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Half-Sandwich Hydride Complexes of Ruthenium with Bidentate Phosphinoamine Ligands: Proton-Transfer Reactions to $[(C_5R_5)RuH(L)]$ [R = H, Me; L = dippae, (*R*,*R*)-dippach]

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The complexes $[(C_5R_5)RuH(dippae)]$ [R = H (**1a**), Me (**2a**); dippae = 1,2-bis(diisopropylphosphinoamino)ethane] and $[(C_5R_5)RuH((R,R)\text{-dippach})]$ [R = H (**1b**), Me (**2b**); (*R*,*R*)-dippach = (*R*,*R*)-1,2-bis(diisopropylphosphinoamino)-cyclohexane] have been prepared and characterized. The cationic ruthenium(IV) dihydride derivatives $[(C_5R_5)RuH_2(dippae)][BPh_4]$ [R = H (**3a**), Me (**4a**)] and $[(C_5R_5)RuH_2((R,R)\text{-dippach})][BPh_4]$ [R = H (**3b**), Me (**4b**)] are also reported. No significant intramolecular interaction between the amino protons and the hydrogen atoms bound to the metal has been observed in any of these compounds. The X-ray crystal structure of **4a** was determined. The proton-transfer processes over the monohydrides **2a** and **2b** with $HBF_4{\cdot}OEt_2$ have been studied by NMR spectroscopy. Dicationic dihydride complexes $[CpRuH_2(LH)]^{2+}$ [LH = dippaeH$^+$ (**5a**), (*R*,*R*)-dippachH$^+$ (**5b**)] and $[Cp^*RuH_2(LH)]^{2+}$ [LH = dippaeH$^+$ (**6a**), (*R*,*R*)-dippachH$^+$ (**6b**)] result respectively from the protonation of either the monohydrides **1a**,**b** or **2a**,**b** or the dihydrides **3a**,**b** or **4a**,**b** at one of the NH groups of the phosphinoamine ligands by an excess of HBF_4. These dicationic derivatives exhibit fluxional behavior in solution. In the course of the protonation of **1a** with $HBF_4{\cdot}OEt_2$, a cationic dihydrogen complex and a dihydrogen-bonded derivative have been identified as intermediates by NMR spectroscopy. Another dihydrogen species, namely, $[CpRu(H{\cdots}HOOCPh)((R,R)\text{-dippach})]$, was also identified in the course of the reaction of **1b** with benzoic acid in toluene-d_8. The reaction of **1a** with 0.5 equiv of 1,1,1,3,3,3-hexafluoroisopropanol generates a hydride species having a very short $(T_1)_{min}$ of 6.5 ms at 400 MHz, an experimental fact for which no satisfactory explanation has yet been found.

Introduction

The protonation reactions of half-sandwich ruthenium hydride systems of the type $[(C_5R_5)RuHLL']$ (R = H or Me; L, L′ = tertiary phosphine or CO) have been the subject of many thorough synthetic, as well as mechanistic, and theoretical studies.[1−8] From these studies, it has been possible to establish the stepwise nature of this process and the identification of several intermediate species. Thus, the proton-transfer reaction from a donor HX to a hydride HML_n is preceded by the formation of a dihydrogen-bonded complex $XH{\cdots}HML_n$.[6,9,10] This species is converted to a dihydrogen complex forming a contact ion pair stabilized by hydrogen bonding with the anion $L_nM(H_2)^+{\cdots}X^-$, prior to the formation of the free $[L_nM(H_2)]^+$ and X^- ions as

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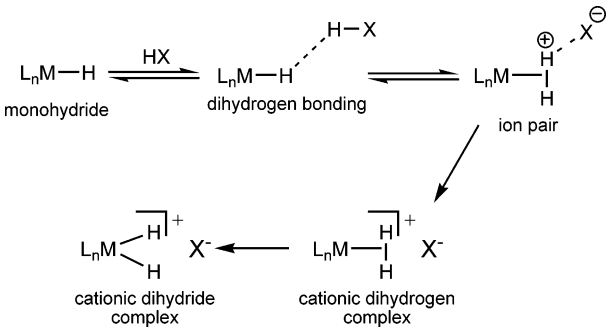
reaction products. In most cases, the dihydrogen complex undergoes isomerization to a ruthenium(IV) dihydride complex.[1,3,5]



In a recent work, we described the preparation and characterization of hydride complexes of the type [TpRuH(L)] and [TpRu(H_2)(L)][BAr′$_4$] [Tp = hydrotris(pyrazolyl)borate; Ar′$_4$ = 3,5-$C_6H_3(CF_3)_2$] bearing the phosphinoamine ligands L = dippae [1,2-bis(diisopropylphosphinoamino)ethane] or L = (*R*,*R*)-dippach [(*R*,*R*)-bis(diisopropylphosphinoamino)cyclohexane].[11] We remarked upon the fact that the TpRu dihydrogen complexes are stable species that do not rearrange to their dihydride tautomers at variance with CpRu or Cp*Ru related systems[12,13] and that this allowed the study of the proton-transfer reactions without the interference of such an isomerization process. We were able to detect by NMR spectroscopy dihydrogen-bonded intermediates, as well as dicationic dihydrogen complexes resulting from protonation at one of the lone pairs of the NH groups of the phosphinoamine ligand. All of the intermediate species identified in these systems were consistent with those recently proposed in the literature for proton-transfer reactions.[1,2,6] We also identified in the course of the protonation of [TpRuH(dippae)] with 0.5 equiv of HBF_4·OEt_2 a remarkable hydride species having an extremely short $(T_1)_{min}$ of 0.5 ms at −62 °C and 400 MHz. In some other rare case, a very short relaxation time of 1.4 ms at −40 °C and 400 MHz for the hydride NMR signal of [{$C_5H_4CH(CH_2CH_2)_2NHMe$}-RuH(PPh_3)$_2$][BF_4] had been previously reported.[14] The causes for these fast relaxation phenomena are still unknown.

We have now completed the study of the proton-transfer reaction on ruthenium hydrides bearing phosphinoamine ligands extending the work to the corresponding cyclopentadienyl and pentamethylcyclopentadienyl derivatives. At variance with the TpRu complexes, the driving force of these reactions is the formation of ruthenium(IV) dihydride complexes. This fact complicates the detection of intermediate species in the process but at the same time affords the opportunity to study new complexes that have no parallel in TpRu chemistry. In this work, we describe the synthesis and characterization of a series of CpRu and Cp*Ru hydride and related complexes containing either the phosphinoamine ligand dippae or the enantiopure (*R*,*R*)-dippach and the study by variable-temperature (VT)-NMR spectroscopy of their proton-transfer reactions.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, and petroleum ether (boiling point range 40−60 °C) were obtained oxygen- and water-free from an Innovative Technology, Inc., solvent purification apparatus. Toluene and fluorobenzene were of anhydrous quality and were used as received. All solvents were deoxygenated immediately before use. The ligands (*R*,*R*)-dippach and dippae were prepared following suitable adaptations of published procedures.[15−19] The complexes [CpRuCl(L)] [L = (*R*,*R*)-dippach, dippae] were obtained by suitable adaptation of the procedures previously reported by us for the preparation of [CpRuCl(dippe)] and [Cp*RuCl(dippe)] [dippe = 1,2-bis(diisopropylphosphino)ethane].[20] HBF_4, benzoic acid, and 1,1,1,3,3,3-hexafluoroisopropanol (HFIPOH) were used as supplied by Aldrich. IR spectra were taken in Nujol mulls on a Perkin-Elmer SPECTRUM 1000 FTIR spectrophotometer. NMR spectra were taken on a Varian Unity 400 MHz or a Varian Gemini 300 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^{1}H and ^{13}C{^{1}H}), 85% H_3PO_4 (^{31}P{^{1}H}), or $CFCl_3$ (^{19}F). Longitudinal relaxation time (T_1) measurements were made by the inversion−recovery method. Activation parameters for fluxional processes were obtained by a dynamic NMR line-shape fitting simulation using the program *DNMR3*[21] incorporated into *SpinWorks 2.2*.[22] Microanalysis was performed on a elemental analyzer model LECO CHNS-932 at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz, Cádiz, Spain.

[CpRuH(L)] [L = dippae (1a), (*R*,*R*)-dippach (1b)]. To a solution of either [CpRuCl(dippae)] (0.5 g, 1.2 mmol) or [CpRuCl((*R*,*R*)-dippach))] (0.5 g, 1 mmol) in ethanol (10 mL) was added an excess of solid $NaBH_4$ (0.1 g). The mixture was heated under reflux for 1 h. Upon cooling, an off-white precipitate was formed. The solids were filtered off, washed with ethanol (2 mL) and petroleum ether (5 mL), and dried in vacuo. Data for **1a**. Yield: 0.4 g, 72%. Anal. Calcd for $C_{19}H_{40}N_2P_2Ru$: C, 49.7; H, 8.77; N, 6.1. Found: C, 49.3; H, 8.50, N, 6.3. IR: ν(RuH) 1986, ν(NH) 3365 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ −13.6 (t, $^2J_{HP}$ = 37 Hz, 1 H, Ru*H*), 0.76 (m, 2 H, N*H*), 0.90, 0.97, 1.14, and 1.23 (m, 24 H, PCH(CH_3)$_2$), 1.57 (m, 4 H, PC*H*(CH_3)$_2$), 2.60 and 3.00 (m, 4 H, (CH_2)$_2$), 4.73 (s, 5 H, C_5H_5). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 132.2 (s). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 298 K): δ 17.1, 18.3, 18.8, and 20.4 (s, PCH(*C*H$_3$)$_2$), 32.2 and 34.8 (m, P*C*H(CH$_3$)$_2$), 44.8 (s, (*C*H$_2$)$_2$), 78.1 (s, C_5H_5). Data for **1b**. Yield: 0.25 g, 70%. Anal. Calcd for $C_{23}H_{46}N_2P_2Ru$: C, 53.8; H, 9.03; N, 5.5. Found: C, 54.0; H, 9.15; N, 5.6. IR: ν(RuH) 2016,

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ν(NH) 3374 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ −13.6 (dd, $^2J_{HP}$ = 37 Hz, $^2J_{HP'}$ = 35.6 Hz, 1 H, Ru*H*), 0.99, 1.18 (m, 24 H, PCH(C*H*$_3$)$_2$), 1.31 (m, 4 H, (C*H*$_2$)$_2$), 1.52 (m, 2 H, N*H*), 1.66 (m, 4 H, PC*H*(CH$_3$)$_2$), 2.87 (m, 2 H, C*HCH*), 4.67 (s, 5 H, C$_5$*H*$_5$). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 127.6 (d, J_{pp}= 42 Hz), 130.1 (d, J_{pp}= 42 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 298 K): δ 17.2, 17.3, 18.6, 18.4, 18.7, 18.9, 19.3, and 20.4 (s, PCH(*C*H$_3$)$_2$), 25.5, 25.6, 27.1, and 28.2 (s, (*C*H$_2$)$_4$), 35.4, 36.6, 36.8, and 37.5 (m, P*C*H(CH$_3$)$_2$), 56.8 and 59.2 (s, *CHC*H), 78.1 (s, *C*$_5$H$_5$).

