. ^e At 223 K.

moieties are binding sites for a variety of small molecules including dinitrogen and dihydrogen. However, the dihydrogen adducts are only stable at low temperatures, and they rearrange irreversibly to the dihydride form at higher temperatures, despite the fact that the value of ν(N₂) for the dinitrogen complexes suggests that the dihydrogen adducts should be stable species. This work parallels recent studies made on the iron systems [CpFeCl(dippe)] and [Cp*FeCl(dippe)],^{8,9} in order to establish analogies and differences in chemical behavior.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane,¹⁰ [CpRuCl(dippe)], and [Cp*RuCl(dippe)]¹¹ were prepared according to the literature. IR spectra were recorded in Nujol mulls on a Perkin-Elmer 881 spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from SiMe₄ (¹H and ¹³C{¹H}) or 85% H₃PO₄ (³¹P{¹H}). Relevant IR and NMR data for compounds prepared in this work are listed in Table 1. Longitudinal relaxation time (T₁) measurements were made using the inversion/recovery method. Microanalyses were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía or by Butterworth Laboratories, Middlessex, UK.

[CpRuH₂(dippe)][BPh₄] (**1**). To a solution of [CpRuCl(dippe)] (0.46 g, 1 mmol) in MeOH under dinitrogen or argon, an excess of Na[BPh₄] (0.5 g, ~1.5 mmol) was added. Dihydrogen was bubbled through the solution. A white, crystalline precipitate was formed almost immediately. It was filtered out, washed with ethanol and petroleum ether, and dried *in vacuo*. The compound can be recrystallized from acetone/EtOH. Yield: 0.58 g, 78%. Anal. Calcd for C₄₃H₅₉BP₂Ru: C, 68.9; H, 7.93. Found C, 69.0; H, 8.05. NMR (CDCl₃) δ: (¹H) -10.370 (t, J(H,P) = 26 Hz, RuH₂, T₁ (400 MHz, 253 K) 674 ms); 5.137 (s, RuC₅H₅). (³¹P{¹H}) 101.3 (s). (¹³C{¹H}) 18.52,

19.20 (s, P(CH(CH₃)₂)₂); 23.12 (t, J(C,P) = 9.6 Hz, PCH₂); 28.26 (t, J(C,P) = 12 Hz, P(CH(CH₃)₂)₂); 83.97 (s, C₅H₅).

[Cp*RuH₂(dippe)][BPh₄] (**2**). **2** was prepared by the same method used for **1**, starting from [Cp*RuCl(dippe)] (0.27 g, 0.5 mmol). Yield: 0.57 g, 70%. Anal. Calcd for C₄₈H₆₉BP₂Ru: C, 70.3; H, 8.48. Found C, 70.1; H, 8.65. NMR (CDCl₃) δ: (¹H) -9.840 (t, J(H,P) = 27.3 Hz, RuH₂, T₁ (400 MHz, 223 K) 870 ms); 1.974 (s, RuC₅(CH₃)₅). (³¹P{¹H}) 93.3 (s). (¹³C{¹H}) 12.49 (s, RuC₅(CH₃)₅); 18.66, 19.96 (s, P(CH(CH₃)₂)₂); 22.53 (t, J(C,P) = 19.6 Hz, PCH₂); 26.90 (t, J(C,P) = 15 Hz, P(CH(CH₃)₂)₂); 99.15 (s, RuC₅(CH₃)₅).

[CpRuH(dippe)] (**3**). To a solution of **1** (0.37 g, 0.5 mmol) in THF, an excess of solid KOBu^t (0.15 g) was added. The mixture was stirred at room temperature for 10 min. Then, the solvent was removed *in vacuo*. The residue was extracted with petroleum ether. Centrifugation, concentration, and cooling to -20 °C afforded white crystals. Yield: 0.15 g, 63%. Anal. Calcd for C₁₉H₃₈P₂Ru: C, 53.1; H, 8.92. Found: C, 52.8; H, 8.73. IR: ν(RuH) 1971 cm⁻¹. NMR (C₆D₆) δ: (¹H) -15.231 (t, J(H,P) = 16.7 Hz, RuH); 4.743 (s, RuC₅H₅). (³¹P{¹H}) 118.5 s. (¹³C{¹H}) 18.69, 18.86, 19.78, 19.98 (s, P(CH(CH₃)₂)₂); 22.78 (t, J(C,P) = 22 Hz, PCH₂); 25.27 (t, J(C,P) = 18 Hz, P(CH(CH₃)₂)₂); 29.47 (t, J(C,P) = 24 Hz, P(CH(CH₃)₂)₂); 76.13 (s, RuC₅H₅).

[Cp*RuH(dippe)] (**4**). **4** was obtained following a procedure identical to that for **3**, starting from **2** (0.5 g, ~0.6 mmol). Yield: 0.23 g, 77%. Anal. Calcd for C₂₄H₄₈P₂Ru: C, 57.7; H, 9.68. Found: C, 57.5; H, 9.54. IR: ν(RuH) 1973 cm⁻¹. NMR (C₆D₆) δ: (¹H) -14.810 (t, J(H,P) = 17.7 Hz, RuH); 2.039 (s, C₅(CH₃)₅). (³¹P{¹H}) 108.35 s. (¹³C{¹H}) 12.07 (s, C₅(CH₃)₅); 16.07, 17.72, 18.96 (s, PCH(CH₃)₂)₂); 21.29 (t, J(C,P) = 23.2 Hz, PCH₂); 25.2 (t, J(C,P) = 23.3 Hz, P(CH(CH₃)₂)₂); 27.7 (s, J(C,P) = 26 Hz, P(CH(CH₃)₂)₂); 89.31 (s, C₅(CH₃)₅).

[CpRu(H₂)(dippe)][BF₄] (**5**). **5** was obtained and characterized in solution by protonation of the monohydride **3** in acetone-*d*₆ or CD₂Cl₂ at -80 °C using a slight excess of HBF₄·OEt₂. The isotopomer [CpRu(HD)(dippe)][BF₄] was obtained in a similar fashion, using HBF₄·OEt₂/D₂O. Yield: quantitative. NMR (acetone-*d*₆, 223 K) δ: (¹H) -10.44 (s, br, Ru(H₂), T₁ (400 MHz, 223 K) 34 ms), 5.65 (s, C₅H₅). (³¹P{¹H}) 109.75 (s).

[Cp*Ru(H₂)(dippe)][BF₄] (**6**). The preparation of **6** is analogous to that for **5**, using the monohydride **4** as starting material. Yield: quantitative. NMR (CD₂Cl₂, 223 K) δ: (¹H) -10.64 (s, br, Ru(H₂), T₁ (400 MHz, 223 K) 26 ms); 1.947 (s, C₅(CH₃)₅). (³¹P{¹H}) 102.06 (s).

Kinetics of the Dihydrogen to Dihydride Isomerization. Samples of **5** or **6**, prepared as described above, were immersed into a liquid N₂/ethanol bath, in order to "freeze" the isomerization process during transport and handling. The sample was removed from the bath and inserted into the precooled probe of the Varian Unity-400 at 203 K. Once shims

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were adjusted, the probe was warmed to the desired temperature. The NMR temperature controller was previously calibrated against a methanol sample, the reproducibility being ± 0.5 °C. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded for at least 3 half-lives at regular intervals using the spectrometer software for accurate time control. Peak intensities were analyzed from stacked plots of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. First-order rate constants were derived from the least-squares best-fit lines of the $\ln(\text{intensity})$ vs time plots. The uncertainty in the isomerization rate constants represents one standard deviation ($\pm\sigma$) derived from the slope of the best-fit line. Uncertainties in the activation enthalpies and entropies were calculated from the uncertainties in the slope and intercept of the best-fit lines of the Eyring plots.

