Monocyclopentadienylhydride Derivatives of Ruthenium: Stereoselective Proton Transfer and Proton–Hydride Exchange in an Extremely Short Dihydrogen Bond

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JULY 2004

Impact Factor: 12.11 · DOI: 10.1021/ja031926k · Source: PubMed

6 AUTHORS, INCLUDING:

Blanca Rosa Manzano
University of Castilla-La Mancha
93 PUBLICATIONS **1,823** CITATIONS

Gustavo Espino
Universidad de Burgos
23 PUBLICATIONS **315** CITATIONS

Kurt Mereiter
TU Wien
481 PUBLICATIONS **6,727** CITATIONS

JACS
ARTICLES
Published on Web 05/15/2004

Monocyclopentadienylhydride Derivatives of Ruthenium: Stereoselective Proton Transfer and Proton-Hydride Exchange in an Extremely Short Dihydrogen Bond

Ester Cayuela,† Félix A. Jalón,*,† Blanca R. Manzano,† Gustavo Espino,‡ Walter Weissensteiner,§ and Kurt Mereiter⊥

Contribution from the Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Universidad de Castilla-La Mancha, Avda. Camilo J. Cela 10, 13071 Ciudad Real, Spain; Departamento de Química, Facultad de Ciencias, Plaza Misael Bañuelos s/n, 09001 Burgos, Spain; Faculty of Chemistry, University of Vienna, Währinger Strasse 38, A-1090 Vienna, Austria; and Faculty of Technical Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

Received December 23, 2003; E-mail: felix.jalon@uclm.es

Abstract: Diastereomerically pure complexes of formula CpRuCl(PP*) and CpRuH(PP*) with chiral ferrocenyl diphosphines were prepared and the selectivity of proton-transfer processes over the monohydride compounds with different acids was studied. With 1 equiv of HBF_4 the *cis*-dihydrogen and *trans*-dihydride complexes were formed while with 3 equiv of CF_3CO_2H the *trans*-dihydride derivative was the only product. However, the use of 1 equiv of CF_3CO_2H led to a dihydrogen bonded complex with an extremely short $RuH\cdots HO_2CF_3$ interaction that exhibits proton-hydride exchange. Using the labeled acid CF_3CO_2D, a stereoselective transference of the deuteron was demonstrated that implies the previous epimerization of the monohydride and the subsequent attack of the acid in the position previously occupied by the hydride.

Introduction

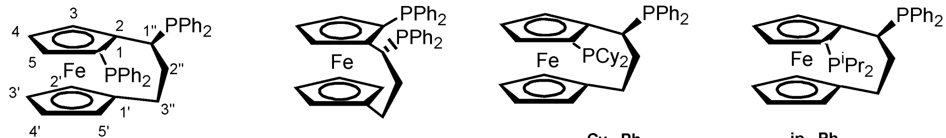
Monocyclopentadienylhydride derivatives of ruthenium have received special attention in recent years, particularly with respect to their chemistry and properties as hydride transition metal complexes. New concepts have been introduced and important advances have been made in the study of these systems. For instance, such complexes were some of the first transition metal systems in which quantum mechanical exchange between the hydrides was observed and studied.[1] Interesting cis to trans isomerism, involving dihydrogen−dihydride transformation, has also been demonstrated.[2] Furthermore, the acid character of the cationic dihydride derivatives has been used to build a large acidity scale in organic solvents.[3]

Studies concerning proton transfer to the neutral monohydride derivatives, mainly with systems containing two phosphorus donor atoms, have demonstrated that the process proceeds through a stereoselective attack cis to the hydride with kinetic control. The cis species slowly evolves to the thermodynamically stable trans dihydride. The nonclassical dihydride derivatives are, in some cases, stable at room temperature, mainly when diphosphine ligands with small bite angle are used.[2a,4] In some rare examples, both cis and trans dihydrides are in equilibrium at room temperature.[2] In other examples, it has been theoretically studied[5] and experimentally demonstrated[5c,6] that the proton transfer occurs through a prior step in which a dihydrogen bond Ru−H···H−A is formed. Interesting ideas concerning the noninnocent role of the conjugated base (A^-) of the proton donor agent (AH) have recently been suggested,[5c,7] but many aspects concerning the kinetic control of this counteranion remain unknown. In this work, our aim was to gain further insights into the protonation process of monohydridediphosphine ruthenium derivatives. To achieve this goal, we used two different but complementary approaches: (i) to use chiral diphosphine ligands. This would create an asymmetric environment in the

† Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Universidad de Castilla-La Mancha.
‡ Departamento de Química, Facultad de Químicas y CyTA.
§ Faculty of Chemistry, University of Vienna.
⊥ Faculty of Technical Chemistry, Vienna University of Technology.

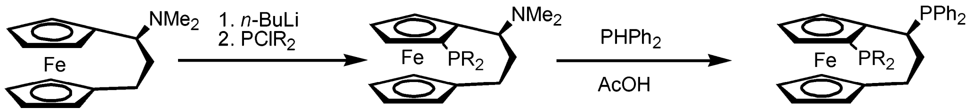
(1) (a) Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353−5361. (b) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077−2091. (c) Maseras, F.; Lledós, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601−636.
(2) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175. (b) Jia G.; Lough, A. J.; Morris R. H. *Organometallics* **1992**, *11*, 161−171.
(3) (a) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883. (b) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171. (c) Berming D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 1432.
(4) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675.
(5) (a) Orlova, G.; Scheiner, S. *J. Phys. Chem. A.* **1998**, *102*, 4813−4818. (b) Orlova, G.; Scheiner, S. *J. Phys. Chem. A.* **1999**, *103*, 514. (c) Belkova, N. V.; Besora, M.; Epstein, L. M.; Lledós, A.; Maseras, F.; Shubina, E. S. *J. Am. Chem. Soc.* **2003**, *125*, 7715−7725.
(6) (a) Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000. (b) Shubina, E. S.; Belkova, N. V.; Bakhmutova, E. V.; Vorontsov, E. V.; Backhmutov, V. I.; Ionidis, A. V.; Bianchini, C.; Marvelli, L.; Peruzzini, M.; Epstein, L. M. *Inorg. Chim. Acta* **1998**, *280*, 302. (c) Gruendeman, S.; Ulrich, S.; Limbach, H.-H.; Golubev, N. S.; Denisiov, G. S.; Epstein, L. M.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1999**, *38*, 2550. (d) Chu, H. S.; Xu, Z.; Ng, S. M.; Lau, C. P.; Lin, Z. *Eur. J. Inorg. Chem.* **2000**, 993.
(7) Basallote, M. G.; Durán, J.; Fernández-Trujillo, M. J.; Máñez, M. A. *Organometallics* **2000**, *19*, 695−698.

Chart 1



(S_c,S_p)-PP^{Ph}PF (R_c,R_p)-PP^{Ph}PF (S_c,S_p)-P^{Cy}P^{Ph}PF (S_c,S_p)-P^{ip}P^{Ph}PF

Scheme 1



R = Cy, (S_c,S_p)-P^{Cy}APF

R = ^{i}Pr, (S_c,S_p)-P^{ip}APF

R = Cy, (S_c,S_p)-P^{Cy}P^{Ph}PF

R = ^{i}Pr, (S_c,S_p)-P^{ip}P^{Ph}PF

coordination sphere that could give valuable information regarding the stereoselectivity of the transfer; (ii) to analyze the proton transfer process using not only the strong acid HBF_4, but also a weaker acid such as CF_3CO_2H. Given that the cis species that could be initially formed can be quite acidic, it was envisaged that a similarity in acidity with the proton-transfer agent could allow the observation of intermediates in this process. The fact that the kinetic acidity of one acid changes with its concentration in the reaction medium has also been used to modulate the degree of the transference.

Results and Discussion

A. Synthesis and Structural Characterization of Ligands and Complexes 1−6. The racemic 1-diphenylphosphino-2,1′-(1-diphenylphosphinopropanediyl)-ferrocene, PP^{Ph}PF (see Chart 1) was prepared according to methods previously reported by some of us.[8] The enantiomerically pure ligands [(S_c,S_p)-1-dicyclohexylphosphino-2,1′-(1-diphenylphosphinopropanediyl)ferro-cene, (S_c,S_p)-P^{Cy}P^{Ph}PF and (S_c,S_p)-1-diisopropylphosphino-2,1′-(1-diphenylphosphinopropanediyl)-ferrocene, (S_c,S_p)-P^{ip}P^{Ph}PF] were synthesized for the first time.

To prepare them, two new chiral ferrocenylaminophosphine derivatives were also obtained as the respective precursors: (S_c,S_p)-1-dicyclohexylphosphino-2,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene, (S_c,S_p)-P^{Cy}APF and (S_c,S_p)-1-diisopropylphosphino-2,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene, (S_c,S_p)-P^{ip}APF (see Scheme 1). These ferrocenylaminophosphine derivatives were obtained by a previous *ortho*-lithiation of the chiral ferrocenylamine (*S*)-1,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene with *n*-buthyllithium. The known[8] high diastereoselectivity of this lithiation allows, by quenching with $PClCy_2$ or PCl^iPr_2, the preparation of the enantiomericaly pure aminophosphines (S_c,S_p)-P^{Cy}APF and (S_c,S_p)-P^{ip}APF, respectively. The reaction of (S_c,S_p)-P^{Cy}APF or (S_c,S_p)-P^{ip}APF with $PHPh_2$ in acetic acid (see Scheme 1) gave the diphosphines (S_c,S_p)-P^{Cy}P^{Ph}PF and (S_c,S_p)-P^{ip}P^{Ph}PF respectively in a type of reaction where, as it has been reported,[8a] the configuration of the chiral center is retained (See Experimental Section for more details).