These compounds are also accessible by deprotonation of the corresponding dihydride complexes [CpRuH$_2$(dippae)][BPh$_4$] (**3a**) or [CpRuH$_2$(dippach)][BPh$_4$] (**3b**) (vide infra): To a solution of the respective dihydride complex **3a** or **3b** (0.5 mmol) in THF (5 mL) was added solid KOBu^t (0.1 g, excess). The mixture was stirred for 10 min at room temperature. Then the solvent was removed in vacuo, the residue extracted with toluene (4 mL), and the resulting solution filtered off. Concentration of the solution, followed by the addition of petroleum ether and cooling to −20 °C, afforded microcrystals, which were filtered off and dried in vacuo. Yield: 60−65% in both cases.

[Cp*RuH(L)] [L = dippae (2a), (*R*,*R*)-dippach (2b)]. To a solution of either [Cp*RuCl(dippae)] (0.6 g, 1.2 mmol) or [Cp*RuCl((*R*,*R*)-dippach)] (0.6 g, 1 mmol) in methanol (10 mL) was added an excess of solid NaOH (1 pellet, ca. 0.2 g). The mixture was stirred at room temperature for 10 min. The resulting white precipitate was filtered off, washed with ethanol (2 mL) and petroleum ether (5 mL), and dried in vacuo. Data for **2a**. Yield: 0.5 g, 78%. Anal. Calcd for $C_{24}H_{50}N_2P_2Ru$: C, 54.4; H, 9.51; N, 5.3. Found: C, 54.6; H, 9.39, N, 5.3. IR: ν(RuH) 1984, ν(NH) 3358 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ −14.2 (t, $^2J_{HP}$ = 36 Hz, 1 H, Ru*H*), 0.79 (m, 2 H, N*H*), 1.12, 1.29 (m, 24 H, PCH(C*H*$_3$)$_2$), 1.91 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 2.71 (m, 4 H, PC*H*(CH$_3$)$_2$), 2.89 and 3.02 (m, 4 H, (C*H*$_2$)$_2$). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 123.7 (s). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 298 K): δ 12.9 (s, C$_5$(*C*H$_3$)$_5$), 16.2, 17.3, 19.5, and 21.3 (s, PCH(*C*H$_3$)$_2$), 31.5 and 33.4 (m, P*C*H(CH$_3$)$_2$), 44.7 (s, (*C*H$_2$)$_2$), 90.4 (s, *C*$_5$(CH$_3$)$_5$). Data for **2b**. Yield: 0.32 g, 70%. Anal. Calcd for $C_{28}H_{56}N_2P_2Ru$: C, 57.6; H, 9.67; N, 4.8. Found: C, 58.3; H, 9.65; N, 5.0. IR: ν(RuH) 1980, ν(NH) 3385 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ −14.1 (dd, $^2J_{HP}$ = 34.9 Hz, $^2J_{HP'}$ = 33.6 Hz, 1 H, Ru*H*), 1.22 (m, 32 H, PCH(C*H*$_3$)$_2$ overlapping with (C*H*$_2$)$_4$), 1.46 (m, 2 H, N*H*), 1.95 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 2.35 (m, 4 H, PC*H*(CH$_3$)$_2$), 3.25 (m, 2 H, C*HCH*). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 298 K): δ 121.3 (d, J_{pp}= 45 Hz), 126.3 (d, J_{pp}= 45 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 298 K): δ 12.8 (s, C$_5$(*C*H$_3$)$_5$), 17.5, 18.1, 18.5, 19.1, 20.2, 20.4, and 20.8 (s, PCH(*C*H$_3$)$_2$), 21.3, 31.4, 31.6, and 33.2 (s, (*C*H$_2$)$_4$), 33.4, 33.5, 36.2, and 36.7 (m, P*C*H(CH$_3$)$_2$), 55.8 and 61.8 (s, *CHC*H), 90.5 (s, *C*$_5$(CH$_3$)$_5$).

As occurs with **1a** and **1b**, the monohydrides **2a** and **2b** are also accessible by deprotonation of the corresponding dihydride complexes [Cp*RuH$_2$(dippae)][BPh$_4$] (**4a**) or [Cp*RuH$_2$(dippach)][BPh$_4$] (**4b**) (vide infra) using KOBu^t in THF. The procedure is entirely analogous to that outlined above for a compounds **1a** and **1b**, starting now from either **4a** or **4b**. Yield: 60−65% in both cases.

[CpRuH$_2$(L)][BPh$_4$] [L = dippae (3a), (*R*,*R*)-dippach (3b)]. Hydrogen gas was bubbled through a solution of either [CpRuCl(dippae)] or [CpRuCl(*R*,*R*-dippach)] (1 mmol) in methanol (15 mL). An excess of solid NaBPh$_4$ (0.4 g) was added. An off-white precipitate was gradually formed. It was filtered off, washed with ethanol and petroleum ether, and dried in vacuo. The products were recrystallized from acetone/ethanol. Data for **3a**. Yield: 0.4 g, 50%. Anal. Calcd for $C_{43}H_{61}N_2BP_2Ru$: C, 66.2; H, 7.88; N, 3.6. Found: C, 66.4; H, 7.78, N, 3.8. IR: ν(RuH) 1967, ν(NH) 3343 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3, 298 K): δ −8.75 (t, $^2J_{HP}$ = 21.1 Hz, 2 H, Ru*H*$_2$), 1.24 (m, 24 H, PCH(C*H*$_3$)$_2$), 2.09 (m, 4 H, PC*H*(CH$_3$)$_2$), 2.81 and 3.15 (m, 6 H, (C*H*$_2$)$_2$ overlapping with N*H*), 5.52 (s, 5 H, C$_5$*H*$_5$). ^{31}P{^{1}H} NMR (161.89 MHz, CD_3COCD_3, 298 K): δ 125.7 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3COCD_3, 298 K): δ 17.2 and 18.1 (s, PCH(*C*H$_3$)$_2$), 33.1 and 33.5 (m, P*C*H(CH$_3$)$_2$), 43.1 (s, (*C*H$_2$)$_2$), 78.7 (s, *C*$_5$H$_5$). Data for **3b**. Yield: 0.51 g, 60%. Anal. Calcd for $C_{47}H_{67}N_2BP_2Ru$: C, 67.7; H, 8.10; N, 3.4. Found: C, 67.6; H, 8.25; N, 3.4. IR: ν(RuH) 2064, ν(NH) 3326, 3342 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3, 298 K): δ −8.76 (dd, $^2J_{HP}$ = 22.4 Hz, $^2J_{HP'}$ = 18.5 Hz, 2 H, Ru*H*$_2$), 1.22 (m, 32 H, PCH(C*H*$_3$)$_2$ overlapping with (C*H*$_2$)$_2$), 1.64 (m, 2 H, N*H*), 1.92 and 2.04 (m, 4 H, PC*H*(CH$_3$)$_2$), 3.08 (m, 2 H, C*HCH*), 5.50 (s, 5 H, C$_5$*H*$_5$). ^{31}P{^{1}H} NMR (161.89 MHz, CD_3COCD_3, 298 K): δ 120.6 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3COCD_3, 298 K): δ 17.9 and 18.9 (s, PCH(*C*H$_3$)$_2$), 25.9 (s, (*C*H$_2$)$_4$), 33.6 and 36.9 (m, P*C*H(CH$_3$)$_2$), 58.4 (s, *CHC*H), 86.7 (s, *C*$_5$H$_5$).

[Cp*RuH$_2$(L)][BPh$_4$] [L = dippae (4a), (*R*,*R*)-dippach (4b)]. These compounds were prepared in a fashion analogous to that reported above for **3a** and **3b**, starting from either [Cp*RuCl(dippae)] or [Cp*RuCl((*R*,*R*)-dippach)]. Data for **4a**. Yield: 0.42 g, 50%. Anal. Calcd for $C_{48}H_{71}N_2BP_2Ru$: C, 67.8; H, 8.42; N, 3.3. Found: C, 67.6; H, 8.39, N, 3.5. IR: ν(RuH) 1989, ν(NH) 3307 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3, 298 K): δ −8.43 (t, $^2J_{HP}$ = 24 Hz, 2 H, Ru*H*$_2$), 1.28 (m, 24 H, PCH(C*H*$_3$)$_2$), 1.72 (m, 2 H, N*H*), 1.97 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 2.82 (m, 4 H, PC*H*(CH$_3$)$_2$), 3.05 (m, 4 H, (C*H*$_2$)$_2$). ^{31}P{^{1}H} NMR (161.89 MHz, CD_3COCD_3, 298 K): δ 122.8 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3COCD_3, 298 K): δ 11.7 (s, C$_5$(*C*H$_3$)$_5$), 18.1 and 19.8 (s, PCH(*C*H$_3$)$_2$), 32.6 (m, P*C*H(CH$_3$)$_2$), 43.6 (s, (*C*H$_2$)$_2$), 99.8 (s, *C*$_5$(CH$_3$)$_5$). Data for **4b**. Yield: 0.45 g, 50%. Anal. Calcd for $C_{52}H_{77}N_2BP_2Ru$: C, 69.1; H, 8.59; N, 3.1. Found: C, 68.9; H, 8.25; N, 3.3. IR: ν(RuH) 2010, 2071, ν(NH) 3350 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3, 298 K): δ −8.54 (dd, $^2J_{HP}$ = 26.4 Hz, $^2J_{HP'}$ = 23.1 Hz, 2 H, Ru*H*$_2$), 1.15 (m, 32 H, PCH(C*H*$_3$)$_2$ overlapping with (C*H*$_2$)$_2$), 1.52 (m, 2 H, N*H*), 1.85 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 2.16 (m, 4 H, PC*H*(CH$_3$)$_2$), 2.81 (m, 2 H, C*HCH*). ^{31}P{^{1}H} NMR (161.89 MHz, CD_3COCD_3, 298 K): δ 123.6 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3COCD_3, 298 K): δ 11.8 (s, C$_5$(*C*H$_3$)$_5$), 17.5, 19.0, 19.3, and 19.9 (s, PCH(*C*H$_3$)$_2$), 32.6 and 33.8 (s, (*C*H$_2$)$_4$), 36.3 (m, P*C*H(CH$_3$)$_2$), 58.4 (s, *CHC*H), 99.6 (s, *C*$_5$(CH$_3$)$_5$).