[CpRu(N₂)(dippe)][BPh₄] (7). To a solution of [CpRuCl(dippe)] (0.46 g, 1 mmol) in dichloromethane under dinitrogen was added AgCF₃SO₃ (0.25 g, ~1 mmol). A precipitate of AgCl was immediately formed. The mixture was stirred under dinitrogen at room temperature for 15 min. Then, it was centrifuged or filtered through Celite, in order to remove all AgCl. Addition of a deoxygenated solution of NaBPh₄ in ethanol, followed by concentration using reduced pressure, yielded a yellow microcrystalline precipitate, which was filtered off, washed with ethanol and petroleum ether, and dried. Attempts made to recrystallize this compound led to dinitrogen loss. In some instances, [CpRu(η^6 -C₆H₅BPh₃)] was isolated. Yield: 0.4 g, 52%. Anal. Calcd for C₄₃H₅₇N₂BP₂Ru: C, 66.6; H, 7.41; N, 3.6. Found: C, 66.6; H, 7.35; N, 3.0. IR: $\nu(\text{N}_2)$ 2145 cm⁻¹. NMR (CD₂Cl₂) δ : (¹H) 5.116 (s, C₅H₅). (³¹P{¹H}) 91.7 (s). (¹³C{¹H}) NMR spectrum not recorded due to significant decomposition.

[CpRu(Me₂CO)(dippe)][BPh₄] (8). To a solution of [CpRuCl(dippe)] (0.46 g, 1 mmol) in acetone under an argon atmosphere was added AgCF₃SO₃ (0.25 g, ~1 mmol). A precipitate of AgCl was immediately formed. The mixture was stirred under argon for 15 min. AgCl was removed by centrifugation or filtration through Celite, as for 7. Addition of NaBPh₄ in ethanol, concentration, and cooling to -20 °C afforded orange crystals. Yield: 0.69 g, 86%. Anal. Calcd for C₄₆H₆₃BOP₂Ru: C, 68.6; H, 7.88. Found: C, 68.7; H, 7.80. IR: $\nu(\text{C}=\text{O})$ 1650 cm⁻¹. NMR (acetone-*d*₆) δ : (¹H) 4.930 (s, C₅H₅); (CH₃)₂CO of coordinated acetone not observed due to exchange with solvent. (³¹P{¹H}) 92.9 (s). (¹³C{¹H}) NMR spectrum not recorded due to significant decomposition.

[CpRu(η^6 -C₆H₅BPh₃)] (9). A dichloromethane solution of 7 or 8 was stirred in the air for 10–15 min. Then, it was concentrated using reduced pressure. Addition of petroleum ether to the dark green solution produced the precipitation of a green-brown solid, which was filtered off, washed with petroleum ether, and dried *in vacuo*. Recrystallization from dichloromethane/petroleum ether afforded dark green-brown crystals. Yield: quantitative. Anal. Calcd for C₂₉H₂₅N₂BRu: C, 71.7; H, 5.19. Found: C, 71.9; H, 5.15. NMR (CDCl₃) δ : (¹H) 4.747 (s, C₅H₅); 5.627, 6.228 (m, Ru(η^6 -C₆H₅B(C₆H₅)₃)); 7.063 (t), 7.168 (t), 7.310 (d, Ru(η^6 -C₆H₅B(C₆H₅)₃)). (¹³C{¹H}) 78.32 (s, C₅H₅); 80.91, 83.68, 92.13 (s, Ru(η^6 -C₆H₅B(C₆H₅)₃)); 123.41, 126.25, 135.60 (s, Ru(η^6 -C₆H₅B(C₆H₅)₃)).

[Cp*Ru(N₂)(dippe)][BPh₄] (10). An acetone solution of [Cp*RuCl(dippe)] (0.27 g, 0.5 mmol) was treated with solid AgCF₃SO₃ (0.12 g, ~0.5 mmol) under dinitrogen. A precipitate of AgCl was immediately formed. The mixture was stirred under dinitrogen for 15 min. AgCl was removed by filtration through Celite. Then, a deoxygenated solution of NaBPh₄ (0.35 g) in ethanol was added. Concentration using dinitrogen bubbling yielded a green precipitate, which was filtered off, washed with ethanol and petroleum ether, and dried under a dinitrogen stream. All attempts made to recrystallize this compound led to dinitrogen loss and isolation of the dioxygen complex [Cp*Ru(O₂)(dippe)][BPh₄]. Yield: 0.21 g, 50%. Anal. Calcd for C₄₈H₆₇N₂BP₂Ru: C, 68.1; H, 7.93; N, 3.3. Found: C, 67.7; H, 7.75; N, 2.5. IR: $\nu(\text{N}_2)$ 2120 cm⁻¹. NMR (CD₂Cl₂)

δ : (¹H) 1.808 (s, C₅(CH₃)₅). (³¹P{¹H}) 79.3 (s). (¹³C{¹H}) NMR spectrum not recorded due to significant decomposition.

[CpRu(CO)(dippe)][BPh₄] (11). CO was bubbled through a solution of [CpRuCl(dippe)] (0.23 g, ~0.5 mmol) in EtOH (20 mL). An excess of Na[BPh₄] (0.34 g) dissolved in EtOH (10 mL) was added, producing a yellow crystalline precipitate. It was filtered, washed with EtOH and petroleum ether, and dried *in vacuo*. Yellow crystals were obtained upon recrystallization from acetone/EtOH. Yield: 0.27 g, 70%. Anal. Calcd for C₄₄H₅₇BOP₂Ru: C, 68.1; H, 7.41. Found: C, 68.2; H, 7.50. IR: $\nu(\text{CO})$ 1959 cm⁻¹. NMR (CDCl₃) δ : (¹H) 5.148 (s, C₅H₅). (³¹P{¹H}) 95.848 (s). (¹³C{¹H}) 18.57, 18.73, 19.00, 19.47 (s, P(CH(CH₃)₂)₂); 23.28 (t, $J(\text{C},\text{P}) = 18.5$ Hz, PCH₂); 27.87 (t, $J(\text{C},\text{P}) = 15.6$ Hz, P(CH(CH₃)₂)₂); 29.08 (t, $J(\text{C},\text{P}) = 12.6$ Hz, P(CH(CH₃)₂)₂); 85.86 (s, C₅H₅); 201.72 (t, $J(\text{C},\text{P}) = 15.4$ Hz, CO).

[CpRu(CNBu⁺)(dippe)][BPh₄] (12). To a solution of [Ru(C₅H₅)Cl(dippe)] (0.23 g, ~0.5 mmol) in MeOH (20 mL) was added a slight excess of CNBu⁺ (0.15 mL). Addition of solid Na[BPh₄] (0.34 g) produced a yellow, crystalline precipitate. It was filtered, washed with ethanol and petroleum ether, and dried *in vacuo*. The product was recrystallized from acetone/EtOH. Yield: 0.36 g, 88%. Anal. Calcd for C₄₈H₆₆NBP₂Ru: C, 69.4; H, 8.01; N, 1.7. Found: C, 69.4; H, 8.10; N, 1.5. IR: $\nu(\text{CN})$ 2104 cm⁻¹. NMR (acetone-*d*₆) δ : (¹H) 1.450 (s, CNC(CH₃)₃); 5.250 (s, C₅H₅). (³¹P{¹H}) 98.479 (s). (¹³C{¹H}) 19.341, 19.388, 19.702, 20.153 (s, P(CH(CH₃)₂)₂); 24.353 (t, PCH₂); 24.533 (m, P(CH(CH₃)₂)₂); 24.745 (m, P(CH(CH₃)₂)₂); 30.565 (s, CNC(CH₃)₃); 58.55 (s, CNC(CH₃)₃); CNC(CH₃)₃ not observed; 84.00 (s, C₅H₅).

[CpRu(C₂H₄)(dippe)][BPh₄] (13). Ethylene was bubbled through a solution of [CpRuCl(dippe)] (0.23 g, mmol) in MeOH (20 mL) containing an excess of Na[BPh₄]. A yellow-white precipitate was formed almost immediately. The mixture was stirred for 10 min under ethylene. The microcrystalline precipitate was filtered off, washed with ethanol and petroleum ether, and dried *in vacuo*. Recrystallization from dichloromethane/EtOH afforded green crystals, suitable for X-ray structure analysis. Yield: 0.28 g, 74%. Anal. Calcd for C₄₅H₆₁BP₂Ru: C, 69.7; H, 7.93. Found: C, 69.7; H, 7.90. NMR (acetone-*d*₆) δ : (¹H) 2.498 (t, $J(\text{H},\text{P}) = 2.6$ Hz, C₂H₄); 5.320 (s, C₅H₅). (³¹P{¹H}) 88.7 (s). (¹³C{¹H}) 19.23, 19.27, 19.66, 20.42 (s, P(CH(CH₃)₂)₂); 21.84 (t, $J(\text{C},\text{P}) = 19.9$ Hz, PCH₂); 28.19 (t, $J(\text{C},\text{P}) = 13.3$ Hz, P(CH(CH₃)₂)₂); 33.19 (t, $J(\text{C},\text{P}) = 13$ Hz, P(CH(CH₃)₂)₂); 33.42 (s, C₂H₄); 85.30 (s, C₅H₅). This compound, as well as 11 and 12, can also be obtained by starting from the acetone adduct 8 in dichloromethane. The corresponding complex is isolated in similar yields by ethanol addition, concentration, and cooling to -20 °C.