(8) (a) Sturm, T.; Weissensteiner, W.; Spindler, F.; Mereiter, K.; López-Agenjo, A. M.; Manzano, B. R.; Jalón, F. A. *Organometallics* **2002**, *21*, 1766. (b) Mernyi, A.; Kratky, Ch.; Weissensteiner, W.; Widhalm, M. *J. Organomet. Chem.* **1996**, *508*, 209−218.

Scheme 2

$$CpRuCl(PPh_3)_2 + PP^* \longrightarrow CpRuCl(PP^*) + 2\,PPh_3$$

$$PP^* = PP^{Ph}PF, \mathbf{1};\ (S_c,S_p)\text{-}P^{Cy}P^{Ph}PF, \mathbf{2};\ (S_c,S_p)\text{-}P^{ip}P^{Ph}PF, \mathbf{3}$$

Ligands and precursors indicated in Scheme 1 were characterized as optically active compounds by polarimetry and as pure species by mass spectrometry and NMR. The elemental analyses were in accordance with their chemical formula. In general, if the signals are not obscured by other resonances, the ^1H and $^{13}C\{^1H\}$ NMR spectra showed the expected signals for the Cp and the alkylic interannular chain. The PPh_2 and PR_2 groups showed complex patterns due to the diastereotopic character of the phosphine substituents. PPh_2 and PR_2 groups exhibited the characteristic resonances in the respective $^{31}P\{^1H\}$ NMR spectra that are mutually coupled in the case of the diphosphine derivatives.

The existence of the interannular alkylic chain makes these ligands conformationally rigid,[8] which is especially convenient for our structural studies because of the simplification that this feature causes in the NMR spectra at low temperature due to the existence of only one conformation (see below). In the sole conformation of these ligands, the PPh_2 group attached to the interannular chain is slightly above the disubstituted Cp ring and, as a consequence, the $C^{2''}$ carbon of the chain points toward the C^1−$C^{5'}$ axis as indicated in Chart 1. Previous nOe studies on palladium[9] and ruthenium[10] complexes with related ligands demonstrated that the stated conformation persists when the diphosphine is coordinated to metallic centers.

The halide complexes **1**−**3** were prepared by thermally induced substitution reactions in toluene (Scheme 2) in an analogous way to procedures previously described for other similar monocyclopentadienyldiphosphines.[11]

The reaction of **1**−**3** with an excess of $LiAlH_4$ in THF allowed the isolation of the monohydride complexes **4**−**6** by metathetical exchange of chloride by hydride (Scheme 3). In

(9) Gómez-de la Torre, F.; Jalón, F. A.; López-Agenjo, A.; Manzano, B. R.; Rodríguez, A.; Sturm, T.; Weissensteiner, W.; Martínez-Ripoll, M. *Organometallics* **1998**, *17*, 4634−4644.

(10) Jalón, F. A.; López-Agenjo, A.; Manzano, B. R.; Moreno-Lara, M.; Rodríguez, A.; Sturm, T.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1999**, 4031−4039.

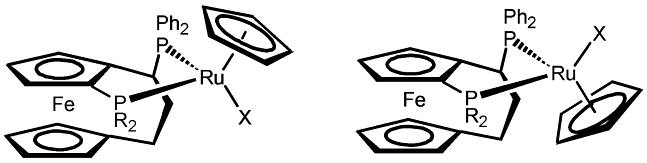
(11) (a) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003−1016. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376−2382.

Scheme 3

$$\mathrm{CpRuCl(PP^*) + LiAlH_4 \longrightarrow CpRuH(PP^*) + LiCl + ``AlH_3"}$$

$$\mathrm{PP^* = PP^{Ph}PF}, \mathbf{4}; (S_c,S_p)\text{-}\mathrm{P^{Cy}P^{Ph}PF}, \mathbf{5}; (S_c,S_p)\text{-}\mathrm{P^{ip}P^{Ph}PF}, \mathbf{6}$$

Chart 2



endo X ***exo X***

X = Cl; R = Ph (**1**), Cy (**2**), ^{i}Pr (**3**)
X = H; R = Ph (**4**), Cy (**5**), ^{i}Pr (**6**)

contrast with other similar reactions, in which the trihydride derivatives were formed in addition to the monohydrides,[12] in this case the reaction leads selectively to the monohydride complexes.

All of the neutral complexes **1**−**6** are soluble in polar solvents such as acetone and THF while the monohydride compounds are more soluble in nonpolar solvents such as toluene. The monohydride complexes **4**−**6** undergo hydride/chloride metathesis with chlorocarbon solvents.[13]

Complexes **1**−**6** were characterized by NMR and IR spectroscopy. The molecular structure of **4** was determined by X-ray diffraction (see below). Elemental analyses are consistent with the proposed formulas.

The observation of consistent NMR resonances confirms that complexes **1**−**5** exist in solution as single species, despite the fact that two diastereomers are possible given the stereogenic character of the Ru center due to the asymmetry of the diphosphine ligands (see Chart 2). The absolute configuration of the ruthenium center was determined according to the method described below. The asymmetry and rigidity of the diphosphine ligands probably impose an energetic difference that is sufficiently high to see only one of the diastereomers in solution by NMR methods. This diastereospecificity contrasts with the results found by other authors in the preparation of chiral monocyclopentadienyl derivatives.[14] However, for complex **6** the two diastereomeric forms were observed in acetone or toluene solutions in a 100:6 ratio even though only the major component (R_{Ru}, *endo* H) in solution was obtained after crystallization. To study the possible existence of an equilibrium between the *exo* and *endo* stereoisomers of **6**, solutions in acetone-d_6 and toluene-d_8 were monitored by NMR spectroscopy over a period of several hours at room temperature and in toluene-d_8 at 80 °C. The ratio between these isomers did not change. However, when methanol-d_4 was added to an acetone-d_6 solution of this complex at room temperature (1:1 v/v ratio of solvents), the signals due to the minor component of the mixture (*exo* H, S_{Ru}) disappeared immediately from the spectra, showing the effect of the solvent in the equilibrium constant of epimerization and the relatively high velocity of this process. According to these data, the formation of the *exo* isomer probably occurs under kinetic control. The epimerization process of monocyclopentadienyl ruthenium derivatives has hardly been studied and the examples that have been investigated are centered on halide or pseudohalide derivatives. This process is considered to be difficult in phosphine derivatives[14a,15] but is feasible in complexes bearing ligands that are prone to allowing a reversible and partial dissociation.[16] The dramatic effect of the methanol in our experiments can be understood by taking into account the known solvolysis effect of this solvent. This solvent probably favors the partial dissociation of the diphosphine, allowing the epimerization process to give the thermodynamically more stable form (*endo* H, R_{Ru}). In addition to the aforementioned process, a slow incorporation of deuterium into the hydride group of **6** was observed in the acetone-d_6/methanol-d_4 solution. After 12 h, the D/H ratio was 8/2. The other groups in the complex were not deuterated in this time and only the OH group of the solvent incorporated protium. This process was reversible and when the solution of **6** + **6**-*d* was evaporated to dryness and wet acetone-d_6 was used to dissolve the complex, the deuterium was almost totally removed from this complex. As discussed below, an acid−base process is probably the mechanism involved in this isotopic exchange.

The monohalide complexes **1**−**3** exhibit in the IR spectra only one small vibration band in the 270−290 cm^{-1} region and this is characteristic of the Ru−Cl stretching mode. The more characteristic vibration of the monohydride complexes **4**−**6** is the Ru−H stretching, which appears in the range 1950−2000 cm^{-1} and is observed as a small band.[17]

The $^{31}P\{^1H\}$ NMR spectra of **1**−**6** show two doublets with a J_{PP} of about 54 Hz for the halide and J_{PP} = 41.5−50.7 Hz for the hydride derivatives. These values are in the range usually found for diphosphine coordinated in three-legged piano-stool compounds[14a,15,18] (see data in the Experimental Section). The shift of these resonances to higher frequency with respect to the free ligand provides evidence of the coordination of the diphosphines.