NMR Study of Proton-Transfer Reactions. Solutions of the respective monohydride complexes **1a**,**b** or **2a**,**b** in CD_2Cl_2 unless otherwise stated, prepared under an argon atmosphere in NMR tubes, were frozen by immersion into liquid nitrogen. The corresponding amount of HBF_4 or of other acid was added via syringe or micropipette. The solvent was allowed to melt. Then, the tubes were shaken, to mix the reagents, and stored in an ethanol/liquid nitrogen bath. The samples prepared in this way were studied by NMR at low temperatures. The sample was removed from the bath and inserted into the precooled probe of the Varian UNITY-400 spectrometer at 185 K. Once shims were adjusted, the probe was warmed to the desired temperature. The NMR temperature controller was previously calibrated against a methanol sample, with the reproducibility being ±0.5 °C.

X-ray Structure Determinations. Crystal data and experimental details are given in Table 1. X-ray diffraction data were collected on a Bruker SMART APEX 3-circle diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) with a CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by ω scan frames with $\delta(\omega)$ = 0.30°. Corrections for

Table 1. Summary of Crystallographic Data for **4a**

compound	**4a**
formula	$C_{48}H_{71}N_2BP_2Ru$
fw	849.89
T (K)	293(2)
cryst size (mm)	0.23 × 0.32 × 0.34
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell param	$a = 11.9028(6)$ Å
	$b = 20.125(1)$ Å
	$c = 19.618(1)$ Å
	$\beta = 97.640(1)°$
V (Å^3)	4657.7(4)
Z	4
ρ_{calc} (g cm^{-3})	1.212
radiation/λ (Å)	Mo Kα/0.710 73
μ(Mo Kα) (cm^{-1})	4.38
F(000)	1808
max, min transm factors	1.000, 0.876
θ range for data collection	$1.5 < \theta < 25.1$
reflns collcd	34 883
unique reflns	8191 ($R_{int} = 0.040$)
no. of obsd reflns [$I > 2\sigma(I)$]	7145
no. of param	508
final R, wR values [$I > 2\sigma(I)$]	0.0537, 0.1176
final R, wR values (all data)	0.0667, 0.1245
GOF	1.059
weighting scheme	$1/[\sigma^2(F_o^2) + (0.0536P)^2 + 5.9715P]$ where $P = (F_o^2 + 2F_c^2)/3]$
max, ave shift/error	0.01, 0.00
residual electron density peaks (e Å^{-3})	−0.41, 0.87

absorption and crystal decay (insignificant) were applied by the semiempirical method from equivalents using the program *SADABS*.[23] The structures were solved by direct methods, completed by subsequent difference Fourier synthesis, and refined on F^2 by full-matrix least-squares procedures using the program *SHELXTL*.[24] The two hydrogen atoms bonded to the metal were localized in a regular difference Fourier map and isotropically refined with restricted Ru−H bond lengths. The program *ORTEP-3*[25] was used for plotting.

Results and Discussion

Preparation and Characterization of Hydride Complexes 1−4. The monohydride complexes [CpRuH(L)] [L = dippae (**1a**), (*R*,*R*)-dippach (**1b**)] were prepared by reaction of the corresponding chloro complex [CpRuCl(L)] with $NaBH_4$ in refluxing ethanol. The pentamethylcyclopentadienyl homologous derivatives [Cp*RuH(L)] [L = dippae (**2a**), (*R*,*R*)-dippach (**2b**)] were better prepared by reaction of the chloro complexes [Cp*RuCl(L)] with an excess of NaOH in methanol at room temperature. All of these neutral monohydride complexes are also accessible by the deprotonation reaction of the corresponding cationic dihydride complex [(C_5R_5)RuH(L)] (R = H, Me; L = dippae, (*R*,*R*)-dippach] (vide infra) using KOBu^t in THF. Complexes **1a**,**b** and **2a**,**b** are very air-sensitive white microcrystalline solids that gradually darken even when stored under argon at −20 °C. The hydride ligand appears as one high-field triplet in the ^{1}H NMR spectra of complexes containing dippae as the coligand, namely, **1a** and **2a**, whereas their $^{31}P\{^1H\}$ NMR spectra display one sharp singlet. The free chiral and enantiomerically pure phosphinoamine (*R*,*R*)-dippach has C_2 symmetry. However, when bound to ruthenium in complexes **1b** and **2b**, the phosphorus atoms become inequivalent, and hence two doublets of an AM spin system are observed in their respective $^{31}P\{^1H\}$ NMR spectra. Consistent with this, the signal for the hydride ligand in these complexes appears in the ^{1}H NMR spectra as a high-field doublet of doublets (X part of an AMX spin system). In any case, the values found for the coupling constants $^2J_{HP}$ and $^2J_{HP'}$ are very similar (i.e., 37 and 35.6 Hz for **1b**). These NMR patterns have been previously observed by us for the recently reported monohydride complex [TpRuH((*R*,*R*)-dippach)].[11] As we did also with TpRuH derivatives, we wanted to determine the occurrence or absence of weak NH···HRu interactions. NMR NOESY and ROESY experiments failed to show any significant NH···HRu contact in these cases, just as happens also with the TpRu hydrides bearing dippae and (*R*,*R*)-dippach. The minimum longitudinal relaxation times $(T_1)_{min}$ of the hydride protons were measured by the inversion−recovery method. These are listed in Table 2.

Table 2. ^{1}H NMR Chemical Shifts and $(T_1)_{min}$ Values for the Hydride Protons in Monohydride and Dihydride Complexes

compound	δ RuH (ppm)	$(T_1)_{min}$ (ms)[a]
Monohydrides[b]		
[CpRuH(dippae)] (**1a**)	−13.6	398
[CpRuH((*R*,*R*)-dippach)] (**1b**)	−13.6	430
[Cp*RuH(dippae)] (**2a**)	−14.2	370
[Cp*RuH((*R*,*R*)-dippach)] (**2b**)	−14.1	425
Dihydrides[c]		
[$CpRuH_2$(dippae)][BPh_4] (**3a**)	−8.75	306
[$CpRuH_2$((*R*,*R*)-dippach)][BPh_4] (**3b**)	−8.82	373
[Cp*RuH_2(dippae)][BPh_4] (**4a**)	−8.43	281
[Cp*RuH_2((*R*,*R*)-dippach)][BPh_4] (**4b**)	−8.77	297

[a] At 400 MHz. [b] In toluene-d_8. [c] In acetone-d_6.

For the monohydride complexes, the values of $(T_1)_{min}$ are in between 370 and 430 ms. These values are somewhat shorter than those reported for other half-sandwich monohydride complexes of ruthenium (i.e., 520 ms for [{C_5H_4-$CH(CH_2CH_2)_2NMe$}$RuH(PPh_3)_2$][14] or 480 ms for [CpRuH-(PPh_3)$_2$][26]) but of the same order of magnitude as those measured for the TpRu monohydride derivatives [TpRuH-(dippae)] (397 ms) and [TpRuH((*R*,*R*)-dippach)] (373 ms).[11] As has been proposed for these TpRuH complexes, in here the cause for the relatively short $(T_1)_{min}$ values measured should also be the sum of interactions of the hydride with all other neighboring nuclei within the molecule. Again, the contributions of the interactions of the hydride with the phosphinoamine protons NH···HRu, in particular, do not appear to be of particular relevance in the overall relaxation processes.

The dihydride complexes [$CpRuH_2$(L)][BPh_4] [L = dippae (**3a**), (*R*,*R*)-dippach (**3b**)] and [Cp*RuH_2(L)][BPh_4] [L = dippae (**4a**), (*R*,*R*)-dippach (**4b**)] were prepared by reaction of the corresponding chloro complex [CpRuCl(L)] or [Cp*RuCl(L)] with H_2 and $NaBPh_4$ in methanol in the form

(23) Sheldrick, G. M. *SADABS*, University of Göttingen: Göttingen, Germany, 2001.
(24) Sheldrick, G. M. *SHELXTL*, version 6.10; Crystal Structure Analysis Package; Bruker AXS: Madison, WI, 2000.
(25) Farruggia, L. J. ORTEP-3 for Windows, version 1.076. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(26) Desrosiers, P. J.; Cai, L.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

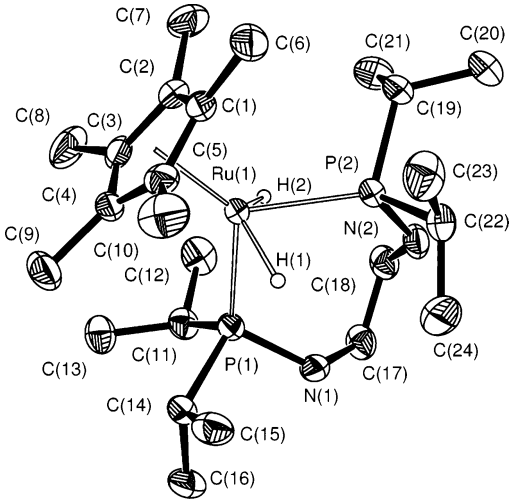


Figure 1. ORTEP drawing (30% thermal ellipsoids) of the cation $[Cp^*RuH_2(dippae)]^+$ in complex **4a**. Hydrogen atoms, except hydride ligands, have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: bond lengths Ru(1)−P(1) 2.3215(10); Ru(1)−P(2) 2.3099(10); Ru(1)−H(1) 1.53(3); Ru(1)−H(2) 1.55(3); P(1)−N(1) 1.697(4); P(2)−N(2) 1.672(4); bond angles P(1)−Ru(1)−P(2) 98.41(4); P(1)−Ru(1)−H(1) 67.4(14); P(1)−Ru(1)−H(2) 72.6(14); P(2)−Ru(1)−H(1) 71.6(18); P(2)−Ru(1)−H(2) 69.0(13); H(1)−Ru(1)−H(2) 117(2); torsion angles P(1)−N(1)−C(17)−C(18) 55.4(5); P(2)−N(2)−C(18)−C(17) −99.8(4); N(1)−C(17)−C(18)−N(2) 48.7(5).

of off-white microcrystalline solids. The crystal structure of **4a** was determined. An ORTEP view of the complex cation $[Cp^*RuH_2(dippae)]^+$ is shown in Figure 1, together with a listing of selected bond lengths and angles.