[Cp*Ru(CO)(dippe)][BPh₄] (14). An experimental procedure identical to that for 11 was followed for the preparation of this compound, starting from [Cp*RuCl(dippe)] (0.27 g, 0.5 mmol). Yield: 0.37 g, 87%. Anal. Calcd for C₄₉H₆₇BOP₂Ru: C, 69.6; H, 7.98. Found: C, 69.5; H, 7.89. IR: $\nu(\text{CO})$, 1926 cm⁻¹. NMR (CDCl₃) δ : (¹H) 1.840 (s, C₅(CH₃)₅). (³¹P{¹H}) 83.43 (s). (¹³C{¹H}) 10.839 (s, C₅(CH₃)₅); 17.502, 18.284, 18.709, 19.406 (s, P(CH(CH₃)₂)₂); 21.123 (t, $J(\text{C},\text{P}) = 18.3$ Hz, PCH₂); 24.693 (t, $J(\text{C},\text{P}) = 10.7$ Hz, P(CH(CH₃)₂)₂); 28.89 (t, $J(\text{C},\text{P}) = 15.3$ Hz, P(CH(CH₃)₂)₂); 98.52 (s, C₅Me₅); 206.98 (t, $J(\text{C},\text{P}) = 15.5$ Hz, CO).

[Cp*Ru(CNBu⁺)(dippe)][BPh₄] (15). 15 was obtained in a fashion analogous to that for 12, starting from [Cp*RuCl(dippe)] (0.27 g, 0.5 mmol) in MeOH. Yield: 0.36 g, 81%. Anal. Calcd for C₅₃H₇₆NBP₂Ru: C, 70.6; H, 8.50; N, 1.6. Found: C, 70.5; H, 8.56; N, 1.5. IR: $\nu(\text{CN})$ 2105 cm⁻¹. NMR (CDCl₃) δ : (¹H) 1.410 (s, CNC(CH₃)₃); 1.820 (s, C₅(CH₃)₅). (³¹P{¹H}) 86.050 (s). (¹³C{¹H}) 11.01 (s, C₅(CH₃)₅); 18.20, 18.79, 19.15, 19.92 (s, P(CH(CH₃)₂)₂); 21.48 (t, $J(\text{C},\text{P}) = 19.2$ Hz, PCH₂); 25.14 (t, $J(\text{C},\text{P}) = 9.9$ Hz, P(CH(CH₃)₂)₂); 29.59 (t, $J(\text{C},\text{P}) = 14.0$ Hz, P(CH(CH₃)₂)₂); 30.88 (s, CNC(CH₃)₃); 57.48 (s, CNC(CH₃)₃); 95.34 (s, C₅(CH₃)₅); 155.94 (t, $J(\text{C},\text{P}) = 17$ Hz, CNC(CH₃)₃).

Table 2. Summary of Data for the Crystal Structure Analyses of 2, 12, and 13

compound	2	12	13
formula	C ₄₈ H ₆₉ BP ₂ Ru	C ₄₈ H ₆₆ NBP ₂ Ru	C ₄₆ H ₆₁ BP ₂ Ru
fw	819.90	830.88	775.80
crystal size (mm)	0.32 × 0.25 × 0.33	0.22 × 0.33 × 0.36	0.26 × 0.21 × 0.35
crystal system	monoclinic	triclinic	orthorhombic
space group	<i>P2</i> ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>Pbca</i> (No. 61)
cell parameters	<i>a</i> = 14.325(2) Å <i>b</i> = 21.567(4) Å <i>c</i> = 14.496(5) Å β = 101.18(2)°	<i>a</i> = 13.724(3) Å <i>b</i> = 16.549(4) Å <i>c</i> = 10.338(2) Å α = 95.41(2)° β = 102.17(2)° γ = 85.05(2)°	<i>a</i> = 22.471(6) Å <i>b</i> = 19.916(5) Å <i>c</i> = 18.351(8) Å
volume (Å ³)	4394(3)	2280(2)	8212(8)
<i>Z</i>	4	2	8
ρ_{calcd} (g cm ⁻³)	1.239	1.210	1.255
λ (Mo K α) (Å)	0.710 69	0.710 69	0.710 69
μ (Mo K α) (cm ⁻¹)	4.51	4.36	4.79
<i>F</i> (000)	1744	880	3280
transmission factors	0.946–1.000	0.967–1.000	0.902–1.000
scan speed (ω) (deg min ⁻¹)	8	8	8
2θ interval	5° < 2θ < 45°	5° < 2θ < 45°	5° < 2θ < 45°
no. of measd reflctns	8346	6310	7952
no. of unique reflctns	8014 (R_{int} = 0.074)	6009 (R_{int} = 0.085)	7945 (R_{int} = 0.090)
no. of obsd reflctns ($I > 3\sigma$)	4206	4147	2879
no. of params	469	472	442
reflctn/param ratio	8.97	8.79	6.51
R^a	0.048	0.062	0.055
R_w ($w = \sigma_F^{-2}$) ^b	0.062	0.076	0.065
max Δ/σ in final cycle	0.69	16.99	0.02
gof	1.80	2.51	1.75

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

[CpRu*(C₂H₄)(dippe)][BPh₄] (16).** **16** was obtained following a procedure identical to that for **13**, starting from [Cp**Ru*Cl(dippe)] (0.27 g, 0.5 mmol). It was not recrystallized due to decomposition. Yield: 0.42 g, quantitative. Anal. Calcd for C₅₀H₇₁BP₂Ru: C, 71.0; H, 8.46. Found: C, 70.7; H, 8.37. NMR (acetone-*d*₆, under ethylene) δ : (¹H) 1.752 (s, C₅(CH₃)₅); 1.968 (t, *J*(H,P) = 2.8 Hz, C₂H₄). (³¹P{¹H}) 75.07 (s). (¹³C{¹H}) 10.42 (s, C₅(CH₃)₅); 19.229, 19.274, 19.661, 20.420 (s, P(CH(CH₃)₂)₂); 22.04 (t, *J*(C,P) = 19.8 Hz, PCH₂); 28.07 (s, P(CH(CH₃)₂)₂); 28.34 (s, P(CH(CH₃)₂)₂); 33.30 (s, C₂H₄); 85.30 (s, C₅(CH₃)₅).

Experimental Data for the X-ray Crystal Structure Determinations. A summary of crystallographic data for compounds **2**, **12**, and **13** is given in Table 2. X-ray measurements were made on crystals of the appropriate size, which were mounted onto a glass fiber, and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo K α graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω - 2θ scan method. Lorentz, polarization, and absorption (ψ scan method) corrections were applied. Decay was negligible during data collection for **12**, but a deterioration correction was applied in the case of **2** and **13**. Reflections having $I > 3\sigma(I)$ were used for structure analysis. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN¹² software system and ORTEP¹³ for plotting. All the structures were solved by the Patterson method and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. For **2**, most of the hydrogen atoms were included at idealized positions and not refined. Only one of the hydride atoms was located using a difference Fourier map. Attempts made to locate both hydrides using high-angle difference Fourier maps were unsuccessful. Disorder was found for the *tert*-butyl group of the isocyanide ligand in **12**. This disorder was satisfactorily modeled using