^{1}H NMR data are compiled in the Experimental Section and the $^{13}C\{^1H\}$ NMR information is given in the Supporting Information. The assignment of the resonances was carried out on the basis of information extracted from ^{1}H ^{1}H COSY, selectively decoupled $^1H\{^{31}P\}$ NMR spectra, nOe and DEPT experiments. For **4**−**6**, a doublet of doublets or an apparent triplet is observed in the high field region of the ^{1}H NMR spectra

(12) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278−1279.
(13) The same property has been reported for $CpRuH(PMe_3)_2$: Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980−3987.
(14) (a) Consiglio, G.; Morandini, F.; Bangerter, F. *Inorg. Chem.* **1982**, *21*, 455−457. (b) Morandini, F.; Consiglio, G.; Lucchini, V. *Organometallics* **1985**, *4*, 1202−1208.
(15) Morandini, F.; Consiglio, G.; Straub, B.; Ciani, G.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2293−2298.
(16) (a) Onitsuka, K.; Ajioka, Y.; Matsushima, Y.; Takahashi, S. *Organometallics* **2001**, *20*, 3274−3282. (b) Carmona, D.; Vega, C.; Lahoz, F. J.; Atencio, R.; Oro, L. A.; Lamata, P.; Viguri, F.; San José, E. *Organometallics* **2000**, *19*, 2273−2280. (c) Slugovc, Ch.; Simanko, W.; Mereiter, K.; Schmid, R.; Kirchner, K.; Xiao, L.; Weissensteiner, W. *Organometallics*, **1999**, *18*, 3865−3872. (d) Brunner, H.; Neuhierl, T.; Nuber, B. *J. Organomet. Chem* **1998**, *563*, 173−178. (e) Mezzetti, A.; Consiglio, G.; Morandini, F. *J. Organomet. Chem.* **1992**, *430*, C15−C18.
(17) Bruce, M. I.; Butler, I. R.; Cullen, W. R.; Koutsantonis, G. A.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1988**, *41*, 963−969.
(18) Torres-Lubián, R.; Rosales-Hoz, M. J.; Arif, A. M.; Ernst, R. D.; Paz-Sandoval, M. A. *J. Organomet. Chem.* **1999**, *585*, 68−82.

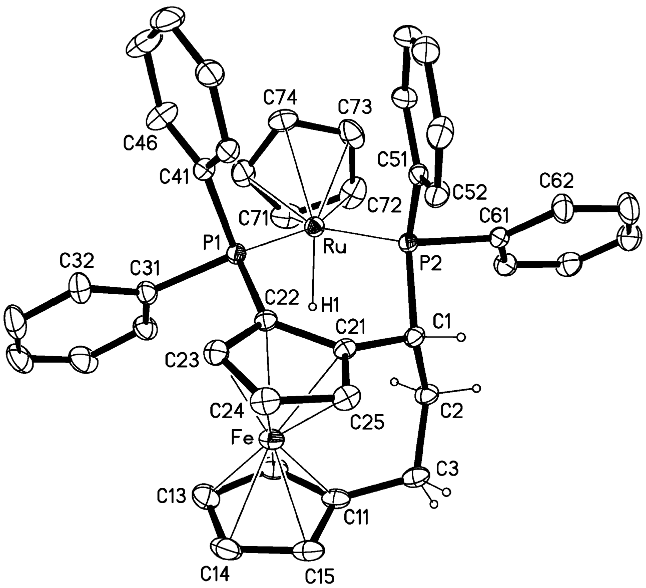


Figure 1. Molecular structure of complex **4** in the crystalline state showing 20% thermal ellipsoids. Hydrogen atoms of the aromatic rings have been omitted for clarity. Only the S_{Ru},R_c,R_p enantiomer is represented.

(−12.75 to −14.15 ppm). These signals correspond to the resonance of the hydride ligand coupled to the two chemically different phosphorus atoms. The coupling constants (J_{HP} = 34.1−34.9 Hz) are consistent with the expected structure for these complexes.[3b,12]

B. Stereochemical Studies of 4. The structure of complex **4** was studied both in the solid state (X-ray diffraction) and in solution (nOe experiments) in order to demonstrate the absolute configuration of this complex.

1. X-ray Study of 4. Compound **4** crystallized as a racemic and contains in its lattice both $S_{Ru}-R_c-R_p$ and $R_{Ru}-S_c-S_p$ forms of the complex. Only one of the two enantiomers existing in the unit cell of space group $P\bar{1}$ is shown in Figure 1 (see Table 1 for salient crystal data). The hydride hydrogen could be located from the diffraction data and was refined in positional parameters yielding a chemically reasonable structure.

As expected, the complex exhibits a three-legged piano stool structure (see Figure 1). A selection of bond distances and bond angles is compiled in Table 2. Bond distances around the ruthenium center can be considered as normal.[13,19] The relative disposition of the CpRuH moiety with respect to the ferrocenyl ligand shows that the absolute configuration of the metal is *S*,[20] when (R_c,R_p)−PP^{Ph}PF is the coordinated enantiomer (*endo* H in Chart 2). The bite angle of the diphosphine is 87.94(5)°, smaller than observed in comparable derivatives bearing diphosphines with three spacer carbons that are in the range of 90−97°.[21] The bond angles between the donor atoms (P−Ru−H = 81 and 87°, H−Ru−Cp$_c$, = 122° and P−Ru−Cp$_c$ = 130.6 and 132.0° (Cp$_c$ = Cp centroid)) are in the range of this type of

Table 1. Details for the Crystal Structure Determinations of CpRuH(PP^{Ph}PF), **4**, and CpRu(CF_3CO_2)(PP^{Ph}PF), **13**

	CpRuH(PP^{Ph}PF), **4**	CpRu(CF_3CO_2)(PP^{Ph}PF), **13**
formula	$C_{42}H_{38}FeP_2Ru$	$C_{44}H_{37}F_3FeO_2P_2Ru$
fw	761.58	873.60
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	11.318(4)	11.350(5)
b, Å	11.675(4)	11.543(5)
c, Å	13.253(5)	16.084(7)
α, deg	93.94(2)	82.07(2)
β, deg	97.22(2)	88.66(2)
γ, deg	106.93(2)	62.05(2)
V, Å^3	1651.8(9)	1841.6(14)
Z	2	2
ρ_{calc}, g cm^{-3}	1.531	1.575
T, K	297(2)	297(2)
μ, mm^{-1}	1.024	0.945
F(000)	780	888
θ_{max}, deg	30.0	30.0
no. of reflns measured	24309	33751
no. of unique reflns	9439	10525
no. of reflns $I > 2\sigma$(I)	7923	8557
no. of params	419	478
R_1 ($I > 2\sigma$(I))^a	0.0329	0.0328
R_1 (all data)	0.0431	0.0449
wR_2 (all data)	0.0880	0.0901
diff Four. Peaks min/max, e Å^{-3}	−0.97/0.66	−0.57/0.65

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for CpRuH(PP^{Ph}PF), **4**, and CpRu(CF_3CO_2)(PP^{Ph}PF), **13**

	4	**13**
<Ru−(C(71)−C(75))>	2.247(3)	2.196(2)
Ru−P(1)	2.2277(12)	2.343(1)
Ru−P(2)	2.2348(11)	2.305(1)
Ru−H(1)/Ru−O(1)	1.51(2)	2.183(2)
<Fe−(C(11)−C(15)>	2.032(3)	2.045(2)
<Fe−(C(21)−C(25))>	2.032(2)	2.038(2)
P(1)−C(22)	1.811(2)	1.825(2)
P(1)−C(31)	1.841(2)	1.837(2)
P(1)−C(41)	1.839(2)	1.843(2)
P(2)−C(1)	1.862(2)	1.866(2)
P(2)−C(51)	1.837(2)	1.847(2)
P(2)−C(61)	1.838(2)	1.840(2)
C(1)−C(21)	1.512(3)	1.504(3)
C(1)−C(2)	1.550(3)	1.548(3)
C(2)−C(3)	1.526(3)	1.534(3)
C(3)−C(11)	1.492(4)	1.501(3)
P(1)−Ru−P(2)	87.94(5)	92.03(4)
P(1)−Ru−H(1)/Ru−O(1)	80.6(9)	93.78(5)
P(1)−Ru−H(1)/Ru−O(1)	87.1(9)	86.41(5)

monohydrides.[13] One of the most important aspects to be discussed in this structure is the conformation of the diphosphine ligand. As it can be observed in Figure 1, two of the phenyl groups have practically parallel $C_{ipso}-C_{para}$ axis with a pseudo-axial orientation in the six-member coordination metallacycle. These two phenyl groups block the position trans to the Ru−H bond that is one of the possible directions of attack in the proton-transfer process (trans attack). The other two phenyl groups are situated in a pseudoequatorial position in the coordination metallacycle. According with the conformational rigidity of this ligand, very probably this conformation persists in solution but nOe experiments have been carried out in order to demonstrate this statement.

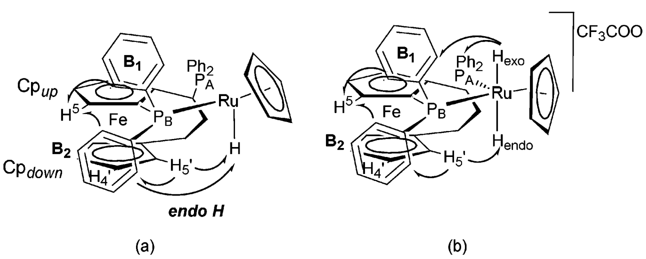
2. Stereochemical nOe Studies for 4. Bidimensional (NOE-SY) and monodimensional nOe studies have proven to be successful methods to determine the single or more populated

(19) Brammer, L.; Klooster, W. T., Lemke, F. R. *Organometallics* **1996**, *15*, 1721−1727.
(20) The Cahn−Ingold−Prelog criteria extended to π-bonded ligands have been considered in this assignment. Priority order of the ligands, Cp > PPh_2Cp > PPh_2R > H. Lecomte, C.; Dusausoy, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* **1974**, *73*, 67. Brunner, H. *Enantiomer* **1997**, *2*, 133. Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194−1208.
(21) (a) Chang, Ch. W.; Lin, Y. Ch.; Lee, G. H.; Wang, Y. *Organometallics* **2000**, *19*, 3692. (b) Hung, M. Y.; Ng, S. M. *Organometallics* **2000**, *19*, 3692. (c) Zanetti, N. C.; Spindler, F.; Spencer, J.; Togni, A.; Rihs, G. *Organometallics* **1996**, *15*, 860. (d) Lister, S. A.; Redhouse, A. D.; Simpson, S. J. *J. Acta Crystallgr.* **1992**, *C48*, 1661.