The cation exhibits a four-legged piano-stool structure, with hydride ligands arranged in a transoid disposition with an angle H(1)−Ru(1)−H(2) of 123(2)°. This angle is similar to the value found by neutron diffraction for the dihydride complex $[CpRuH_2(PMe_3)_2][BF_4]$ [118.8(4)°][27] and by X-ray diffraction for $[Cp^*RuH_2(PPh^iPr_2)_2][BAr'_4]$ [124.5(17)°].[28] The Ru−H separations of 1.53(3) and 1.55(3) Å are consistent with those found in other half-sandwich ruthenium dihydride complexes, i.e., 1.50(3) and 1.53(3) Å in $[Cp^*RuH_2(PPh^iPr_2)_2][BAr'_4]$[28] or 1.599(8) and 1.604(9) Å for $[Cp^*RuH_2(PMe_3)_2][BF_4]$ (neutron diffraction).[27] The ruthenium atom and the dippae ligand are part of a seven-membered ring. The P(1)−Ru(1)−P(2) angle has a value of 98.41(4)°, which is intermediate between 87.53(7)° in $[Cp^*RuH_2(dippe)][BPh_4]$[5] and 107.96(2)° in $[Cp^*RuH_2(PPh^iPr_2)_2][BAr'_4]$[28] and is larger than the value of 93.88(4)° found for $[TpRu(H_2)(dippae)][BAr'_4]$,[11] in which the Tp ligand imposes a cis arrangement of the phosphorus atoms. Hence, the seven-membered ring, in combination with the transoid stereochemistry, increases the value of the P(1)−Ru(1)−P(2) angle, placing complex **4a** structurally in between transoid dihydride complexes with bidentate phosphines and those bearing monodentate phosphines.

The ^1H NMR spectra of complexes **3a** and **4a** display one high-field triplet resonance for the equivalent hydride ligands

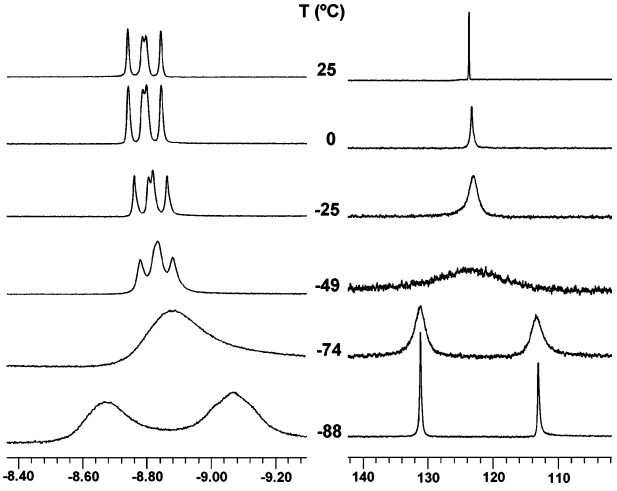


Figure 2. VT ^1H (400 MHz, hydride region) and $^{31}P\{^1H\}$ (161.89 MHz) NMR spectra in acetone-d_6 of **3b**.

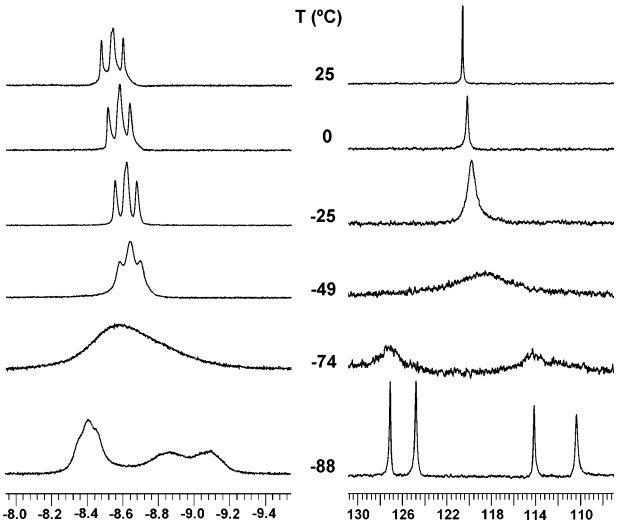


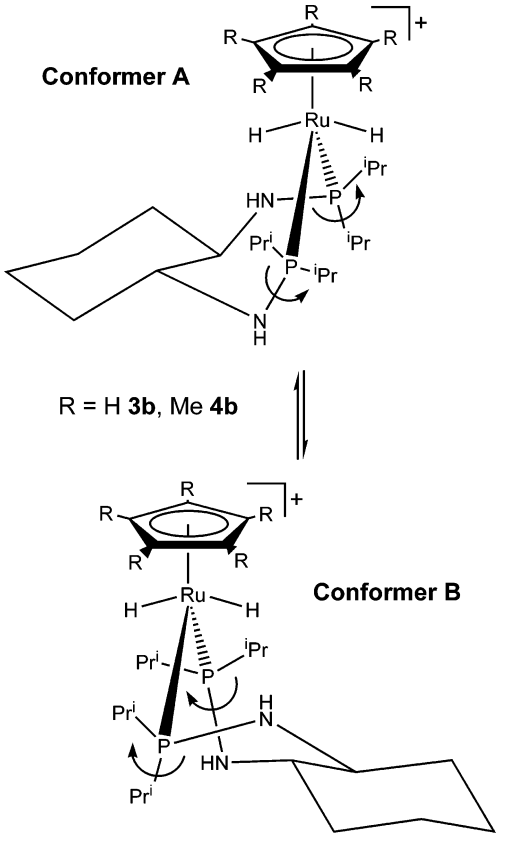
Figure 3. VT ^1H (400 MHz, hydride region) and $^{31}P\{^1H\}$ (161.89 MHz) NMR spectra in acetone-d_6 of **4b**.

and one singlet in the $^{31}P\{^1H\}$ NMR spectra, as is expected for systems having pseudo-C_{2v} symmetry in solution. The simplicity of the $^{13}C\{^1H\}$ NMR spectra for these complexes is also consistent with this. However, for complexes **3b** and **4b**, which bear the chiral phosphinoamine (*R*,*R*)-dippae, the situation is different. The hydride protons give rise to a doublet of doublets in their room temperature ^1H NMR spectra, whereas the $^{31}P\{^1H\}$ NMR spectra consist of one apparent singlet. The NMR spectra for both **3b** and **4b** are temperature-dependent and exhibit a somewhat different behavior as a function of the presence of either Cp (**3b**) or Cp* (**4b**) as the coligand. The VT ^1H (hydride region) and $^{31}P\{^1H\}$ NMR spectra of **3b** and **4b** are respectively shown in Figures 2 and 3.

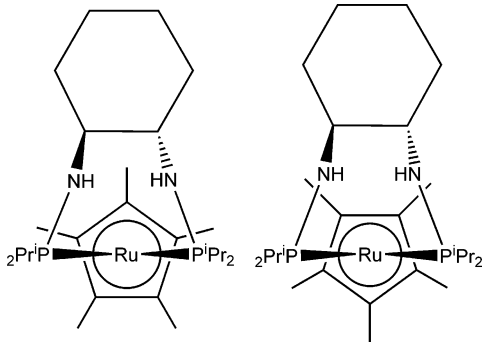
At variance with this, the resonances in the ^1H and $^{31}P\{^1H\}$ NMR spectra of **3a** and **4a** undergo broadening at low temperature, but no decoalescence occurs. When the temperature is lowered in the case of compound **3b**, decoalescence of the ^1H NMR hydride resonance to two broad signals at −88 °C is observed, whereas the room temperature $^{31}P\{^1H\}$ NMR resonance decoalesces to two broad singlets

(27) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721−1727.
(28) Aneetha, H.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Sapunov, V. N.; Schmid, R.; Kirchner, K.; Mereiter, K. *Organometallics* **2002**, *21*, 5334−5346.

(Figure 2). Likewise, for compound **4b**, the hydride resonance splits into three broad signals in the intensity ratio 2:1:1 at −88 °C. At this temperature, the $^{31}P\{^1H\}$ NMR spectrum consists of four separate singlet resonances (Figure 3), so the P−P coupling is not resolved. For both **3b** and **4b**, the ^1H NMR signals corresponding to the protons of either Cp or Cp* remain as singlets in the temperature range studied. The fact that the hydride resonances appear as doublet of doublets at room temperature indicates the magnetic inequivalence of the phosphorus atoms. The presence of one singlet in the $^{31}P\{^1H\}$ NMR spectra indicates averaging of the chemical shifts of rapidly exchanging phosphorus atoms. The dynamic process responsible for this behavior has been interpreted in terms of freezing of the equilibrium between rapidly exchanging conformers in solution resulting from the restricted rotation around the Ru−P bond, which causes a flipping motion of the diaminocyclohexane fragment. A similar phenomenon has been invoked as an explanation for the dynamic behavior of [Ru(OAc)$_2$((*R*,*R*)-dppach)] [dppach = 1,2-bis(diphenylphosphinoamino)ethane].[29]



Values of 37−39 kJ mol^{-1} have been estimated by means of NMR line-shape fitting for the free energy of activation $\Delta G^{\ddagger}_{298}$ of these processes. Conformers A and B are related by a 180° rotation around the Ru−Cp or Ru−Cp* axis but only assuming free rotation of the Cp or Cp* groups. At low temperature, the two hydride ligands are inequivalent and each of them gives rise to separate resonances. The observed differences between the VT-NMR spectra of **3b** and **4b** are then most likely due to the existence of a rotation barrier around the Ru−Cp* bond in the case of **4b**, which generates two diastereomers depending on the orientation of the methyl groups of the Cp* ring relative to the ruthenium−phosphinoamine fragment, as shown.



Each of the diastereomers gives rise to two resonances in the slow-exchange $^{31}P\{^1H\}$ NMR spectrum corresponding to an AM spin system and to two separate hydride resonances in the ^1H NMR spectrum. The rotation barrier of around Ru−Cp in **3b** must be lower in energy than that in **4b** because of the lower steric hindrance of the hydrogen substituents compared to the methyl groups in Cp*. Hence, a decoalescence similar to that observed in the NMR spectra of **4b** should be expected but only at temperatures well below −88 °C.