Table 3. Selected Bond Distances and Angles for [CpRu*H₂(dippe)][BPh₄]**

Intramolecular Distances ^a (Å)			
Ru(1)–P(1)	2.296(2)	Ru(1)–C(3)	2.225(7)
Ru(1)–P(2)	2.298(2)	Ru(1)–C(4)	2.237(7)
Ru(1)–C(1)	2.272(7)	Ru(1)–C(5)	2.275(7)
Ru(1)–C(2)	2.240(8)		
Intramolecular Bond Angles ^a (deg)			
P(1)–Ru(1)–P(2)	87.53(7)	P(2)–Ru(1)–C(1)	104.2(2)
P(1)–Ru(1)–C(1)	165.9(2)	P(2)–Ru(1)–C(2)	116.3(2)
P(1)–Ru(1)–C(2)	144.0(2)	P(2)–Ru(1)–C(3)	150.8(2)
P(1)–Ru(1)–C(3)	112.3(2)	P(2)–Ru(1)–C(4)	159.7(2)
P(1)–Ru(1)–C(4)	105.1(2)	P(2)–Ru(1)–C(5)	122.8(2)
P(1)–Ru(1)–C(5)	129.9(3)		
P(1)–Ru(1)–H(1)	75.13		

^a Estimated standard deviations in the least significant figure are given in parentheses.

two positions for atoms C(22), C(23) and C(24), with half-occupancy. These atoms were isotropically refined without bonded hydrogens. Slight disorder was also observed for the Cp group, but so small that no attempt to model it was made. In the case of complex **13**, the hydrogen atoms in the cyclopentadienyl and ethylene ligands were located on a regular difference Fourier map. Most of the other hydrogen atoms were included at idealized positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were +0.67 and –0.55 e Å⁻³ for **2**, +1.35 and –1.25 e Å⁻³ for **12**, and +0.87 and –0.61 e Å⁻³ for **13**. Selected bond lengths and angles for each compound are listed in Tables 3–5.

Results and Discussion

The complexes [Cp*Ru*Cl(dippe)] and [Cp**Ru*Cl(dippe)] react with dihydrogen in MeOH or EtOH, in the presence of NaBPh₄, yielding white, crystalline [Cp*Ru*H₂(dippe)][BPh₄] (**1**) or [Cp**Ru*H₂(dippe)][BPh₄] (**2**), respectively. The hydride protons appear on the ¹H NMR spectra as triplets centered at –10.370 ppm and –9.840 ppm for **1** and **2**, respectively. The ³¹P{¹H} NMR

(12) Molecular Structure Corp., TEXSAN, *Single-Crystal Structure Analysis Software*, version 5.0; The Woodlands, TX, 1989.

(13) Johnson, C. K. ORTEP, *A Thermal Ellipsoid Plotting Program*, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

Table 4. Selected Bond Distance and Angles for [CpRu(CNBU^t)(dippe)][BPh₄]

Intramolecular Distances ^a (Å)			
Ru–P(1)	2.306(2)	Ru–C(4)	2.23(1)
Ru–P(2)	2.312(2)	Ru–C(5)	2.24(1)
Ru–C(1)	2.24(1)	Ru–C(20)	1.93(1)
Ru–C(2)	2.24(1)	N–C(20)	1.15(1)
Ru–C(3)	2.22(1)	N–C(21)	1.48(1)
Intramolecular Bond Angles ^a (deg)			
P(1)–Ru–P(2)	84.55(8)	P(2)–Ru–C(1)	150.5(4)
P(1)–Ru–C(1)	101.0(3)	P(2)–Ru–C(2)	113.4(3)
P(1)–Ru–C(2)	106.8(3)	P(2)–Ru–C(3)	96.4(3)
P(1)–Ru–C(3)	139.9(4)	P(2)–Ru–C(4)	114.4(5)
P(1)–Ru–C(4)	159.9(4)	P(2)–Ru–C(5)	149.6(4)
P(1)–Ru–C(5)	125.8(4)	P(2)–Ru–C(20)	92.3(3)
P(1)–Ru–C(20)	88.0(3)	C(20)–N–C(21)	170(1)

^a Estimated standard deviations in the least significant figure are given in parentheses.

Table 5. Selected Bond Distances and Angles for [CpRu(η²-C₂H₄)(dippe)][BPh₄]

Intramolecular Distances ^a (Å)			
Ru(1)–P(1)	2.338(3)	Ru(1)–C(4)	2.24(1)
Ru(1)–P(2)	2.339(3)	Ru(1)–C(5)	2.27(1)
Ru(1)–C(1)	2.25(1)	Ru(1)–C(6)	2.24(1)
Ru(1)–C(2)	2.20(1)	Ru(1)–C(7)	2.25(1)
Ru(1)–C(3)	2.27(1)	C(1)–C(2)	1.43(2)
Intramolecular Bond Angles ^a (deg)			
P(1)–Ru(1)–P(2)	82.1(1)	P(2)–Ru(1)–C(1)	80.1(3)
P(1)–Ru(1)–C(1)	100.5(3)	P(2)–Ru(1)–C(2)	114.8(3)
P(1)–Ru(1)–C(2)	91.0(3)	P(2)–Ru(1)–C(3)	130.8(3)
P(1)–Ru(1)–C(3)	95.9(3)	P(2)–Ru(1)–C(4)	97.2(3)
P(1)–Ru(1)–C(4)	110.3(4)	P(2)–Ru(1)–C(5)	94.3(3)
P(1)–Ru(1)–C(5)	147.1(3)	P(2)–Ru(1)–C(6)	123.6(3)
P(1)–Ru(1)–C(6)	152.9(3)	P(2)–Ru(1)–C(7)	155.2(3)
P(1)–Ru(1)–C(7)	116.3(4)	C(1)–Ru(1)–C(2)	37.5(4)

^a Estimated standard deviations in the least significant figure are given in parentheses.

spectra consist of one singlet for both compounds. Longitudinal relaxation time (T_1) measurements made for the hydride protons in these compounds support a "classical" dihydride structure, since the minimum values for T_1 are 674 and 870 ms, respectively, (400 MHz, acetone-*d*₆). Oxidative addition of the dihydrogen molecule to these complexes has taken place furnishing organoruthenium(IV) dihydrides, with no spectral evidence for dihydride/dihydrogen equilibria at low temperatures. Spectra are consistent with a "four-legged" piano stool geometry for the dihydride cations, as has been found for the homologue iron derivatives [CpFeH₂(dippe)]⁺ and [Cp*FeH₂(dippe)]⁺,⁸ as well as for other half-sandwich ruthenium dihydrides such as [CpRuH₂(PMe₃)₂]⁺¹⁴ or [Cp*RuH₂(dppm)]⁺ (dppm = 1,1-bis(diphenylphosphino)ethane).¹⁵ In all these cases, the hydride ligands adopt a transoid disposition. For **1** and **2**, ¹H and ³¹P{¹H} NMR spectra do not allow one to distinguish unequivocally a cisoid (*C*_s symmetry) or transoid (*C*_{2v} symmetry) disposition. Some authors have used asymmetric phosphines to solve the cisoid/transoid ambiguity in the dihydride structures.^{5a} We have used ¹³C{¹H} NMR spectroscopy to discern these two possibilities.^{8,16} The presence in the ¹³C{¹H} NMR spectra of only four signals for the phosphine carbon atoms, apart from those due to the C₅H₅ or C₅Me₅ ligands,

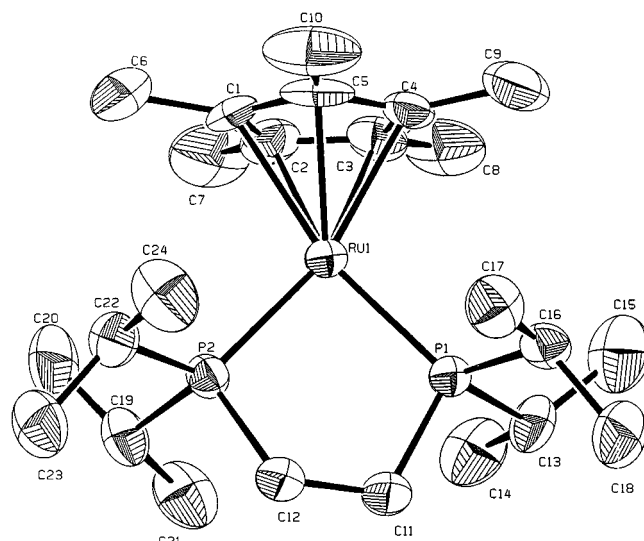


Figure 1. ORTEP drawing of the cation [Cp*RuH₂(dippe)]⁺ with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

indicates a *C*_{2v} symmetry characteristic of a transoid arrangement of hydrides. An X-ray crystal structure analysis of **2** has confirmed this structural assignment. A view of the cation [Cp*RuH₂(dippe)]⁺ is shown in Figure 1. Selected bond lengths and angles are listed in Table 3. Despite the fact that hydride atoms could not be located, the disposition of the phosphine ligand with the P(1)–Ru–P(2) plane almost perpendicular (87.9°) to the plane defined by the C₅ ring of the C₅Me₅ group indicates a "four-legged" piano stool having transoid hydrides. This structure is essentially identical to that adopted by the iron derivative [Cp*FeH₂(dippe)]-[BPh₄],⁹ and it compares well with that of [CpRuH₂(PMe₃)₂][BF₄], recently reported.¹⁴ The P(1)–Ru–P(2) angle of 87.53(7)° is smaller in our case than the value of 110.6(1)° found in [CpRuH₂(PMe₃)₂][BF₄]. In this complex, the phosphine ligands are bidentate and do not have the "bite angle" imposed by the backbone ethane group in bidentate dippe.