Scheme 4

$$\mathrm{CpRuHL_2} + \mathrm{HA} \longrightarrow cis\text{-}[\mathrm{CpRu}(\eta^2\text{-}\mathrm{H_2})\mathrm{L_2}]\mathrm{A} \longrightarrow trans\text{-}[\mathrm{CpRuH_2L_2}]\mathrm{A}$$

Chart 3



configuration of molecules in solution.[22] We and others have demonstrated that the assignment of resonances of the *ortho* phenyl protons and the determination of the nOe's of these protons with their neighboring groups is a very effective way to show the conformation of ferrocenylaminophosphine[9,23] and ferrocenyldiphosphine ligands[24] coordinated to metallic centers. We assigned the resonances of the ortho protons of **4** by examining selectively decoupled ^{1}H{^{31}P} NMR spectra. In this way, irradiation of the ^{31}P NMR resonances induces decoupling in the resonances at 7.78, 7.89 (P_A) and 6.73, 8.45 (P_B) ppm (see Chart 3a). In the corresponding monodimensional nOe spectra, an nOe is observed between the resonance at 6.73 and the Cp resonances at 2.58, 3.30 (Cp_{down}) and 3.93 ppm (Cp_{up}) and between the resonance at 8.45 and the Cp resonance at 3.93 ppm. The Cp resonance at 2.58 is substantially more shielded to lower frequency than the rest of the Cp resonances. This situation is due to the shielding effect of phenyl B_2 on $H_{5'}$.[10] On the basis of this information, the resonance at 6.73 can be assigned to the ortho proton of phenyl B_2 in Chart 3a. In agreement with this assignment, an nOe between this resonance and the hydride signal is also observed and all this evidence supports the (R_{Ru}, *endo* H) absolute configuration of **4** when the (S_c−S_p)-PP^{Ph}PF enantiomer is coordinated (see Chart 3a). We can conclude that the configuration determined in the solid-state persists in solution. The short distances between $H_{5'}$ and one of the ortho protons of phenyl B_2 (2.78 Å) and between this ortho proton and the hydride (2.50 Å), as seen in the X-ray structure of **4**, support the nOe results. The ^{1}H NMR spectrum of **4** at low temperature does not show signs of the existence of other conformations or other stereoisomers, a situation that reflects the rigidity of the diphosphine in **4** and the existence of a single configuration.

Analogous experiments were carried out with the major isomer of **6** and an endo orientation for the hydride ligand (R_{Ru}−S_c−S_p diastereomer) was also found.

C. Proton-Transfer Processes. The reaction of monohydrides $\mathrm{CpRuHL_2}$ with Brönsted acids (HA) leads to cationic dihydrides through proton-transfer reactions.[25] The mechanism of such reactions is assumed to start with attack at the Ru−H bond (cis attack) by kinetic control. The cis isomers have a nonclassical nature for these Ru derivatives. However, unless L_2 is a bidentate ligand with a small bite angle, a slow cis to trans isomerization usually occurs that irreversibly transforms these dihydrides into the classical trans species (see Scheme 4).

The cis to trans isomerization in this type of dihydride has been explained in terms of the formation of trigonal bipyramidal intermediates,[2a] dissociative processes with the partial breaking of Ru−L bonds[26] or the deprotonation of the cis isomer with subsequent attack at the trans position.[27] This last mechanism seems to be more probable in the case of acidic cis dihydrogen complexes.

With this information in mind, we carried out the reactions of our monohydrides **4**−**6** with acids of different strength such as HBF_4 or CF_3CO_2H (also CF_3CO_2D). The corresponding transfer reactions were monitored by NMR at low temperature (−80 or −70 °C) in NMR tubes using acetone-d_6 as solvent. To compare the results, some of the reactions were followed during a slow increase in the temperature or were carried out directly at room temperature.

1. Proton Transfer from HBF_4. Initially, we used HBF_4 as a donor in the proton transfer, with **4** acting as the acceptor. The choice of this strong acid was based on the fact that the majority of examples where the *cis*-dihydride has been stabilized have involved the use of this acid.[2a,28] The reaction carried out at −70 °C in acetone-d_6, using a slight excess of acid with respect the 1:1 ratio of reactants, led to a mixture of three hydride derivatives in which, besides **4**, signals for two new species appeared in the ^{1}H and ^{31}P{^{1}H} spectra (see Figure 2a).

The major component of this mixture, **8**, shows hydride resonances as two doublets of doublets at −7.90 and −8.36 ppm, whereas the other new component, **7**, exhibits a broad signal at −8.3 ppm (obscured by one of the hydride resonance of **8**). The ^{1}H{^{31}P}NMR spectrum showed that the multiplicity of the hydride signals of **8** was due to J_{HP} coupling constants. The T_1(min) of the hydride resonances of the three derivatives was calculated and showed clearly different values: **4** (188 ms, 209 K), **7** (15 ms, 225 K) and **8** (320 ms, 243 K). The low value obtained for **7** allows the assignment of this resonance to the dihydrogen molecule coordinated in the *cis*-[CpRu(η^2-H_2)(PP^{Ph}PF)]BF_4, **7**. A H−H distance of 1.13 Å (low rotation regime) or 0.90 Å (rapid rotation regime)[29] was calculated for this coordinated molecule and is in accordance with that expected for this type of complexes.[30] The T_1(min) value, the chemical shift, the J_{PH} coupling constants of the hydride

(22) (a) Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727−734. (b) Friedbolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; John Wiley & Sons: New York, 1999.
(23) Hess, A.; Sehnert, J.; Weyhermuller, T.; Metzler-Nolte, N. *Inorg. Chem.* **2000**, *39*, 5437−5443.
(24) (a) Abbenhuis, H. C. L.; Burkhard, U.; Gramlich, V.; Koellner, C.; Pregosin, P. S. *Organometallics* **1995**, *14*, 759−766. (b) Manzano, B. R.; Jalón, F. A.; Gómez-de la Torre, F.; López-Agenjo, A.; Rodríguez, A. M.; Mereiter, K.; Weissensteiner, W.; Sturm, T. *Organometallics* **2002**, *21*, 789−802.
(25) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155−248.
(26) De los Rios, I.; Jimémez-Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, *15*, 4565−4574.
(27) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 9554.
(28) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865−5867. (b) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (c) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martin-Vaca, B. M.; Borge, J.; García-Granada, S. *Inorg. Chim. Acta* **2003**, *347*, 181−188. (d) Mathew, N.; Jagirdar, B. R.; Ranganathan, A. *Inorg. Chem.* **2003**, *42*, 187−197. (e) Aneetha, H.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2002**, *663*, 151−157. (f) Mathew, N.; Jagirdar, B. R. *Organometallics* **2000**, *19*, 4506−4517.
(29) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133 (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031−7036. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