The values of $(T_1)_{min}$ for **3a**,**b** and **4a**,**b** were also determined and appear listed in Table 2. Values range from 281 to 397 ms, which are short for "classical" dihydride complexes but of the same order of magnitude as those found for the monohydride complexes **1a**,**b** and **2a**,**b**. Again, no significant NH···HRu interactions were found by ROESY experiments. Taking into consideration the values of $(T_1)_{min}$ for the monohydrides as a reference, we can estimate the H···H separation in the dihydride complexes in a manner similar to that used for the derivatives [TpRu(H$_2$)(L)][BAr′$_4$] [L = (*R*,*R*)-dippach, dippae] using the expression[26,30,31]

$$\frac{1}{T_1(\mathrm{H_2})_{obs}} = \frac{1}{T_1(\mathrm{H_2})_{true}} + \frac{1}{T_1(\mathrm{H})_{obs}} \qquad (1)$$

The term $1/T_1(H)_{obs}$ in eq 1 corresponds to the value of $(T_1)_{min}$ measured for the hydride resonance of either **1a**,**b** or **2a**,**b**, considering that the contribution to the relaxation of the hydride ligand in these complexes comes mainly from dipole−dipole interactions with the metal and through space with all of the remaining atoms. The resulting corrected values for $(T_1)_{min}$ of the hydride protons can be used for the calculation of the H···H separation using the equation

$$r_{H\cdots H} = 5.815[(T_1)_{min}/\nu]^{1/6} \qquad (2)$$

(29) Kuznetsov, V. F.; Jefferson, G. R.; Yap, G. P. A.; Alper, H. *Organometallics* **2002**, *21*, 4241−4248.

(30) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155−284.

(31) Cayuela, E.; Jalón, F.; Manzano, B. R.; Espino, G.; Weissensteiner, W.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 7049−7062.

Table 3. Observed and Corrected $(T_1)_{min}$ Values[a] and Calculated H···H Separations in Dihydride Complexes

compd	obsd $(T_1)_{min}$ for RuH_2 (ms)[b]	$(T_1)_{min}$ for RuH in monohydride (ms)[c]	corrected $(T_1)_{min}$ for RuH_2 (ms)	$r_{H\cdots H}$ (Å)
3a	306	398	1323	2.24
3b	373	430	2814	2.55
4a	281	370	1168	2.20
4b	297	425	986	2.14

[a] At 400 MHz. [b] In acetone-d_6. [c] In toluene-d_8.

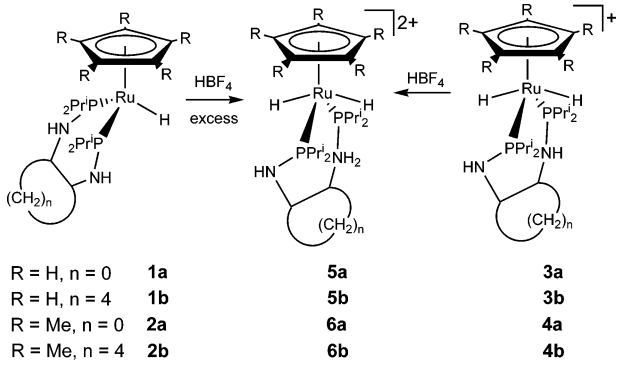
In this equation, ν represents the NMR frequency of operation, which in our case is 4×10^8 Hz. All of the results are summarized in Table 3.

It is clear that the extra hydridic proton in all of these dihydride complexes contributes very little to the overall dipole−dipole relaxation, leading to H···H separations longer than 2.1 Å in all cases, consistent with their formulation as ruthenium(IV) dihydrides. Furthermore, the value of 2.20 Å calculated for the H···H separation in **4a** can be compared to the value of 2.631 Å found in the solid state by X-ray diffraction.

Study of Proton-Transfer Reactions. We have studied by VT ^{1}H and ^{31}P{^{1}H} NMR spectroscopy the protonation reactions of **1a**,**b** and **2a**,**b** with HBF_4·OEt_2. We have also performed some experiments in selected cases using other acids of different strength in order to get an insight into the processes of proton transfer to hydride complexes.

The monohydride complexes **1a**,**b** and **2a**,**b** react with an excess of HBF_4·OEt_2 in CD_2Cl_2, furnishing dicationic dihydrides $[CpRuH_2(LH)]^{2+}$ [LH = dippaeH$^+$ (**5a**), (*R*,*R*)-dippachH$^+$ (**5b**)] and $[Cp^*RuH_2(LH)]^{2+}$ [LH = dippaeH$^+$ (**6a**), (*R*,*R*)-dippachH$^+$ (**6b**)], respectively, in which one of the NH groups of the phosphinoamine ligands has been protonated. The same species were obtained by treatment of the monocationic dihydrides **3a**,**b** or **4a**,**b** with HBF_4·OEt_2 in CD_2Cl_2 or acetone-d_6.

We had previously observed the protonation of the NH groups of the phosphinoamine ligands in the course of the proton-transfer reactions over the complexes [TpRuH(L)] [L = dippae, (*R*,*R*)-dippach], leading to dicationic species of the type $[TpRu(H_2)(LH)]^{2+}$, which in some instances undergo tautomerization to $[TpRuH(LH_2)]^{2+}$.[11] These dicationic hydride complexes are characterized by a downfield shift of the relevant ^{31}P{^{1}H} NMR resonances and the occurrence of fast proton-exchange equilibria. In the case of CpRu and Cp*Ru derivatives, this has also been observed. In Table 4 are summarized selected ^{1}H and ^{31}P{^{1}H} NMR data for the dicationic derivatives **5a**,**b** and **6a**,**b**.



In all cases, the hydride signals exhibit long $(T_1)_{min}$ values (greater than 300 ms at 400 MHz), consistent with their formulation as "classical" dihydrides. Complexes **5a** and **6a** containing dippae as the coligand display one singlet resonance in their ^{31}P{^{1}H} NMR spectra at room temperature. These resonances are shifted ca. 30 ppm downfield with respect to the position of the signal of the corresponding dihydride complex. One high-field triplet is observed in the ^{1}H NMR spectra for the hydride ligands. When the temperature is lowered, the ^{31}P{^{1}H} and the ^{1}H NMR hydride resonances get gradually broader, but no decoalescence is observed. At variance with this, the VT-NMR spectra of complexes with (*R*,*R*)-dippach, **5b** and **6b**, show different profiles. For reference, the VT ^{1}H (hydride region) and ^{31}P{^{1}H} NMR spectra of **6b** are shown in Figure 4.

For both **5b** and **6b**, two separate resonances are observed in the ^{31}P{^{1}H} NMR spectra at low temperatures. These resonances are ca. 70 ppm apart from each other. The signals at very low field are attributed to the phosphorus atoms next to the protonated NH groups. At these low temperatures, the hydride ligands are inequivalent and give rise to two separate resonances in the ^{1}H NMR spectra, which couple separately to each of the phosphorus atoms. As the temperature is raised, the resonances in the ^{1}H and ^{31}P{^{1}H} NMR spectra get progressively broader. At 25 °C, the ^{31}P{^{1}H} NMR spectra are featureless whereas the hydride resonances have become one triplet. The activation parameters for the dynamic process responsible for this behavior were determined by means of NMR line-shape fitting. For **5b**, values of 19.1 ± 0.8 kJ mol^{-1} and −110 ± 4 J K^{-1} mol^{-1} were obtained for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively, whereas for **6b**, $\Delta H^{\ddagger}$ was 23 ± 1 kJ mol^{-1} and $\Delta S^{\neq}$ −85 ± 6 J K^{-1} mol^{-1}. These parameters led to the free energy of activation $\Delta G^{\ddagger}_{298}$ values of 52 ± 2 kJ mol^{-1} for **5b** and of 49 ± 3 kJ mol^{-1} for **6b**. The largely negative values obtained for $\Delta S^{\ddagger}$ are consistent with a process

Table 4. Selected ^{1}H and ^{31}P{^{1}H} NMR Data for Dicationic Dihydride Complexes in CD_2Cl_2 at the Indicated Temperatures

compound	^{1}H NMR	^{31}P{^{1}H} NMR
$[CpRuH_2(dippaeH)]^{2+}$ (**5a**)	at 25 °C: δ −8.79 (t, $^2J_{HP}$ = 22.4 Hz, RuH_2), 5.30 (s, C_5H_5)	at 25 °C: δ 158.5
$[CpRuH_2((R,R)\text{-dippachH})]^{2+}$ (**5b**)[a]	at 25 °C: δ −8.40 (t, $^2J_{HP}$ = 22.4 Hz, RuH_2), 5.82 (s, C_5H_5)	at 25 °C: featureless
	at −88 °C: δ −8.37 (dd, $^2J_{HP}$ = 28 Hz, $^2J_{HP'}$ = 14 Hz), −8.73 (t, $^2J_{HP}$ = 22 Hz) (RuH_2), 6.02 (s, C_5H_5)	at −88 °C: δ 187.8 (br), 115.8 (br)
$[Cp^*RuH_2(dippaeH)]^{2+}$ (**6a**)[a]	at 25 °C: δ −7.98 (t, $^2J_{HP}$ = 25 Hz, RuH_2), 2.07 (s, $C_5(CH_3)_5$)	at 25 °C: δ 155.0
$[Cp^*RuH_2((R,R)\text{-dippachH})]^{2+}$ (**6b**)	at 35 °C: δ −8.04 (t, $^2J_{HP}$ = 25.3 Hz, RuH_2), 2.01 (s, $C_5(CH_3)_5$)	at 35 °C: 161 (very broad)
	at −88 °C: δ −8.04 (dd, $^2J_{HP}$ = 28 Hz, $^2J_{HP'}$ = 15 Hz), −8.68 (t, $^2J_{HP}$ = 26 Hz) (RuH_2), 1.91 (s, $C_5(CH_3)_5$)	at −88 °C: δ 192.4 (s), 119.7 (s)

[a] In acetone-d_6.