The dihydrides **1** and **2** are quite stable toward reductive elimination of dihydrogen, but they are cleanly deprotonated by KOBu^t in THF, yielding the neutral monohydrides [CpRuH(dippe)] (**3**) and [Cp*RuH(dippe)] (**4**). These compounds are white, crystalline, air-sensitive materials, soluble in nonpolar solvents. They react slowly with chlorinated solvents to yield the corresponding chloro complex, [CpRuCl(dippe)] or [Cp*RuCl(dippe)]. The IR spectra of the monohydrides display one strong ν(RuH) band at 1971 cm⁻¹ for **3** and 1973 cm⁻¹ for **4**, whereas the hydride resonance appears on the ¹H NMR spectra as high-field triplet. These complexes are also prepared directly from [CpRuCl(dippe)] or [Cp*RuCl(dippe)], either by reaction with NaBH₄ in MeOH or with ¹PrMgCl in THF. The latter procedure implies a β-elimination reaction from an unstable ruthenium–isopropyl complex formed *in situ*, a process known to occur for other related ruthenium¹⁷ and iron¹⁸ complexes.

The monohydrides **3** and **4** are protonated by HBF₄·OEt₂ in acetone-*d*₆ at room temperature, furnish-

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(15) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161.

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ing the dihydride cations $[\text{CpRuH}_2(\text{dippe})]^+$ or $[\text{Cp}^*\text{RuH}_2(\text{dippe})]^+$, as inferred from NMR spectroscopy. If the protonation is carried out at -80°C , then the dihydrogen complexes $[\text{CpRu}(\eta^2\text{-H}_2)(\text{dippe})][\text{BF}_4]$ (**5**) and $[\text{Cp}^*\text{Ru}(\eta^2\text{-H}_2)(\text{dippe})][\text{BF}_4]$ (**6**) are obtained. The presence of a dihydrogen ligand in these complexes is characterized by a broad resonance in the corresponding ^1H NMR spectra at -10.443 ppm for **5** and at -10.640 ppm for **6**, having short minimum longitudinal relaxation times of 34- and 14 ms, respectively (acetone- d_6 , 400 MHz). These values of T_1 are typical of "nonclassical" hydrides.^{2,19} The values of the $\mathcal{J}(\text{H},\text{D})$ coupling constants observed for the isotopomers $[\text{CpRu}(\text{HD})(\text{dippe})]^+$ and $[\text{Cp}^*\text{Ru}(\text{HD})(\text{dippe})]^+$, 20.5 and 21 Hz, respectively, are also consistent with the formulation as dihydrogen complexes. In contrast with this, no resolvable HD coupling was observed for the isotopomers of the dihydrides **1** and **2**, as expected. The $^{31}\text{P}\{^1\text{H}\}$ NMR display one sharp resonance, these spectral data being consistent with a "three-legged" piano stool, similar to that found for the dihydrogen complex $[\text{Cp}^*\text{Ru}(\eta^2\text{-H}_2)(\text{dppm})][\text{BF}_4]$ by neutron diffraction.²⁰

Protonation of neutral hydrides of the type $[\text{CpRuHP}_2]$ or $[\text{Cp}^*\text{RuHP}_2]$ has proven to be an useful route to cationic ruthenium(II) dihydrogen complexes and/or ruthenium(IV) dihydrides. In those instances in which the thermal stability of both species is similar, equilibrium mixtures of dihydrogen/dihydride are observed.^{5b} Otherwise, irreversible isomerization to the stable dihydride form takes place.^{5a} This is what happens in our case, and as temperature rises, the dihydrogen complexes **5** and **6** rearrange irreversibly to the corresponding dihydride. In fact, all attempts made to isolate either **5** or **6** as solids led to the corresponding dihydride isomer. The kinetics of the dihydrogen to dihydride isomerization has been studied by NMR spectroscopy. In a typical experiment, samples of the neutral hydride **3** or **4** in acetone- d_6 were treated with a slight excess of $\text{HBF}_4\cdot\text{OEt}_2$ at -80°C . The samples were then inserted into the spinner and lowered into the NMR precooled probe. At temperatures below -60°C , the sole product observed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR was the dihydrogen isomer **5** or **6**. As the temperature rises, the signals corresponding to the dihydrogen species decrease and new signals, attributable to the dihydride tautomer, increase their intensities with time. Kinetic data acquired following the rate of disappearance of the phosphorus resonance of the $\eta^2\text{-H}_2$ complex **5** or **6** in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were consistent with a first-order process. Data were collected over 3 half-lives or more at different temperatures, and rate constants were obtained from the slope of the least-squares best-fit lines of the $\ln(\text{intensity})$ vs time plots. These rate constants are invariant with the starting concentration of complex and with the concentration of acid. The rate constants at 267 K are $(1.76 \pm 0.03) \times 10^{-3} \text{ s}^{-1}$ for the isomerization of **5**, and $(2.27 \pm 0.06) \times 10^{-2} \text{ s}^{-1}$ for **6**. Thus, the rearrangement is faster for the Cp^* derivative, an observation that is not consistent with data in the literature for complexes of the type $[\text{LRu}(\text{H}_2)\text{P}_2]^+$ ($\text{L} = \text{Cp}$ or Cp^* ; $\text{P} = \text{phosphine ligand}$), where the isomerization has shown to be faster for Cp derivatives in

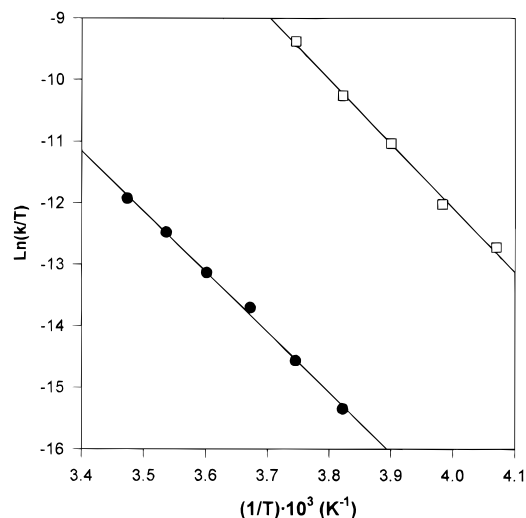
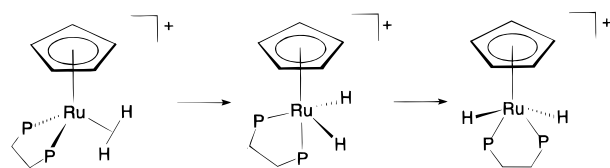


Figure 2. Plot of $\ln(k/T)$ vs $1/T$ (K^{-1}) for the irreversible isomerization of $[\text{CpRu}(\eta^2\text{-H}_2)(\text{dippe})]^+$ to $[\text{CpRuH}_2(\text{dippe})]^+$ (\bullet) and of $[\text{Cp}^*\text{Ru}(\eta^2\text{-H}_2)(\text{dippe})]^+$ to $[\text{Cp}^*\text{RuH}_2(\text{dippe})]^+$ (\square).