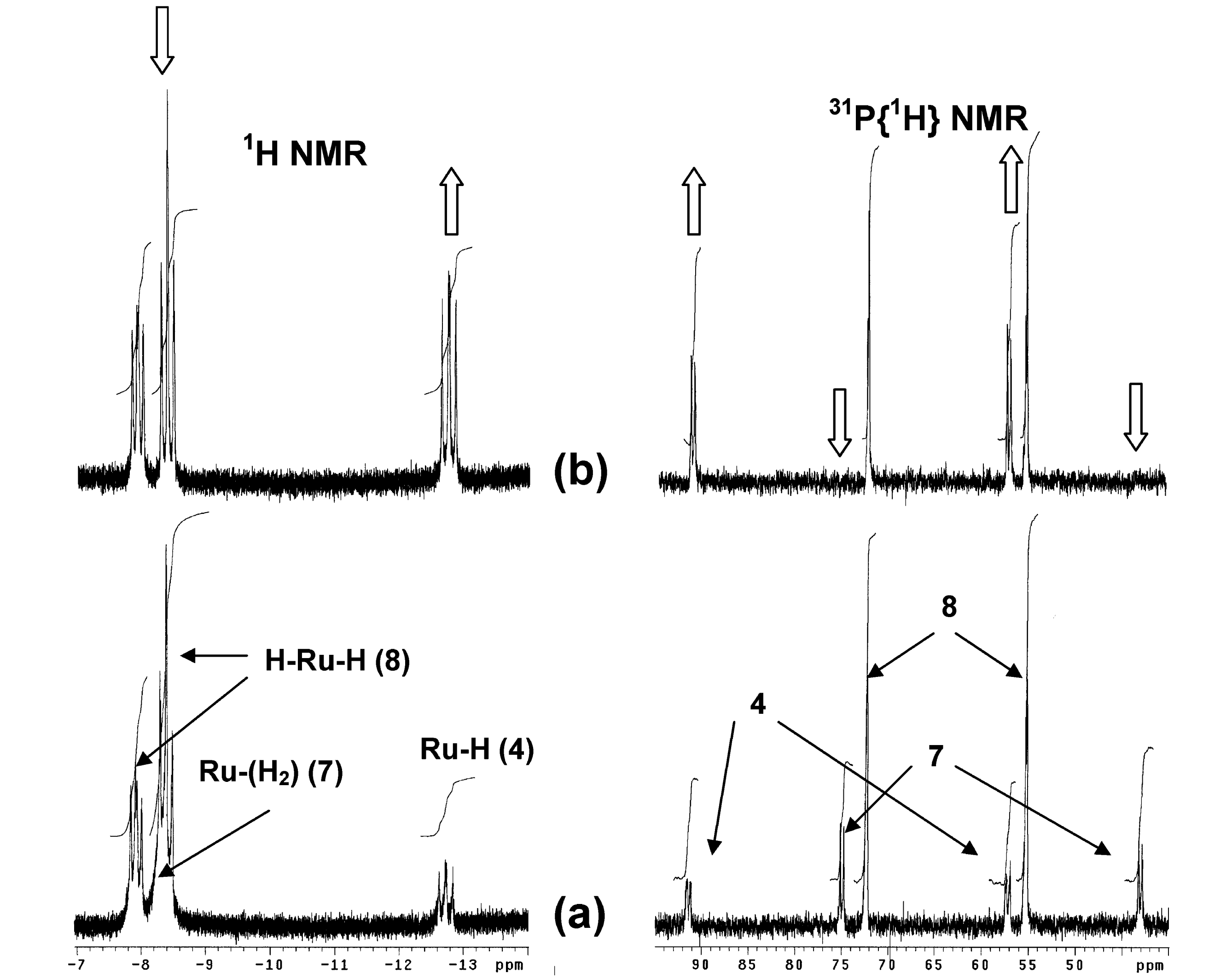


Figure 2. High field ^{1}H and ^{31}P{^{1}H} NMR spectra (acetone-d_6) at -70 °C after the adition of a stoichiometric amount of HBF_4 to **4**, showing the hydride resonances of **4** (starting material), **7** and **8** (products of the protonation). (a) without CF_3CO_2Na. (b) after the adition of this salt. Empty arrows indicate the increase or decrease of the resonance intensities of **4**.CF_3CO_2H and **7**.

Scheme 5

$$\underset{\mathbf{4}}{\mathrm{CpRuH(PP^{Ph}PF)} + \mathrm{HBF_4}} \xrightleftharpoons{-70\ ^\circ\mathrm{C}} \underset{\mathbf{7}}{cis\text{-}[\mathrm{CpRu}(\eta^2\text{-}\mathrm{H_2})(\mathrm{PP^{Ph}PF})]\mathrm{BF_4}} \longrightarrow \underset{\mathbf{8}}{trans\text{-}[\mathrm{CpRuH_2(PP^{Ph}PF)}]\mathrm{BF_4}}$$

resonances and other structural aspects, which will be discussed below, show that **8** is the isomer *trans*-[$CpRuH_2(PP^{Ph}PF)$]BF_4. When the temperature was increased to room temperature, the resonance of **7** practically disappeared and **8** was the major component. This effect is consistent with the expected behavior in the proton transfer to the monohydride **4**, with the formation of a dihydrogen compound under kinetic control (**7**) that evolves irreversibly to the trans isomer, **8**, when the temperature is increased.

On the basis of this information, it can be concluded that the protonation of **4** with HBF_4 is not complete and the reaction sequence reflected in Scheme 5 is established. An estimated value of the equilibrium constant of the process **4** + HBF_4 $\leftrightarrow$ **7**, $K(-70\ °C) = 43.3$ L mol^{-1}, has been evaluated on the basis of the spectrum integrations.

To obtain initial information about the effect that the presence of a weaker acid has on this system, a solution of CF_3CO_2Na in acetone-d_6 (see Experimental Section) was added to this mixture of hydrides at -70 °C (the amount of CF_3CO_2Na was approximately the stoichiometric). After the addition, the resonances due to the nonclassical dihydride **7** disappeared completely in the ^{1}H and ^{31}P NMR spectra increasing those of **4**, whereas the signals of **8** were practically unaffected (See Figure 2). The initial incomplete protonation of **4**, and the complete transformation of **7** to **4** when the counteranion $CF_3CO_2^-$ is added, suggests a relatively high thermodynamic acidity of the H_2 molecule in **7** that can be estimated higher than that of CF_3CO_2H and lower, but close, than the acidity of HBF_4. Although in this description of the deprotonation experiment of **7** with the anion $CF_3CO_2^-$ we have referred to the formation of **4** as the product, in the next section, we will see that **4** is very much associated to the CF_3CO_2H acid resulting

(30) See Jia, G.; Lau, C. P. *J. Organomet. Chem.* **1998**, *565*, 37−48 and references therein.

Scheme 6

$$\underset{\mathbf{4}}{\mathrm{CpRuH(PP^{Ph}PF)}} + \mathrm{CF_3CO_2H} \xrightarrow{-70\ ^{\circ}\mathrm{C}} \underset{\mathbf{9}}{[\mathrm{CpRu(H\cdots HO_2CF_3)(PP^{Ph}PF)}]} + \underset{\mathbf{10}}{trans\text{-}[\mathrm{CpRuH_2(PP^{Ph}PF)}]\mathrm{CF_3CO_2}}$$

from this deprotonation leading to the concatenate (**4**·CF_3CO_2H) we will number as **9** (see below and Scheme 6).

In an effort to better evaluate the effect of CF_3CO_2H in our proton-transfer studies and to analyze the possible role of the counteranion, we used this acid in conjunction with **4** in two different molar ratios.

2. Proton Transfer with a Stoichiometric Amount of CF_3CO_2H. Proton-Hydride Exchange. When a stoichiometric amount of the acid was used at −70 °C, new hydride resonances, similar to those of **8**, appeared in the ^{1}H NMR spectrum. It seems reasonable that these new signals correspond to the *trans*-dihydride with CF_3CO_2 as a counteranion, i.e., *trans*-[CpRuH$_2$-(PPh^{Ph}PF)]CF_3CO_2, **10**. In addition, other resonances were observed due to a new product, **9**, and these appeared to be similar to those of the starting monohydride **4**. A signal due to the proton of the acid (around 4 ppm) was also observed. In Scheme 6, the products formed in this proton transfer are indicated. As the temperature was increased, only the resonances of the acid proton and the hydride of **9** broadened, whereas those of **10** remained sharp (see Figure 3). The broadening of these two resonances is reversible and when the temperature was decreased they became sharp. As expected, an increase in the intensity of the resonances of the dihydride **10** was also observed when the temperature was raised.

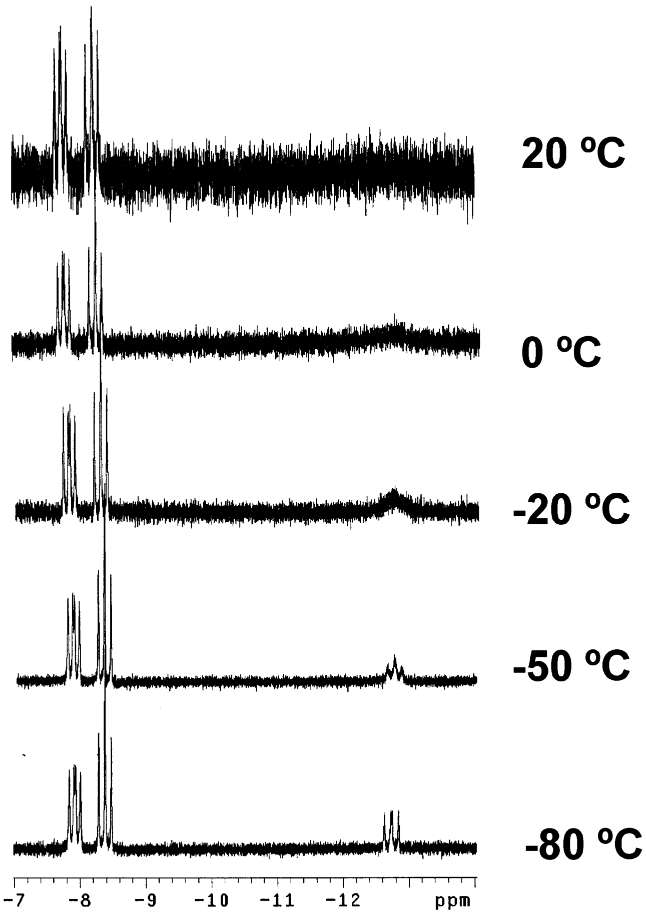


Figure 3. Variable temperature ^{1}H NMR study in the high field region after the addition of a stoichiometric amount of CF_3CO_2H to **4**, showing the hydride resonances of the products of protonation **9** and **10**.