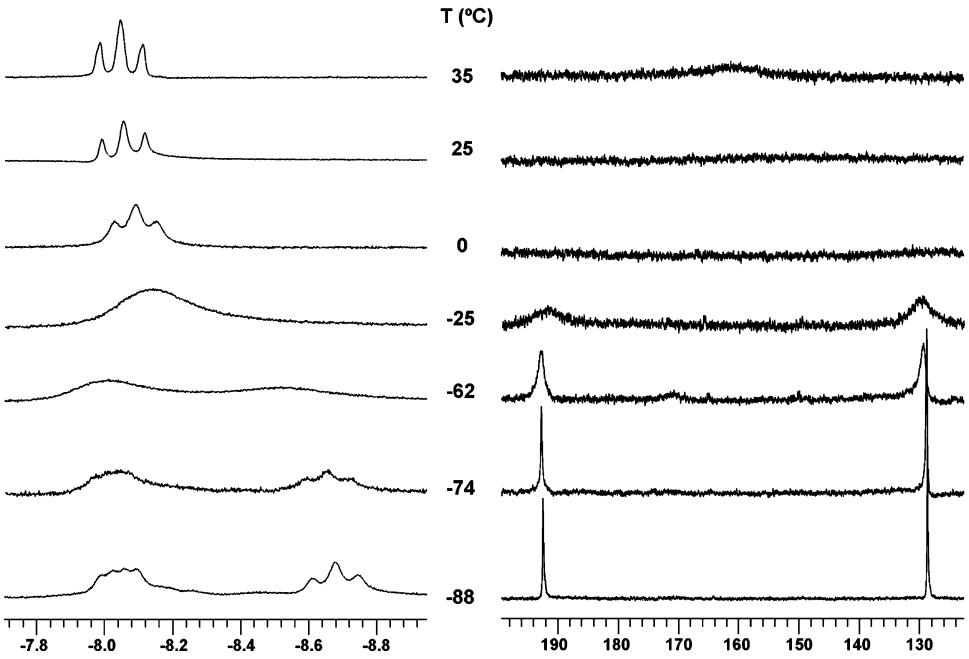
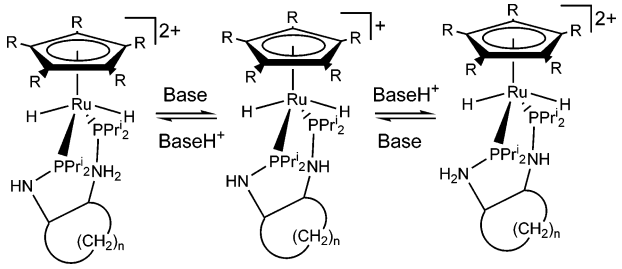


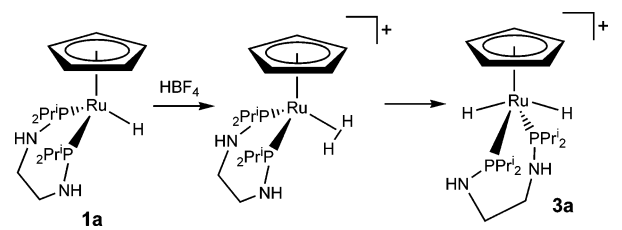
Figure 4. VT ^{1}H NMR (left, hydride region, 400 MHz) and VT ^{31}P{^{1}H} NMR (right, 161.89 MHz) of [Cp*RuH$_2$((*R*,*R*)-dippachH)]$^{2+}$ (**6b**) in CD_2Cl_2.

in which the controlling step is associative in character. We have interpreted this in terms of an intermolecular rather than intramolecular base-assisted proton exchange between the two NH sites, as shown.



Several species may act as the base in this process: the BF_4^- ion, diethyl ether, or even the solvent (CD_2Cl_2 or acetone-d_6). As the temperature is raised, the rapid exchange between NH and NH_2 protons renders the phosphorus atoms equivalent in the NMR time scale, accounting for the averaged spectra at room temperature. All attempts made to isolate the dicationic dihydrides as solids failed. Presumably, they are exceedingly acidic species that are only stable in solution, as was also pointed out for the derivatives [TpRu(H$_2$)(dippaeH)]$^{2+}$ and [TpRu(H$_2$)(dippachH)]$^{2+}$.[11]

In the absence of an excess of HBF_4, i.e., using stoichiometric amounts of HBF_4 in CD_2Cl_2, all of the monohydride complexes **1a**,**b** and **2a**,**b** react, yielding the corresponding dihydride complexes **3a**,**b** or **4a**,**b** (in the form of $[BF_4]^-$ salts in solution) as the final thermodynamic products of the proton-transfer processes. In the course of the protonation of **1a**, it was possible to detect at low temperature the presence of the dihydrogen complex [CpRu(H$_2$)(dippae)]$^+$ as a metastable intermediate in the formation of the dihydride derivative **3a**.



The dihydrogen adduct is characterized by the presence of one broad resonance at −9.55 ppm with a short $(T_1)_{min}$ of 20 ms in the low-temperature ^{1}H NMR spectra and one singlet at 113.3 ppm in the ^{31}P{^{1}H} spectrum. The value of the coupling constant $^1J_{HD}$ of 26 Hz measured for the isotopomer [CpRu(HD)(dippae)]$^+$ is also consistent with the presence of a η^2-H$_2$ ligand. In the course of the protonation of **1b** with a stoichiometric amount of HBF_4 at −88 °C, a broad resonance with a short T_1 of ca. 20 ms attributable to an intermediate dihydrogen complex was also observed in the ^{1}H NMR spectrum, but only for a brief period of time. This signal disappears when the temperature is raised to −74 °C, suggesting that the dihydrogen complex [CpRu(H$_2$)((*R*,*R*)-dippach)]$^+$ is kinetically much less stable than its counterpart containing dippae. This fact also made impossible the measurement of the corresponding $^1J_{HD}$ coupling constant. No signals attributable to metastable intermediate dihydrogen complexes were observed when the protonation reactions of the Cp* monohydrides **2a**,**b** with HBF_4 in CD_2Cl_2 were monitored by NMR spectroscopy in an analogous fashion.

Going back to the proton-transfer reaction to **1a**, at −88 °C both the ^{1}H and ^{31}P{^{1}H} NMR spectra show the presence of the dihydrogen derivative [CpRu(H$_2$)(dippae)]$^+$, plus small amounts of the dihydride **3a** (Figure 5).

The triplet resonance near −14 ppm present in the ^{1}H NMR spectrum and the broad signal at 133 ppm in the ^{31}P{^{1}H} NMR spectrum were, in principle, attributed to the nonprotonated monohydride complex **1a**. When the temper-

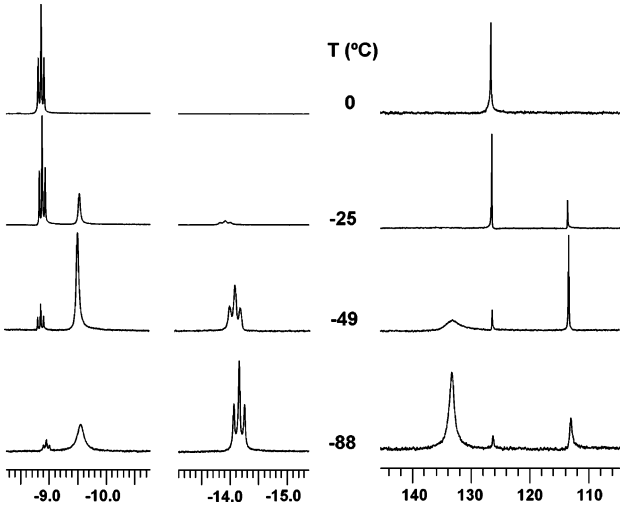


Figure 5. VT ^{1}H NMR (left, hydride region, 400 MHz) and VT ^{31}P{^{1}H} NMR (right, 161.89 MHz) of a sample made up by the addition of HBF_4 to a frozen CD_2Cl_2 solution of **1a** below −90 °C, followed by subsequent warming to the indicated temperatures.

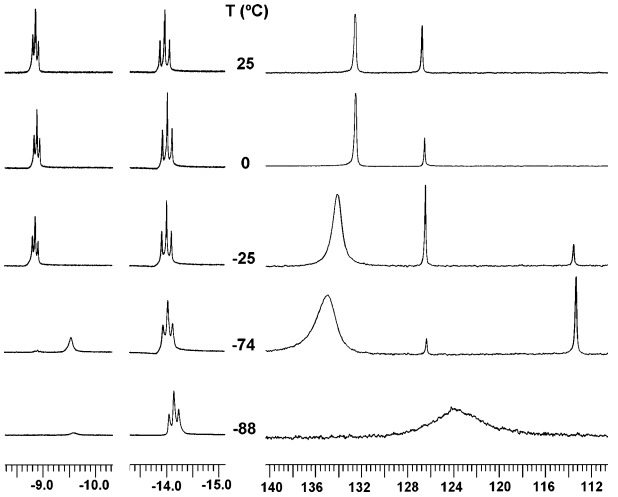
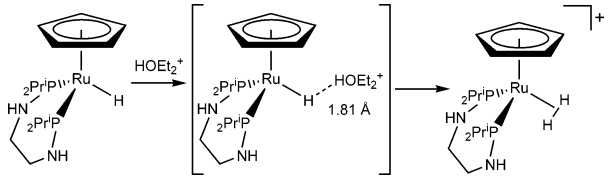


Figure 6. VT ^{1}H NMR (left, hydride region, 400 MHz) and VT ^{31}P{^{1}H} NMR (right, 161.89 MHz) of a sample made up by the addition of less than 0.5 equiv of HBF_4 to a CD_2Cl_2 solution of **1a**.

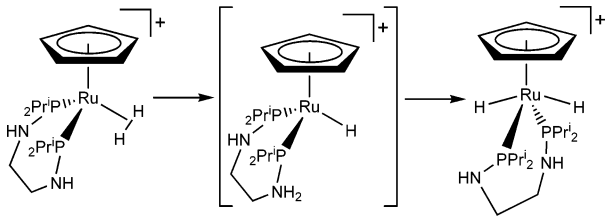
ature is raised, the dihydrogen resonance in the ^{1}H NMR spectrum and the associated signal in the ^{31}P{^{1}H} NMR spectrum disappear as $[CpRu(H_2)(dippae)]^+$ irreversibly rearranges to the dihydride derivative **3a**. At −49 °C, a significant broadening of the ^{1}H and ^{31}P{^{1}H} NMR resonances initially ascribed to the starting monohydride complex **1a** is observed. At this temperature, the measured T_1 for the hydride resonance at −14.15 ppm was 190 ms, a value significantly shorter than the 398 ms measured for the hydride ligand in **1a** (400 MHz, toluene-d_8). These data are consistent with the formation of an intermediate dihydrogen-bonded species prior to the proton transfer to yield the dihydrogen complex $[CpRu(H_2)(dippae)]^+$. Proton−hydride exchange in an extremely short dihydrogen bond has been reported to cause a very significant reduction in the measured $(T_1)_{min}$.[30] An alternative explanation for the increase in the relaxation rate could be a fast equilibrium between the monohydride and dihydrogen complexes. If this were the case, an averaging of the T_1 values for both the monohydride and dihydrogen resonances would be expected.[32] In our system, because the measured T_1 for the dihydrogen protons at this temperature is 23 ms and the ^{31}P{^{1}H} NMR signal for $[CpRu(H_2)(dippae)]^+$ remains sharp, this alternative seems less likely than the well-precedented hypothesis in favor of the formation of a dihydrogen-bonded intermediate.[2,6−10] An experiment of protonation of **1a** performed with less than 0.5 equiv of HBF_4 showed more clearly the formation of the dihydrogen-bonded intermediate in the temperature range −88 to −25 °C (Figure 6).