Scheme 1. Mechanism of the Dihydrogen to Dihydride Isomerization for Complexes of the Type $[\text{CpRu}(\text{H}_2)\text{P}_2]^+$, According to Chinn and Heinekey^{5a}

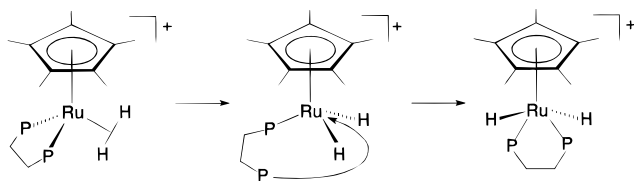


comparison with their Cp^* homologues.^{2,5a} Typical reported activation enthalpies range from 10 to 20 kcal mol^{-1} , with small, negative activation entropies. These small entropies of activation are in support of an intramolecular mechanism for the isomerization process, in which the H_2 ligand in the transition state has lost rotational freedom, accounting in this way for the negative value of ΔS^\ddagger .² Activation parameters for our system were derived from an Eyring plot for each of the series of rate constants determined at different temperatures, ranging from 262 to 288 K in the case of $[\text{CpRu}(\text{H}_2)(\text{dippe})]^+$ and from 246 to 267 K for $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dippe})]^+$ (Figure 2). Thus, for the isomerization of **5**, ΔH^\ddagger and ΔS^\ddagger were found to be $18.4 \pm 0.5 \text{ kcal mol}^{-1}$ and $-1.9 \pm 0.1 \text{ eu}$, respectively. These values compare well with those reported in the literature for related complexes, i.e., ΔH^\ddagger $16.1 \pm 1.8 \text{ kcal mol}^{-1}$ and ΔS^\ddagger $-2.8 \pm 7.9 \text{ eu}$ for the irreversible rearrangement of $[\text{CpRu}(\text{H}_2)(\text{PPh}_3)_2]^+$ to $[\text{CpRuH}_2(\text{PPh}_3)_2]^+$.^{5a} In contrast with this, the values of ΔH^\ddagger and ΔS^\ddagger for the isomerization of **6** were $21 \pm 1 \text{ kcal mol}^{-1}$ and $+11.5 \pm 0.3 \text{ eu}$, respectively. Whereas ΔH^\ddagger remains of the same order of that of the Cp complex, although slightly higher, ΔS^\ddagger is larger and positive. The mechanism of dihydrogen to dihydride isomerization suggested in the literature for half-sandwich ruthenium complexes is intramolecular and independent of external acid or phosphine concentration. The ground-state $\eta^2\text{-H}_2$ complex traverses a relatively high energy transition state along the pathway to dihydride (Scheme 1).^{2,5a} The geometry of the transition state is responsible for the higher energy barrier observed for the isomerization of Cp^* complexes compared to their Cp homologues, since steric interactions between large phosphines and the ring methyl

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Scheme 2. Alternative Dihydrogen to Dihydride Isomerization Mechanism Proposed for the Irreversible Rearrangement 2 → 6



groups would be enhanced in such geometry. Our kinetic data are consistent with this mechanism in the case of the isomerization of the Cp **5**. However, this does not seem to apply to the Cp* complex. If the mechanism shown in Scheme 1 were operating here, the rearrangement should be expected to occur slower for this compound than for the Cp complex. However, isomerization occurs faster in this case than for the complex containing the less sterically demanding Cp group, suggesting that an alternative mechanism of lower activation energy is feasible. The isopropyl substituents of dippe are possibly too bulky to allow the proposed geometry for the transition state shown in Scheme 1 to be adopted in the case of **6**. The positive value for ΔS^\ddagger seems to be in support of a dissociative mechanism in this case. An alternative dissociative mechanism has been proposed for the isomerization of the acidic dihydrogen complex [CpRu(H₂)(CO)(PMe₃)]⁺, in which solvent-promoted deprotonation of the coordinated H₂ is thought to produce [CpRuH(CO)(PMe₃)] in low concentration, this being reprotonated at the metal to give the dihydride tautomer.²¹ However, this mechanism appears only feasible for very acidic dihydrogen complexes. Furthermore, our kinetic measurements were carried out in the presence of an excess of acid, the rate constants being invariant with acid concentration, so this sort of mechanism does not seem likely to operate. In the light of our data, we propose a dissociative and intramolecular mechanism of isomerization for the Cp* complex, in which one of the phosphorus atoms of the dippe ligand dissociates from the metal yielding a 16-electron dihydride transient species, namely, [Cp*RuH₂(η^1 -dippe)]⁺, in which the diphosphine ligand is acting as monodentate. Further attack of the pendant phosphorus atom on the metal produces the final dihydride tautomer, as shown on Scheme 2. Phosphine chelate ring opening is a well-established process that has been shown to occur fast in solution in a number of complexes.²² Therefore, the key step in this process should be the formation of a short-lived 16-electron dihydride intermediate, which has never been detected. Phosphine dissociation processes leading to coordinatively unsaturated metal complexes, as well as the formation of 16-electron hydride complexes, are well-precedented facts in ruthenium chemistry.²³ Bulky phosphines, either monodentate or bidentate, and stronger donors such as the Cp* ligand contribute to stabilize these species, i.e., [Cp*RuX(PR₃)] (X = Cl; R = ⁱPr, Cy),²⁴ a class of π -stabilized, yet reactive half-sandwich ru-

thenium derivatives,²⁵ which has no homologues having the less sterically demanding, poorer donor Cp ligand. Furthermore, the complex [Cp*RuH₂(PPh₃)]⁺, formally analogous to [Cp*RuH₂(η^1 -dippe)]⁺, has been proposed to be one of the intermediate species resulting from the protonation of [Cp*RuH₃(PPh₃)] by CF₃CH₂OH.²⁶ There are also recent examples of 16-electron ruthenium dihydrogen complexes.²⁷ The mechanism suggested here is only likely to operate for systems containing ligands that are both sterically demanding and good electron donors. The driving force for the dihydrogen to dihydride rearrangement seems to be the high thermodynamic stability of the dihydride form, which is enhanced by ligands matching such steric and electronic requirements.² In other cases, the isomerization is expected to occur according to the mechanism shown in Scheme 1, although other alternative possibilities cannot be ruled out. What appears clear from this study is that the dihydrogen complexes **5** and **6** are the kinetic products of the protonation of the monohydrides **3** and **4**, respectively, whereas the dihydrides **1** and **2** are the thermodynamic products of such reactions. This observation is fully consistent with the affirmation by Chinn and Heinekey that the dihydrogen complex is always the kinetic product of protonation, irrespective of the ligand environment, and that the final product is thermodynamically determined.^{5a}

The dihydrogen ligand in **5** or **6** is not displaced by dinitrogen to yield the corresponding dinitrogen derivatives. However, [CpRuCl(dippe)] reacts with AgBF₄ or AgCF₃SO₃ in ethanol or methanol under dinitrogen to furnish the novel half-sandwich dinitrogen complex [CpRu(N₂)(dippe)]⁺, which was isolated as tetraphenylborate salt **7**. This yellow, crystalline material exhibits one strong ν (N₂) band at 2145 cm⁻¹ in the IR spectrum. This value is higher than that for the homologous iron complex [CpFe(N₂)(dippe)][BPh₄] (2112 cm⁻¹)⁹ and in the range observed for other ruthenium dinitrogen complexes, i.e., [RuH(N₂)(depe)₂][BPh₄] (2163 cm⁻¹, depe = 1,2-bis(diethylphosphino)ethane),²⁸ [RuH(N₂)(pp₃)] [BPh₄] (2182 cm⁻¹, pp₃ = P(CH₂CH₂PPh₂)₃),²⁹ or [RuH₂(N₂)(PPh₃)₃] (2147 cm⁻¹).³⁰ No half-sandwich ruthenium dinitrogen complex has yet been reported, as far as we are aware, although it has been possible to estimate the value of ν (N₂) for the hypothetical complex [CpRu(N₂)(dppe)]⁺, as 2193 cm⁻¹.⁴ The dinitrogen ligand is labile in solution, as has been observed for other ruthenium dinitrogen complexes,⁷ being displaced by acetone to give [CpRu(Me₂CO)(dippe)][BPh₄] (**8**). This orange, crystalline compound was better prepared by reaction of [CpRuCl(dippe)] with AgBF₄ or AgCF₃SO₃ in acetone under argon, followed by addition of NaBPh₄