The reversible broadening of the resonances of the acid and the hydride of **9** suggests the existence of a proton-hydride exchange. The participation of **10** in this exchange can be ruled out and its formation seems to be irreversible. The exchanging resonances in the spectrum are too far apart (about 5000 Hertz) to observe clearly a state of coalescence. However, an approximate value of 57 kJ/mol at 0 °C for the free energy of activation for this exchange can be estimated from the broadening of the resonances.[31] Although the aforementioned protium−deuterium exchange observed in the hydride group of **4** in methanol-d_4 clearly has a lower rate, it could follow a similar mechanism.

As far as the mechanism of the proton-hydride exchange observed in our system is concerned, the most reasonable explanation would be the participation of a dihydrogen complex as an intermediate. However, the chemical shift and J_{HP} coupling constants of the monohydride **9** remained practically unchanged when the temperature was raised. This allows us to rule out a rapid equilibrium between **9** and a significant amount of the *cis*-dihydrogen compound (the δ value of this dihydrogen complex should be very similar to that of **7** and differs from that found in **9**). However, the participation of a dihydrogen complex as a short-living intermediate cannot be excluded. It is necessary to consider that in some cases where dihydrogen bonds have been found, a parallel process of proton-hydride exchange has also been observed.[32] The formation of a dihydrogen bond could not alter the δ value of the starting hydride[32a,33] but an additional relaxation would be expected.

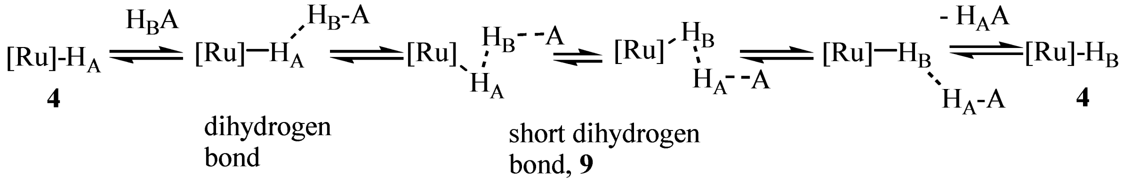
In our case, the T_1(min) for the hydride of complex **4** before the addition of the acid was calculated to be 188 ms at 209 K, whereas after the addition of CF_3CO_2H, that is in **9**, the value was reduced to 49 ms at 234 K. The T_1 values for the proton resonance of the acid (at about 4 ppm) are similar to those of the hydride of **9** at each temperature. This situation is a consequence of the proton-hydride exchange described above.

(31) To calculate this value, k was previously estimated according with $k = \pi W$, being W the broadening in excess of the natural line width and then the activation free energy was calculated with the following equation: $\Delta G_{T\ddagger} = aT[10.319 + \log(T/k)]$ ($a = 1.914 \times 10^{-2}$). Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(32) (a) Caballero, A.; Jalón, F. A.; Manzano, B. R. *Chem. Commun.* **1998**, 1879−1880. (b) Ayllón, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B., Clot, E. *Organometallics* **1999**, *18*, 3981−3900. (c) Lee, J. C Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11 014−11 019.

(33) (a) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105−1112. (b) Belkova, N. V.; Ionidis, A. V.; Epstein, L. M.; Shubina, E. S.; Gruendemann, S.; Golubev, N. S.; Limbach, H.-H. *Eur. J. Inorg. Chem.* **2001**, 1753−1761.

Scheme 7



[Ru] = CpRu(PP^{Ph}PF)
A = $CF_3CO_2^-$

Scheme 8

$$\mathrm{CpRuH(PP^*) + exc.\ CF_3CO_2H} \xrightarrow{-80°\mathrm{C\ or\ r.t.}} \textit{trans}\text{-}\mathrm{[CpRuH_2(PP^*)]CF_3CO_2}$$

PP* = PP^{Ph}PF, **10**; (S_c,S_p)-P^{Cy}P^{Ph}PF, **11**; (S_c,S_p)-P^{ip}P^{Ph}PF, **12**

In contrast, the value for the dihydride **10** does not change in the presence of free CF_3CO_2H acid (320 ms at 243 K).

As stated in the previous section, **4** was present in the solution, as a minor product, after a slight excess of HBF_4 was added and is apparently regenerated from **7** when CF_3CO_2Na was added. However, the T_1(min) calculated for **4** in the presence of the residual H^+ and after the addition of the CF_3CO_2 salt is 45 ms, a value similar to that of **9** and clearly lower than the value found for **4** before the addition of the salt. We propose that the observed excess of relaxation is due not only to the presence of H^+ but mainly to the association of **4** with CF_3CO_2H to form **9** as it is indicated in Scheme 6. According to the approximate method described by Morris,[29] the additional relaxation found for **9** supposes that the average proton-hydride distance is 1.43 Å. This value is substantially lower than that normally expected for a dihydrogen bond (around a minimum of 1.70 Å) and higher than that in a dihydrogen compound (1.13 Å in **8**). Short proton-hydride bonds of about 1.50 Å have been theoretically calculated[5a,32b] and theoretical studies have also suggested that in "CpRu" systems strong dihydrogen bonds can be formed depending on the donor character of the acid.[5a] However, to the best of our knowledge, these species with short proton-hydride interactions have never been found previously and complex **9** represents the first example. This system could be considered as a step, described here for the first time, in the proton-transfer process, e.g., an intermediate state between a dihydrogen bond and a coordinated dihydrogen molecule. In this system, the counteranion $CF_3CO_2^-$ could change between the two hydrogen atoms of the dihydrogen bond, thus changing the nature of both in the way represented in Scheme 7, which explains the observed proton-hydride exchange. In this way, this extremely short dihydrogen bond behaves as a dihydrogen molecule polarized by the counteranion. Such a term has been proposed previously but was not experimentally demonstrated by Norton[34] to explain the proton-hydride exchange in one dihydrogen-bonded complex.[32b]

Shubina and Limbach[33b] demonstrated the existence of a hydrogen-bonded ion-pair adduct in the complex CpRu(CO)L-(η^2-H_2)···CF_3CO_2. In contrast with our system, in this example the properties of a nonclassical dihydrogen compound were preserved. Chaudret and Crabtree et al.[35] described pronounced hydride relaxation in Cp′RuH(PPh_3)$_2$ complexes when weak acids are present. As in **9**, evidence for the existence of a proton-hydride interaction was observed in these systems. However, in these examples the proton-hydride exchange was not observed. The T_1(min) measured for one of these complexes was too short to be attributed solely to a dipole−dipole relaxation and other ancillary groups of the complex were also relaxed. A dependence of the relaxation with the concentration of the acid was also observed for one of the complexes. In our opinion, the behavior of **9**, although probably related with the observations of these authors, offers more information about the chemical characteristics of strong dihydrogen bonds.

If we consider the final steps in Scheme 7, the liberated free acid (HA) could attack at the trans position in the monohydride **4** and give the trans isomer **10**. This path would explain the observed transformation of **9** into **10** when the temperature was raised. However, the participation of a dihydrogen complex in equilibrium with **9** as a transient in the proton-hydride exchange, as previously stated, and also responsive of the cis to trans isomerization cannot be excluded.

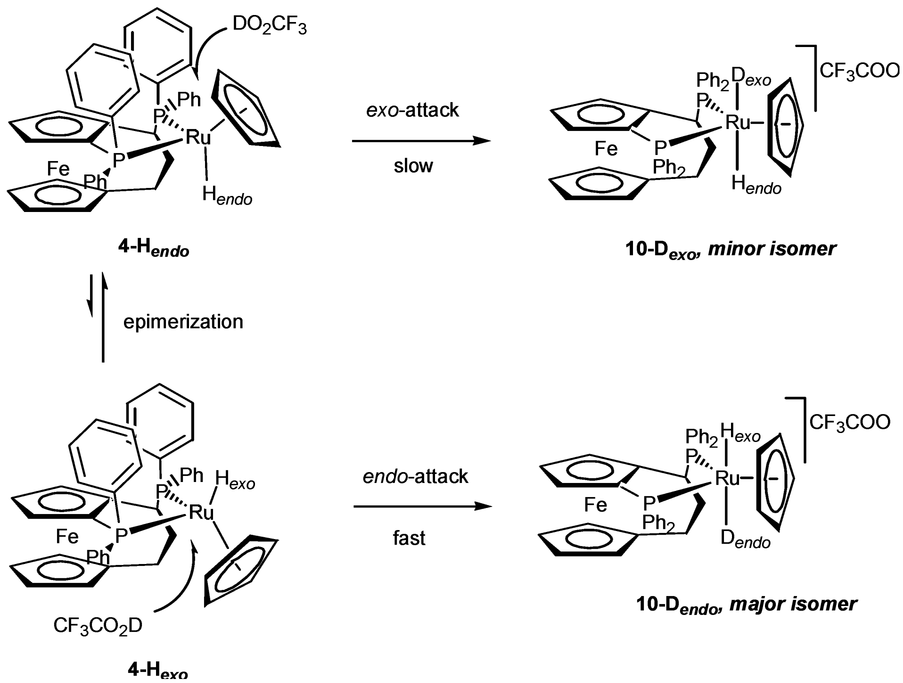
3. Proton Transfer with an Excess of CF_3CO_2H or CF_3CO_2D. Synthesis of Complexes 10−13. Stereoselectivity of the Process. It has been reported that a higher concentration of the acid CF_3CO_2H increases its acidity due to the formation of homoconjugated pairs[5c] and that an increase in the concentration accelerates the proton-transfer process.[7] Given this information, we decided to analyze the results of the proton transfer when an excess of this acid was used. An acid:complex ratio of 3:1 was used in the protonation of the monohydrides **4**−**6**. The only products from these reactions, both at −80 °C and at room temperature, were the trans-dihydride derivatives represented in Scheme 8.