In this experiment, a $(T_1)_{min}$ of 240 ms was measured for the broad triplet resonance at ca. 14 ppm. Above −25 °C, the formation of the dihydride complex **3a** is quantitative, indicating the consumption of all of the HBF_4 added, whereas the resonance at ca. −14 ppm sharpens and increases the value of its T_1, as is indicative of the presence in the mixture of the monohydride **1a**, which remains in excess, as expected. The observed increase in $(T_1)_{min}$ for the resonance at −14 ppm with respect to the values measured in the experiment in which a stoichiometric amount of acid was used ($T_1 \leq$ 190 ms) seems reasonable, given the fact that an averaging of the observed T_1 for the hydridic protons of **1a** and the dihydrogen-bonded species should be expected when the protonation is carried out with a less than 1 equiv of HBF_4. It is very important to note that dihydrogen-bonded intermediates have usually been observed when proton-transfer reactions are performed with relatively weak proton donors.[2,6,7] In this case and also in our previous report on the proton-transfer reactions to [TpRuH(L)] complexes,[11] dihydrogen-bonded intermediates have been detected by NMR spectroscopy when a strong acid such as HBF_4 is used. In these cases, a remarkable shortening in the value of $(T_1)_{min}$ was observed, which was explained in terms of the efficient contribution of the fluorine atoms to the relaxation of dihydrogen-bonded species of the type $[TpRu(H\cdots HBF_4)(L)]$ in equilibrium with contact ion pairs of the type $Ru(H_2)^+\cdots BF_4^-$.[11] In the case of the protonation of **1a**, the shortest T_1 measured for the signal attributed to the dihydrogen-bonded species was 190 ms, a value that is not particularly short. If we apply eq 1 for the determination of T_1 due solely to the H···H interaction, the result is 363 ms, which by application of eq 2 leads to a H···H separation of 1.81 Å, fully consistent with the formation of a standard dihydrogen bond between the hydride ligand and a proton donor.[6,9] Ruling out close contacts with the $[BF_4]^-$ ion in this case, we can propose the formulation as $[CpRu(H\cdots HOEt_2)(dippae)][BF_4]$ for the observed dihydrogen-bonded species in this system.



(32) Bakhmutov, V. I. *Practical NMR Relaxation for Chemists*; Wiley: Chichester, U.K., 2004. Bakhmutov, V. I. *Eur. J. Inorg. Chem.* **2005**, 245−255.

It is interesting to note that, in these systems containing phosphinoamine ligands, metastable intermediate dihydrogen complexes of the type $[(C_5R_5)Ru(H_2)(L)]^+$ are difficult to detect and undergo rapid rearrangement to the corresponding dihydride complexes. In comparison, related systems bearing either monodentate or bidentate phosphine ligands furnish dihydrogen intermediate complexes that are kinetically more stable than those with phosphinoamine ligands.[5,29,33] One possible explanation to this observation is that the NH groups play an active role in the process of isomerization from dihydrogen to dihydride. For instance, the NH group might eventually act as an internal base deprotonating the acidic dihydrogen ligand to yield a cationic monohydride. A direct proton transfer from the NH_2 to the metal would yield the thermodynamically more stable cationic dihydride complex.



Although we have no formal proof for this isomerization pathway, we have previously observed the deprotonation of dihydrogen ligands by NH acting as an internal base in the systems $[TpRu(H_2)(L)]^+$ and $[TpRu(H_2)(LH)]^{2+}$, leading to monohydrides of the type $[TpRuH(LH)]^+$ and $[TpRuH(LH_2)]^{2+}$, respectively.[11] On the other hand, density functional theory studies performed on the model system $[\{C_5H_4CH_2CH_2NH_2\}RuH(PH_3)_2]$ suggest an active role of pendent amino groups in several alternative pathways for the proton-transfer reactions in this system.[34] Therefore, the involvement of amino groups in the mechanism of dihydrogen to dihydride isomerization appears feasible and cannot be ruled out as one possible reason for the observed kinetic instability of dihydrogen complexes with phosphinoamine ligands.

We have also carried out a survey on proton-transfer reactions in some of the complexes using weak acids such as benzoic acid or the acidic alcohol HFIPOH, in order to compare with the results obtained with the strong acid $HBF_4 \cdot OEt_2$.

The VT ^{1}H NMR spectra of a sample of **1a** in toluene-d_8 upon the addition of an excess of PhCOOH (usually more than 2 equiv) display two high-field resonances: one minor triplet at −13.8 ppm and a major triplet at −9.5 ppm in the entire range of temperatures studied (Figure 7). One broad resonance overlapping with the triplet at −9.5 ppm is also visible in between −25 and 0 °C. At 25 °C, only two broad features are observed. The $(T_1)_{min}$'s for all of these signals, including the broad overlapping resonance, are similar in value to those measured for the monohydride **1a** and the dihydride **3a**, which, in principle, rules out the detection,

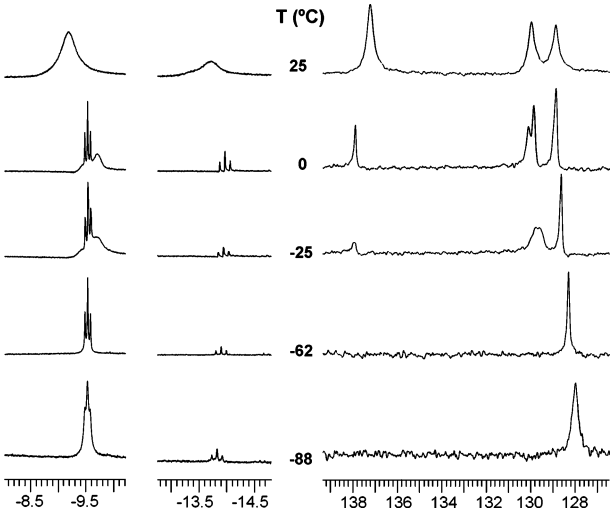


Figure 7. VT ^{1}H NMR (left, hydride region, 400 MHz) and VT $^{31}P\{^1H\}$ NMR (right, 161.89 MHz) of a sample made up by the addition of an excess of PhCOOH to a toluene-d_8 solution of **1a**.

although not the involvement, of a dihydrogen-bonded complex in the observed process.

The VT $^{31}P\{^1H\}$ NMR spectra show one rather broad signal at 127.9 ppm, which gets sharper as the temperature is raised. The position of this signal falls close to that reported for the cationic dihydride complex **2a** in acetone-d_6. At −25 °C, one broad resonance resembling two overlapping singlets arises at 129.4 ppm and one broad resonance is visible at 138.2 ppm. At 0 °C, four signals are observed, whereas at 25 °C, only three rather broad features of approximately the same intensity are present. We have interpreted these observations in terms of a protonation−deprotonation equilibrium involving strongly associated species given the low polarity of the solvent used in this case:

$$[CpRuH(dippae)] + HOOCPh \leftrightarrows [CpRuH_2(dippae)][PhCOO]$$

The equilibrium is shifted to the dihydride at low temperatures, whereas the spectra are dominated by signals attributed mainly to the dihydride in benzoate form, most likely forming a tight ion pair. As the temperature is raised, the equilibrium shifts to the left, which can be interpreted as the attack of the benzoate ion onto the dihydride, that is, a proton transfer back from the dihydride to the benzoate. The possibility exists that the broad resonance visible in the temperature range −25 to 0 °C in the ^{1}H NMR spectra might correspond to an intermediate of the type [CpRu(H)(H···OOCPh)(dippae)] rather than to a dihydrogen-bonded species, given the relatively long $(T_1)_{min}$ value measured for this resonance (400 ms), but, of course, any other possibility cannot be ruled out.

The reaction of the chiral compound **1b** with an excess of PhCOOH shows similarities but also differences with that of **1a** (Figure 8).

As also happens in the previous case, signals attributable to **1b** and also to $[CpRuH_2((R,R)\text{-dippach})][PhCOO]$ are observed in the ^{1}H and $^{31}P\{^1H\}$ NMR spectra at low temperatures. The values of T_1 measured for the hydridic

(33) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2000**, *609*, 161−168.
(34) Ayllón, J. A.; Sayers, S. F.; Sabo-Ettienne, S.; Donnadieu, B.; Chaudret, B.; Clot, E. *Organometallics* **1999**, *18*, 3981−3990.

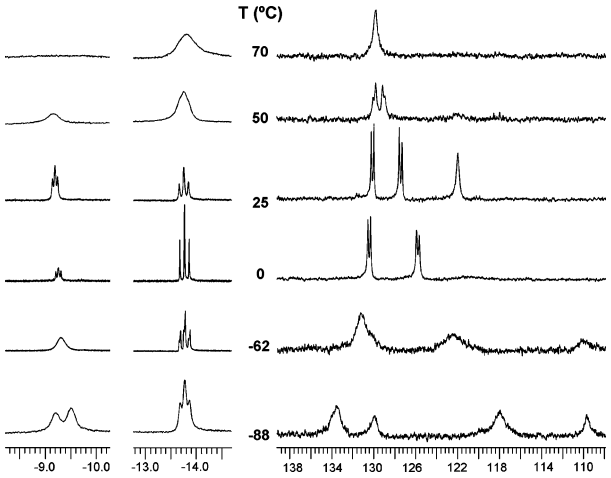


Figure 8. VT ^{1}H NMR (left, hydride region, 400 MHz) and VT ^{31}P{^{1}H} NMR (right, 161.89 MHz) of a sample made up by the addition of 5 equiv of PhCOOH to a toluene-d_8 solution of **1b**.

resonances in the temperature range −88 to 0 °C are consistent with this formulation. However, at 0 °C, an abrupt shortening in the longitudinal relaxation times of both resonances occurs, falling from 560 ms at 0 °C to a common value of 150 ms at 25 °C. At higher temperatures, the signals in the ^{1}H and ^{31}P{^{1}H} NMR spectra get broader. At 70 °C, only one broad resonance is observed in each of the spectra, and the T_1's for the hydridic resonances increase their values smoothly, as shown in Figure 9.