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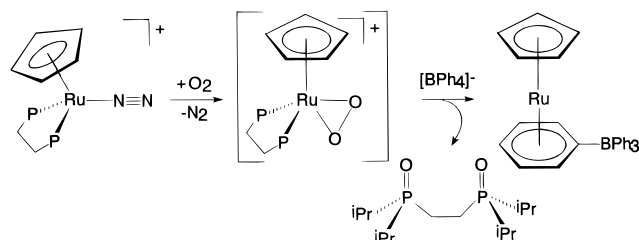
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in EtOH, and it has shown to be an excellent precursor for the preparation of complexes of the type $[\text{CpRu}(\text{L})(\text{dippe})][\text{BPh}_4]$ ($\text{L} =$ neutral donor molecule). One band at 1650 cm^{-1} in the IR spectrum of **8** is ascribed to $\nu(\text{C}=\text{O})$ of coordinated acetone. Both **7** and **8** exhibit one singlet in their respective $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. They are readily interconverted one into the other. Thus, the dinitrogen complex **7** exists in acetone solution under dinitrogen as a mixture with the acetone complex **8**, this being the major product as inferred from $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, or the only product under an argon atmosphere. On the other hand, the acetone complex is completely converted into the dinitrogen adduct in dichloromethane solution under dinitrogen. Both **7** and **8** are extremely air-sensitive in solution. Dichloromethane solutions of **7** and/or **8** become green upon brief exposure to atmospheric oxygen. Examination of these solutions by ^1H NMR spectroscopy showed one Cp resonance at 4.786 ppm and new multiplet signals at 5.621 and 6.212 ppm, as well as a more complex pattern for the phenyl resonances of the tetraphenylborate ion. The multiplets at 5.621 and 6.212 ppm are attributed to protons of a η^6 -coordinated phenyl ring from the tetraphenylborate ion. These spectral data match those reported for the known complex $[\text{CpRu}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)]$ (**9**).^{31,32} Green-brown crystals of this compound were isolated from these dichloromethane solutions by addition of petroleum ether. The dippe ligand is therefore lost together with dinitrogen or acetone in the course of degradation of **7** or **8** to yield **9**. Consistent with this, no signal was observed in the relevant region of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of air-exposed dichloromethane solutions of **7** or **8**. However, no signal attributable to free dippe was observed either. Instead, one single resonance at 59.04 ppm was present. The species responsible for this signal has been identified as $^i\text{Pr}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})^i\text{Pr}_2$, as inferred also from the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra by comparison with an authentic sample. Thus, the formation of **9** is accompanied by the concomitant elimination of the diphosphine dioxide $^i\text{Pr}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})^i\text{Pr}_2$. It is noteworthy that air oxidation of dippe is a very slow process, whereas in our system, the oxidized phosphine is released almost immediately. Therefore, this oxidation process seems to be mediated by the metal complex. There are some precedents for the formation of **9** from complexes of the type $[\text{CpRu}(\text{L})(\text{PPh}_3)_2][\text{BPh}_4]$ ($\text{L} =$ MeOH or $(\text{CH}_3)_2\text{CO}$), but in these cases, the fate of the phosphine ligands was not described.³² In a recent work we reported the synthesis and crystal structure of the dioxygen complex $[\text{Cp}^*\text{Ru}(\eta^2\text{-O}_2)(\text{dippe})][\text{BPh}_4]$, and we noted the fact that no analogous complex containing the Cp ligand had been observed. A reasonable explanation to all these observations can be given based upon the reaction sequence shown in Scheme 3. Dioxygen displaces N_2 from the dinitrogen complex **7** (or acetone from **8**) to furnish $[\text{CpRu}(\eta^2\text{-O}_2)(\text{dippe})]^+$, analogous to $[\text{Cp}^*\text{Ru}(\eta^2\text{-O}_2)(\text{dippe})]^+$. This species possibly undergoes a concerted elimination of $^i\text{Pr}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})^i\text{Pr}_2$, the fragment $[\text{CpRu}]^+$ being trapped by $[\text{BPh}_4]^-$ to yield $[\text{CpRu}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)]$ as final product. All attempts made to detect the intermediate dioxygen complex by

Scheme 3. Proposed Reaction Sequence for the Degradation of the Dinitrogen Complex **7 in Solution**



low-temperature NMR spectroscopy were unsuccessful. The reaction with atmospheric oxygen is very slow at low temperatures, as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. At higher temperatures, the signal corresponding to **7** disappears, being replaced by the resonance of the diphosphine dioxide. No signals attributable to intermediate species were observed, suggesting that the dioxygen complex must be an unstable, short-lived species, which transfers O_2 to the dippe ligand immediately. This process seems to be responsible for the relative ease of decomposition of complexes **7** and **8** in solution, since it takes place even at trace level concentrations of O_2 present in high-purity dinitrogen or argon used for all the manipulations. Although the reaction sequence shown in Scheme 3 seems to be reasonable, it must be regarded with caution, since no direct spectral evidence could be obtained for the intermediate dioxygen complex, and therefore, other possible reaction pathways cannot be ruled out.

The dinitrogen complex $[\text{Cp}^*\text{Ru}(\text{N}_2)(\text{dippe})][\text{BPh}_4]$ (**10**), which was obtained in a manner similar to that for **7**, shows an even greater avidity for dioxygen, but in this case the ultimate metal-containing product is the stable dioxygen complex $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dippe})][\text{BPh}_4]$. Compound **10** is a khaki-green material that displays one strong $\nu(\text{N}_2)$ stretching band at 2120 cm^{-1} in its IR spectrum, a value slightly lower than that found for the cyclopentadienyl derivative **7**. The dinitrogen ligand in **10** is far more labile than in **7**, being readily lost in solution and replaced gradually by dioxygen. For this reason, signals attributable to $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dippe})][\text{BPh}_4]$ were always present in the NMR spectra, despite all efforts made to exclude oxygen. This is possibly the reason for the relatively low dinitrogen content found by microanalysis. It is interesting to note that it has not been possible to obtain the homologous iron complex $[\text{Cp}^*\text{Fe}(\text{N}_2)(\text{dippe})][\text{BPh}_4]$, which does not seem to be a stable species. In contrast to the cyclopentadienyl-ruthenium derivative, the formation of an acetone adduct has not been observed in this case.

The values of $\nu(\text{N}_2)$ found for **7** and **10** suggest, according to the criterion proposed by Morris,^{3,4} that the corresponding dihydrogen complexes **5** and **6** should be stable species and that no homolytic dihydrogen splitting should occur. We have previously noted this for the iron-dinitrogen complex $[\text{CpFe}(\text{N}_2)(\text{dippe})][\text{BPh}_4]$,⁹ but in all these cases, the stable product derived from the interaction with H_2 is the corresponding dihydride complex. However, it has been suggested that in those instances in which the dihydride form is made particularly stable, homolytic splitting may occur even when $\nu(\text{N}_2)$ of the dinitrogen complex is greater than 2060 cm^{-1} .² This is possibly the explanation to the fact that

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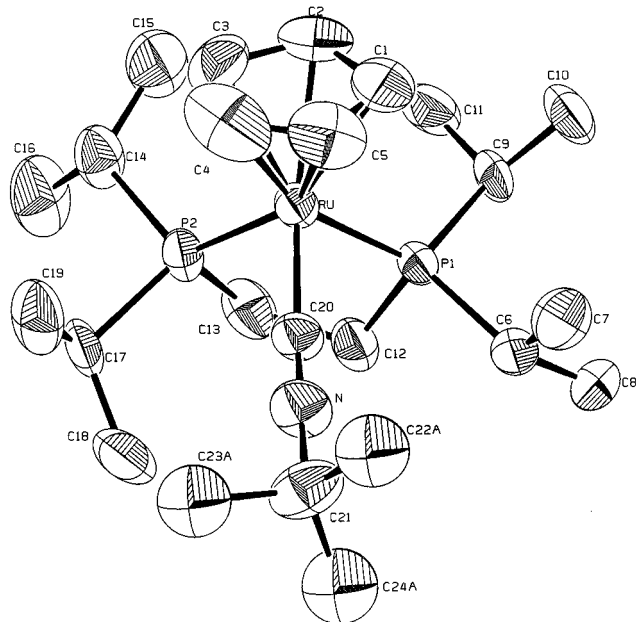


Figure 3. ORTEP drawing of the cation [CpRu(CNBU^t)(dippe)]⁺ with 50% probability thermal ellipsoids. Only one of the two possible orientations of the *tert*-butyl groups is shown. Hydrogen atoms are omitted.

in our case the dihydrides are the stable species, despite what $\nu(\text{N}_2)$ suggests otherwise. Therefore, care must be taken in the application of the $\nu(\text{N}_2)$ criterion for determining the relative stability of dihydrogen or dihydride complexes.