Such species have not been isolated but have been characterized by ^{1}H and ^{31}P NMR spectroscopy. In accordance with the asymmetric environment, these complexes show two different resonances both for the phosphorus atoms and for the two hydrides. The two hydride resonances of each complex differ

(34) Papish, E. T.; Magee, M. P., Norton, J. R. in *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Ed.; Elsevier: Amsterdam, **2001**, 45.

(35) Castellanos, A.; Ayllón, J. A.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B.; Yao, W. B.; Kavallieratos, K.; Crabtree, R. H. *C. R. Acad. Sci. Ser. II C*, **1999**, *2*, 359−368.

Chart 4



slightly in their chemical shifts and are markedly different to those of the corresponding starting monohydrides (see Experimental Section). As expected for these types of complexes, the $^2J_{HP}$ coupling constants of the hydrides are slightly smaller that those of the monohydrides. The same is true for $^2J_{PP}$, which decreases to very small values. The $^2J_{HH}$ values are practically zero and are undetectable in the spectra.

We assigned both the phosphorus (P_A and P_B) and the hydride resonances (H_{exo} and H_{endo}) for **10**−**12** (see Experimental Section) using an analogous procedure to that described for the monohydrides **4**−**6**. The nOe experiments were found to be of special value in this respect. As a representative example, the main nOe's observed for **10** are shown in Chart 3b.

The formation of the trans isomers **10**−**12** as the only species does not exclude a possible prior attack at the Ru−H bond, as occurred when a stoichiometric amount of the acid was used. However, comparing the results when a stoichiometric amount or an excess of the acid was used, a clear increase in the formation rate of the *trans*-dihydrides was observed in the latter case.

To obtain information about the stereochemistry of the proton-transfer process we carried out an identical reaction with **4**, but in this case CF_3CO_2D was used as the acid (at −70 °C). It can be seen from Figure 4a that the deuterium is selectively incorporated in the endo position to give **10-D$_{endo}$**. Surprisingly, this is the position where the hydride was situated in the starting complex **4** and, as a consequence, a simple trans-attack does not explain this result. A cis-attack, with the subsequent formation of a dihydrogen intermediate, followed by a very selective deuterium/protium migration could explain this result, although such an isotopic effect is unexpected.

An isotopic redistribution at −70 °C is not apparent (identical integrations were obtained after 1 h). However, when the temperature was raised to 25 °C the isotopic populations slowly equilibrated (see Figure 4b). This redistribution of isotopes follows an apparent first-order Arrhenius plot ($k = 2.1 \times 10^{-3}$ s^{-1}).

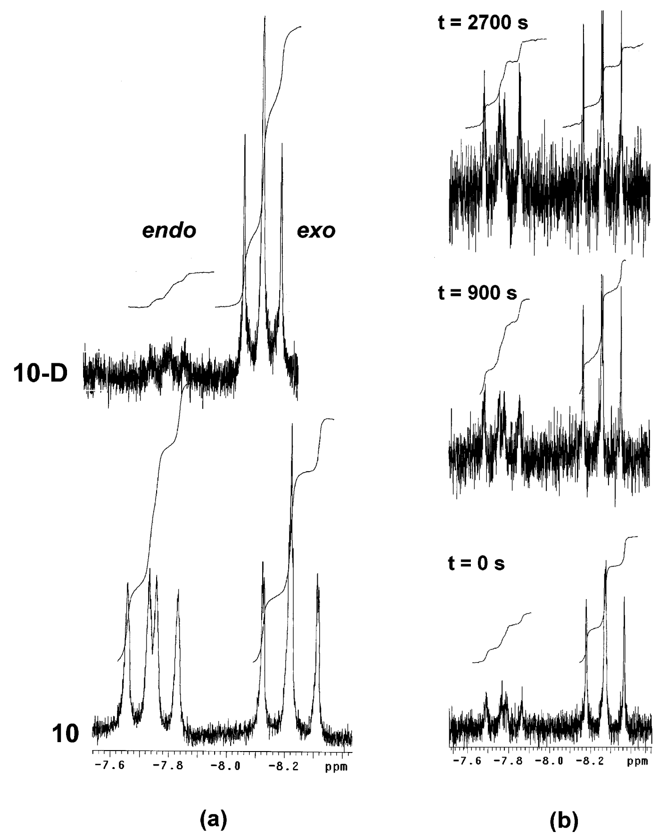


Figure 4. (a) High field ^{1}H NMR spectrum of **10** (*down*) and **10-D** (*up*) at −70 °C showing a selective distribution of deuterium in the *endo*-hydride position of **10-D**. (b) evolution of the isotopic distribution (protium-deuterium) in **10-D** at 25 °C as a function of time (seconds).

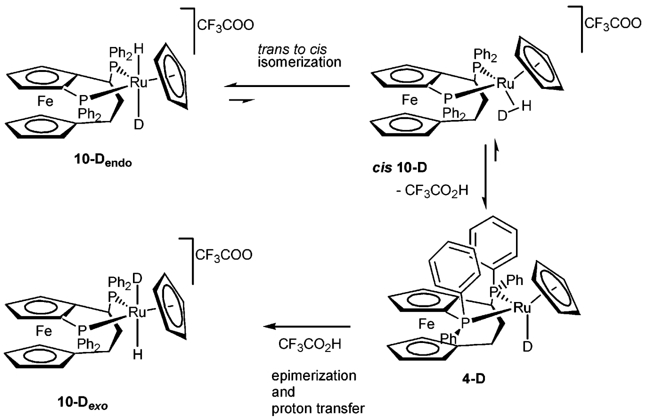
To understand this selective attack, we propose the mechanism depicted in Chart 4. First, complex **4** must be in epimerization equilibrium with the *exo*-hydride isomer. As stated previously, we have demonstrated the existence of an epimerization equilibrium for **6**. The CF_3CO_2H would play the same

Scheme 9

$$trans\text{-}[CpRuH_2(PP^{Ph}PF)]CF_3CO_2 \underset{}{\rightleftharpoons} cis\text{-}[CpRu(\eta^2\text{-}H_2)(PP^{Ph}PF)]CF_3CO_2 \longrightarrow CpRu(CF_3CO_2)(PP^{Ph}PF) + H_2$$

9 → **13**

Chart 5



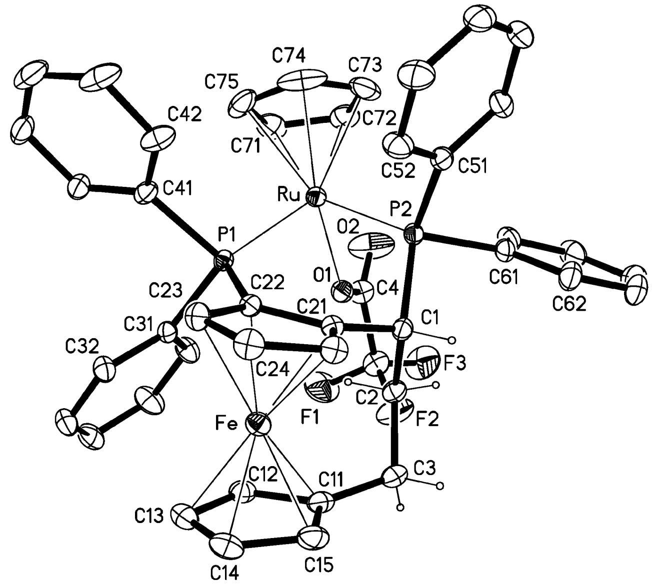


Figure 5. Molecular structure of complex **13** in the crystalline state showing 20% thermal ellipsoids. Hydrogen atoms of the aromatic rings have been omitted for clarity. Only the S_{Ru},R_c,R_p enantiomer is represented.

role in **4** as CD_3OD did in **6**. The latter isomer could be a minor species that is not observed in the NMR spectra. The observed selectivity can be explained if we consider that the proton transfer must follow a *trans*-attack that is substantially more rapid for the exo than for the endo-epimer.

As stated previously, both in the solid state and in solution, **4** presents an endo orientation of the hydride ligand. It is noteworthy that in this epimer the region trans to the hydride is blocked by two phenyl rings of the PPh_2 groups (see Figure 1). Such a situation could make this position less prone to undergo attack by the acid, the difficulty being maximized by the low dissociation degree of the acid and the possible formation of the homoconjugated pairs: $[CF_3CO_2H]_2$.[36]

The isotope redistribution with temperature can be explained by proposing that the proton transfer reaction is reversible, but this would imply that the cationic trans dihydride **10** should be sufficiently acidic when compared with CF_3CO_2H; a situation that is very unlikely. Another possible pathway would involve the existence of a reversible trans to cis isomerization for **10**, as indicated in Chart 5. In this way, the formation of a cis form of **10-D** (dihydrogen compound) would open the door to a deprotonation that would regenerate the monohydride **4** (**4-D** in the chart). A new epimerization and proton-transfer process could then convert **4-D** into the isotopomer of the starting *trans*-dihydride, e.g., to **10-D$_{exo}$**.