In this case, a protonation−deprotonation equilibrium involving tight ion pairs seems to occur also at low temperatures as for **1a**. However, above 0 °C, differences do appear. The drop of the T_1's for both hydridic resonances to a common value of 150 ms is consistent with a rapid exchange involving the formation at this temperature of a long-lived dihydrogen-bonded species with a short H···H contact:

[CpRuH(R,R-dippach)] + HOOCPh

↓↑

[CpRu(H···HOOCPh)(*R,R*-dippach)]

↓↑

[CpRuH$_2$(*R,R*-dippach)][PhCOO]

Using eq 1 for estimation of the contribution of the H···H dipole−dipole interaction to relaxation and eq 2 for determination of the distance, the result is a H···H separation of 1.68 Å, fully consistent with the formation of a dihydrogen bond between benzoic acid and **1b**. The homologous species [TpRu(H···HOOCPh)((*R,R*)-dippach)] containing Tp as the coligand, having a H···H separation of 1.75 Å, has been recently reported by us.[11]

Finally, we have studied the proton-transfer reactions using less than 1 equiv of the acidic alcohol HFIPOH. Figure 10 shows the VT NMR spectra of a sample made up by the addition of 0.5 equiv of HFIPOH to **1a** in CD_2Cl_2.

These spectra bear a great resemblance to those depicted in Figure 5, corresponding to protonation with stoichiometric

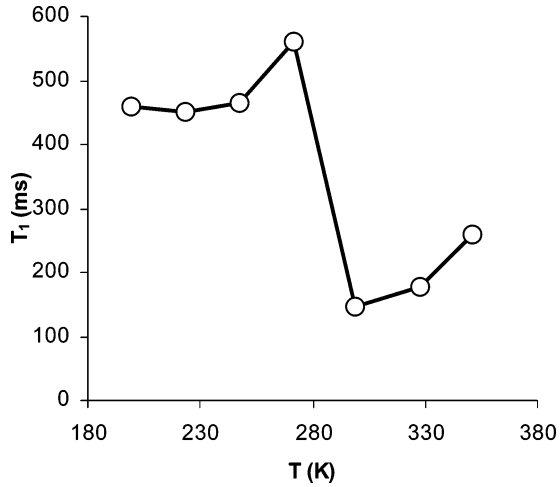


Figure 9. Plot of the variation of T_1 with temperature for the resonance at ca. −14 ppm observed in the reaction of **1b** with an excess of PhCOOH.

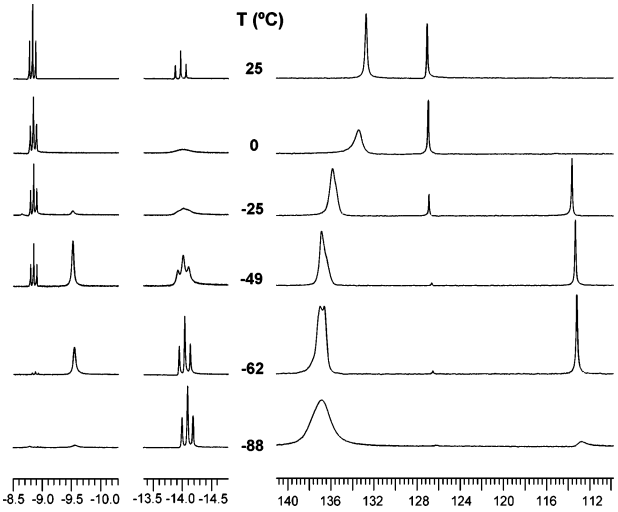


Figure 10. VT ^{1}H NMR (left, hydride region, 400 MHz) and VT ^{31}P-{^{1}H} NMR (right, 161.89 MHz) of a sample made up by the addition of 0.5 equiv of HFIPOH to a CD_2Cl_2 solution of **1a**.

amounts of HBF_4·OEt_2. It is particularly interesting to note here the formation of the dihydrogen complex [CpRu(H$_2$)-(dippae)]$^+$, most likely forming a tight ion pair with the [(CF$_3$)$_2$CHO]$^-$ anion. This species is responsible for the ^{1}H NMR signal at −9.53 ppm and the ^{31}P{^{1}H} NMR resonance at 113.3 ppm. The $(T_1)_{min}$ value of 22 ms is also consistent with this formulation. At the temperature of −49 °C, the formation of the tight ion-paired dihydride species [CpRuH$_2$-(dippae)][(CF$_3$)$_2$CHO] begins, increasing its amount at the expense of the dihydrogen complex as the temperature is raised. In the entire temperature range, a resonance is present at ca. −14 ppm, attributable, in principle, to the monohydride **1a**. This resonance is a triplet at low temperature, becomes broader as the temperature is raised, and then becomes a sharp triplet again at 25 °C. The species responsible for this signal gives a broad resonance centered at 137 ppm in the ^{31}P{^{1}H} NMR spectrum at −88 °C, which gets sharper as the temperature is raised and shifts to a singlet at 132.7 ppm at 25 °C. The latter position is consistent with that of **1a**. Apart from the broadening of these NMR resonances, the signal at −14 ppm displays an unusually short $(T_1)_{min}$ value

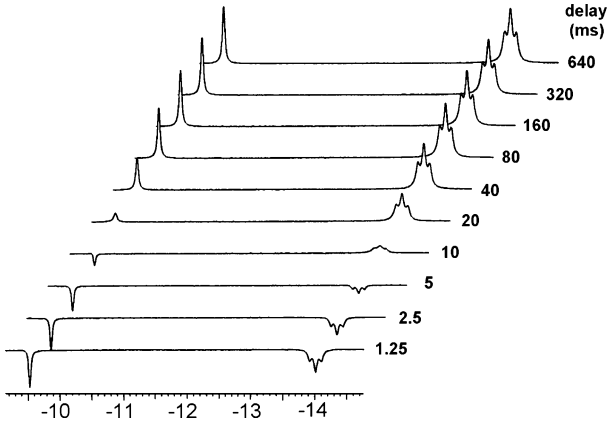


Figure 11. ^{1}H NMR (hydride region, CD_2Cl_2, 400 MHz, −20 °C) profile of **1a** + 0.5 equiv of HFIPOH recorded at variable delay times in a typical inversion−recovery experiment for T_1 determination, showing the faster relaxation of the resonance at higher field compared to that at −9.5 ppm attributed to a dihydrogen complex.

of 6.5 ms. Figure 11 shows clearly the rapid relaxation of the signal at −14 ppm at −20 °C, which has already passed through the null intensity point at a delay of 10 ms, whereas the signal corresponding to the dihydrogen protons at ca. −9.5 ppm is still inverted.

This behavior resembles very much the phenomenon previously observed by us[11] and by other researchers[14] involving species having very short $(T_1)_{min}$'s. We can also rule out here the contributions to relaxation coming from paramagnetic species, so the phenomenon shown in Figure 11 is clearly not an artifact. The reasons why this phenomenon occurs are yet unknown. In here, a minimum longitudinal relaxation time of 6.5 ms is far shorter than that observed for the dihydrogen complex and would involve an unrealistically short H−H distance of 0.74 Å. Everything would suggest that the species responsible for this signal is a dihydrogen-bonded species of the type [CpRu(H···HOCH(CF$_3$)$_2$)(dippae)], except for the anomalously short $(T_1)_{min}$. As a tentative explanation in this particular case, we could eventually propose a multiple simultaneous interaction of the hydride with the hydrogen atom of the alcohol and the fluorine atoms of the CF_3 substituents, maybe favored by additional hydrogen bonding between the HFIPOH molecule and the NH groups of the phosphinoamine ligand. Given the NMR properties of the ^{19}F nucleus compared to those of ^{1}H, an efficient contribution to relaxation would be expected from H···F dipole−dipole interactions. We have carried out a 2D HOESY ^{1}H−^{19}F NMR experiment in order to gather information about this possibility. Only one signal is present in the ^{19}F NMR spectrum of the mixture resulting from the addition of 0.5 equiv of HFIPOH to **1a** in CD_2Cl_2. No H···F interactions were observed other than the expected coupling with the isopropyl proton of HFIPOH. Furthermore, no anomalous shortening of T_1 of the ^{19}F NMR resonance of HFIPOH in the mixture was observed, when compared to the value measured for T_1 of the ^{19}F NMR resonance of pure HFIPOH in a CD_2Cl_2 solution. If indeed fluorine atoms were causing fast relaxation on the hydride proton due to dipole−dipole interactions, a reduction in T_1 of the fluorine atoms should also be expected. Hence, these results rule out in this case the hypothesis that close H···F contacts between the hydride and the fluorine atoms of HFIPOH might be responsible for the anomalous fast relaxation of the hydride proton in **1a**. With these data in our hands, whatever explanation might be suggested at this moment for this fast relaxation phenomenon, it would be merely speculative, and further research is needed. It is important to mention that this phenomenon has only been observed when **1a** reacted with *less than 1 equiv* of HFIPOH. The reaction with a stoichiometric amount or with an excess of HFIPOH only revealed the presence of the dihydrogen complex [CpRu(H$_2$)(dippae)]$^+$, which irreversibly rearranges to the dihydride species as the temperature is raised, with no traces of hydridic species having extra short longitudinal relaxation times.

Conclusions

A series of neutral and cationic CpRu and Cp*Ru hydride complexes bearing chelating phosphinoamine ligands have been prepared and characterized in which no significant interactions between the hydrogen atoms bound to the metal and the NH groups of the phosphinoamine ligands have been detected. Protonation of the monohydride complexes **1a**,**b** or **2a**,**b** or of the dihydrides **3a**,**b** or **4a**,**b** with an excess of HBF_4 leads to dicationic dihydride complexes **5a**,**b** or **6a**,**b** resulting from protonation of one of the NH groups of the phosphinoamine ligand. In the course of the protonation of **1a** with HBF_4, the metastable dihydrogen complex [CpRu(H$_2$)(dippae)]$^+$ was detected as an intermediate. Spectral evidence for the formation of a dihydrogen-bonded species of the type [CpRu(H···HOEt$_2$)(dippae)]$^+$ prior to the proton-transfer process has also been obtained. When a weak acid such as PhCOOH was used in a solvent of low polarity such as toluene-d_8, a protonation−deprotonation equilibrium most likely involving the formation of tight ion pairs occurs. In the case of the reaction of **1b**, the dihydrogen-bonded complex [CpRu(H···HOOCPh)((*R*,*R*)-dippach)] has been identified. A remarkable shortening in the $(T_1)_{min}$ value of the hydride signal of the monohydrides **1a** to 6.5 ms (i.e., shorter than that for the dihydrogen complex [CpRu(H$_2$)(dippae)]$^+$) has been observed upon the addition of 0.5 equiv of HFIPOH in CD_2Cl_2. Paramagnetic contributions to relaxation have been ruled out. Although everything seems to point to the formation of a dihydrogen-bonded species between **1a** and HFIPOH, this is another example of a system having an anomalously short $(T_1)_{min}$, and the reasons for this fast relaxation phenomenon remain as yet unknown.

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Supporting Information Available: Tables of X-ray structural data in CIF format, including data collection parameters, positional and thermal parameters, and bond distances and angles for complex **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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