Other molecules, such as CO, CNBU^t, and C₂H₄, also bind to the [CpRu(dippe)]⁺ or [Cp*Ru(dippe)]⁺ moieties to give the corresponding adducts [CpRu(L)(dippe)]-[BPh₄] (L = CO (**11**), CNBU^t (**12**), C₂H₄ (**13**)) or [Cp*Ru(L)(dippe)]-[BPh₄] (L = CO (**14**), CNBU^t (**15**), C₂H₄ (**16**)), respectively. The carbonyls **11** and **14**, and the isocyanide derivatives **12** and **15** are crystalline, air-stable materials, which exhibit one strong $\nu(\text{CO})$ or $\nu(\text{CN})$ band in their respective IR spectra. Whereas the $\nu(\text{CN})$ band appears at essentially the same wavenumber for **12** and **15**, the $\nu(\text{CO})$ band in the Cp* complex **14** lies at lower frequency (1926 cm⁻¹) than for **11** (1959 cm⁻¹). This behavior was previously observed for the homologous iron complexes [CpFe(L)(dippe)]-[BPh₄] and [Cp*Fe(L)(dippe)]-[BPh₄] (L = CO, CNBU^t),⁹ and it has been explained in terms of the increased electron density at the metal center for Cp* complexes, due to the stronger donor properties of the Cp* ligand compared to Cp. NMR spectral data for these compounds are quite unexceptional, suggesting "three-legged" piano stool structures in all cases, this being evident from an X-ray crystal structure determination for **12**. A view of the cation [CpRu(CNBU^t)(dippe)]⁺ is shown in Figure 3. Selected bond lengths and angles are listed in Table 4. The most significant features of this structure are the disorder present in the *tert*-butyl group, as well as the almost perfectly linear disposition of the isocyanide ligand, having the Ru-C(20)-N and C(20)-N-C(21) angles close to 170°. These two observations are frequent for complexes containing CNBU^t ligands.³³ The C(20)-N and N-C(21) separations of 1.148(9) and 1.48(1) Å, respectively, compare well with

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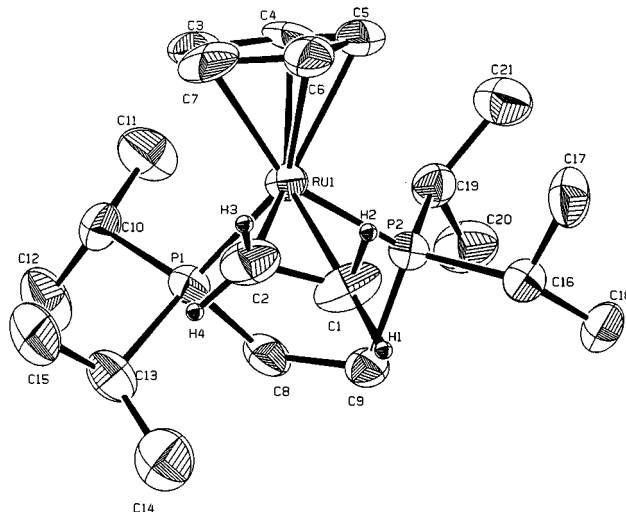


Figure 4. ORTEP drawing of the cation [CpRu(η^2 -C₂H₄)(dippe)]⁺ with 50% probability thermal ellipsoids. Hydrogen atoms, except those on the ethylene ligand, are omitted.

those found in other half-sandwich ruthenium isocyanide complexes, i.e., [CpRuI(CNBU^t)₂] (1.159 and 1.442 Å)³⁴ and [CpRu(CNBU^t)(CO)(PPh₃)]-[PF₆] (1.152 and 1.460 Å).³⁵ These bond distances do not differ much from those found in the free isocyanide, suggesting that there is very little back-bonding from the metal. Consistent with this, the Ru-C(20) bond length of 1.931(8) Å corresponds to a single Ru-C bond, this value being very similar to that found for the complex [CpRu(CNBU^t)(NH₃)(PPh₃)]-[PF₆] (1.934 Å).³⁶ The ethylene adducts [CpRu(η^2 -C₂H₄)(dippe)]-[BPh₄] (**13**) and [Cp*Ru(η^2 -C₂H₄)(dippe)]-[BPh₄] (**16**) deserve a more detailed comment. These are pale green (**13**) or white (**16**) crystalline materials, having no band in their IR spectra that can be unequivocally attributed to coordinated ethylene. Whereas the coordination of ethylene in **13** is irreversible, the Cp* derivative is labile and readily loses C₂H₄, so its characterization in solution was made under an ethylene atmosphere. The instability of ethylene-Cp*Ru adducts was also recently observed for [Cp*Ru(η^2 -C₂H₄)(P~O)₂]-[BPh₄] (P~O = (1,2-dioxan-2-ylmethyl)diphenylphosphine),³⁷ which is only stable under an atmosphere of ethylene, whereas other cyclopentadienylruthenium complexes such as [CpRu(η^2 -C₂H₄)(PPh₃)₂]⁺³⁸ or [CpRu(η^2 -C₂H₄)(PMe₃)₂]⁺³⁹ are stable species. The protons of the C₂H₄ ligand appear in the ¹H NMR spectra as one pseudotriplet centered at 2.498 ppm for **13** and at 1.968 ppm for **16**. These resonances do not experience any appreciable change, apart from broadening, when the temperature is lowered. This suggests a rapid rotation of the coordinated ethylene ligand in both complexes, even at low temperatures. Consistent with this, the ¹³C{¹H} NMR spectra of these compounds display one single resonance for the carbon atoms of coordinated ethylene near 33.5 ppm. All

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attempts to recrystallize the Cp* derivative led to ethylene loss and formation of the dioxygen complex $[\text{Cp}^*\text{Ru}(\eta^2\text{-O}_2)(\text{dippe})][\text{BPh}_4]$,¹¹ due to the enormous avidity of the $[\text{Cp}^*\text{Ru}(\text{dippe})]^+$ moiety for oxygen, even at trace level, as has been already mentioned. In contrast to this, single crystals of the more stable Cp complex **13** were obtained by recrystallization from dichloromethane/ethanol, and an X-ray crystal structure analysis was performed. An ORTEP drawing of the cation $[\text{CpRu}(\eta^2\text{-C}_2\text{H}_4)(\text{dippe})]^+$ is shown in Figure 4. Selected bond lengths and angles are listed in Table 5. The ethylene ligand is bound in the side-on manner, having a C(1)–C(2) separation of 1.43 (2) Å, which is very similar to that found in $[\text{Ru}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_3)_4]$ (1.439 Å)⁴⁰ and slightly longer than in $[\text{RuCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$ (1.375 Å),⁴¹ all these distances being longer than in the free C₂H₄ molecule (1.337 Å), as expected. The Ru–C(1) and Ru–C(2) bond lengths are 2.25(1) and 2.20(1) Å, respectively, corresponding to a symmetrical

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arrangement of the ethylene ligand. The hydrogen atoms on the ethylene group were located out of the ideal plane, which contains the ethylene molecule, and displaced away from the metal atom, as has been observed for other $\eta^2\text{-C}_2\text{H}_4$ complexes. All other bond lengths and angles in the phosphine and cyclopentadienyl ligands, as well as in the tetraphenylborate anion, are in the expected range and unexceptional.

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Supporting Information Available: ORTEPs and tables of X-ray crystallographic data, including atomic coordinates, anisotropic thermal parameters, and interatomic distances and angles for $[\text{Ru}(\text{Cp})(\text{dippe})(\text{C}_2\text{H}_4)][\text{BPh}_4]$ and $[\text{Ru}(\text{Cp})(\text{tBuNC})(\text{dippe})][\text{BPh}_4]$ (51 pages). Ordering information is given on any current masthead page.

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