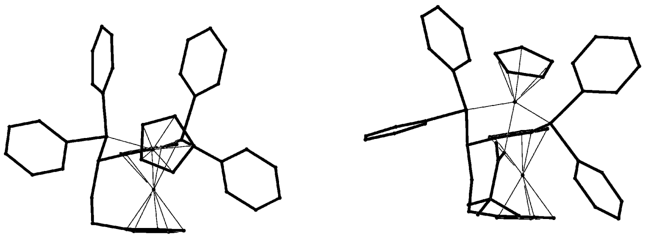
The possible existence of the trans to cis isomerization equilibrium described above was supported by an additional and fortuitous experience. Although the trans dihydride complex **10** appears to be stable in acetone-d_6, when this solution was used to obtain crystals of this complex a new complex of formula $CpRu(CF_3CO_2)(PP^{Ph}PF)$, **13**, was obtained. This can be explained by the reaction indicated in Scheme 9, and confirms the existence of the trans to cis transformation.

Complex **13** was characterized by X-ray diffraction and NMR spectroscopy. To the best of our knowledge the cis to trans transformation of these systems has always been considered as being irreversible. Our results, however, clearly support a situation where, although shifted to the trans form, the cis and trans isomers are in a slow equilibrium.

The results obtained when excess of CF_3CO_2H (or CF_3CO_2D) was used as the acid agent in the transference appear to support a single *trans*-attack − a process in marked contrast to the normally accepted *cis*-attack for these sorts of reactions under kinetic control and also with our results using HBF_4 as the acid. However, on considering all of our results, it would be possible the initial participation of a species with a cis contact, but labile enough not to allow the proton-hydride exchange. Otherwise, the selective attack of the CF_3CO_2D would not be possible. Probably, the increase in the acidity and in the rate of the proton transfer when an excess of acid is used (due to the formation of homoconjugated pairs) makes this transfer occur finally through a trans attack.

D. X-ray Structure of 13. The structure determination of **13** revealed it crystallized as a racemic in the triclinic $P\bar{1}$ space group. Ru shows the usual three-legged piano stool coordination with two P atoms of the PP-ligand and a weakly bonded O from the CF_3COO group (See Figure 5). The CF_3COO group exhibits usual dimensions; it shows relatively large thermal motion parameters for its free oxygen atom O(2) and for the CF_3 group. Tables 1 and 2 compiles the main crystallographic and structural data. The Ru−Fe-complex differs distinctly in conformation from the corresponding to **4**. Whereas in **13**, the Cp rings of

(36) The formation of such sort of homoconjugated pairs has been observed in secondary amines and alcohols: (a) Castaneda, J. P.; Denisov, G. S.; Shreiber, V. M. *J. Mol. Structure* **2001**, *560*, 151. (b) Drichko, N. V.; Kerenskaya, G. I.; Shreiber, V. M. *Chem. Phys. Lett.* **1999**, *304*, 73. (c) Yuchnevich, G. V.; Tarakanova, E. G.; Maiorov, V. D.; Librovich, N. B. *J. Mol. Structure* **1992**, *265*, 237.



4 13

Figure 6. Wire Frame representation of complexes **4** and **13** exhibiting the elevation of the $CpRu(O_2CCF_3)$ fragment in the last and the consequent opening of the trans position to the Ru−X bond.

Ru and ferrocene are mutually inclined by about 45°, they are inclined in **4** by about 90°. This contrasting rearrangement is probably due to the different steric requirements of the hydride (**4**) and the CF_3CO_2 anion (**13**) and this last pushes away the ferrocenyl moiety to liberate a part of the steric hindrance. As a consequence, in **13** when compared with **4**, both the P−C(Cp) and P−C(chain) bonds turn elevating the $CpRuO_2CCF_3$ unit over the ferrocenyl group which separates the two phenyl groups that blocked the *trans*-hydride position in **4** (Figure 6).

Conclusions

Organometallic compounds with three stereogenic centers of formula CpRuX(PP*) (X = Cl, H) bearing enantiomericaly pure or racemic ferrocenyldiphosphine ligands (PP*) have been prepared. In five of the isolated complexes only one diastereomer was observed by NMR spectroscopy. This diastereomer is very probably, as unambiguously demonstrated in the case of **4**, the X-*endo* form. The product of the proton-transfer reactions of the monohydrides was dependent on the acid used, its concentration and the temperature. When HBF_4 was used with $CpRuH(PP^{Ph}PF)$, **4**, the expected cis isomer (nonclassical dihydride) was obtained by kinetic control. This isomer evolved slowly into the trans isomer when the temperature was increased. In contrast, when CF_3CO_2H was used the cis isomer was not observed because it is more acidic than the transfer agent. When an acid:complex ratio of 1:1 was used, a new derivative, $[CpRu(H\cdots HO_2CCF_3)(PP^{Ph}PF)]BF_4$ **9**, with an extremely short dihydrogen bond was formed. Complex **9** represents a new and previously unreported step in the proton-transfer process to transition metal hydrides. A fast and reversible proton-hydride exchange is one of the most relevant properties of this hydrogen bond. This short hydrogen bond is reminiscent of the term introduced by Norton of a coordinated dihydrogen molecule polarized by the counteranion ($CF_3CO_2^-$ in our case). This original species evolved to the trans isomer. For this evolution, we propose a first step involving rupture of the dihydrogen bond that regenerates the monohydride **4** and subsequent trans attack of the liberated acid, although the participation of a dihydrogen complex in equilibrium with **9** as a transient in the proton-hydride exchange cannot be excluded. Using CF_3CO_2D in excess, we have demonstrated that the trans-attack is stereoselective into the endo position of the complex, probably due to steric protection of the exo region of the complex. Because this position is occupied by the hydride in the starting complex, an epimerization of the monohydride **4** is necessary before the trans attack takes place. The feasibility of such epimerization has been demonstrated for **6**. The *trans*-dihydride, *trans*-$[CpRuH_2(PP^{Ph}PF)]CF_3CO_2$ (classical species), **10**, can be considered as thermodynamically stable although it is noteworthy that a slow transformation into $CpRu(CF_3CO_2)(PP^{Ph}PF)$, **13**, suggest that a trans to cis transformation is also possible.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer 2400 CHN microanalyzer. IR spectra were recorded as Nujol mulls on a Perkin-Elmer PE 883 IR spectrometer (*w* = weak). Mass spectra were recorded on a Finnigan MAT 8230 spectrometer (EI). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Chromatographic separations were performed under gravity either on silica gel (Merck, 40−62μ) on alumina (Merck, activity II−III, 0.063−0.200 mm). Petroleum ether with a boiling range of 55−65 °C was used for chromatography. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 300 spectrometer. See Chart 1 for numbering scheme. Chemical shifts (ppm) are relative to TMS (^1H, ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR) (s = singlet, d = doublet, t = triplet, pq = apparent quartet, pt = apparent triplet, m = multiplet). Unless specified otherwise, the ^{13}C resonances are singlets. ^{13}C information is included into the Supporting Information. COSY spectra: standard pulse sequence, acquisition time 0.214 s, pulse width 10 μs, relaxation delay 1 s, 16 scans, 512 increments. The nOe difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, and irradiation power 5−10 dB. For the variable temperature spectra, the temperature of the probe (±1 K) was controlled by a standard unit calibrated with a methanol reference. T_1 values were obtained on the basis of the inversion recovery method. $CpRuCl(PPh_3)_2$ [37] and the racemic ligand $PP^{Ph}PF$,[8a] were prepared according to literature methods. This last was used as racemic to improve the crystallization of the complexes. HBF_4, CF_3CO_2H, and CF_3CO_2D were used as supplied from Aldrich.

Preparation of (S_c,S_p)-1-Dicyclohexylphosphino-2,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene, (S_c,S_p)-P^{Cy}APF. In a 150-mL Schlenk tube, a 2-g portion (7.43 mmol) of (*S*)-1,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene[8b] ($[\alpha]_D^{20}$ = −32°, (*c* = 1, MeOH)) was dissolved under argon in 45 mL of dry diethyl ether. To the degassed solution, 5.1 mL of *n*-butyllithium (8.2 mmol, 1.6 M in hexane) was added dropwise. After being stirred for 16 h at room temperature, 1.8 mL (8.2 mmol) of chlorodicyclohexylphosphine was added dropwise at 0 °C, and the mixture was stirred for additional 24 h at room temperature. The reaction mixture was quenched at 0 °C with 30 mL of saturated aqueous $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (4 × 30 mL). The combined organic layers were washed with 60 mL of brine and dried with $MgSO_4$, the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (40−63 μm, eluent: $CHCl_3/CH_3OH$ 8/2) followed by a chromatography on alumina under argon (eluent: petroleum ether/Et_2NH 99/1). Yield: 1.106 g (2.38 mmol, 32%). Anal. Calcd for $C_{27}H_{40}FeNP$: C, 69.67; H, 8.66; N, 3.01. Found: C, 69.65; H, 8.63; N, 3.06. MS (EI 140 °C) *m*/*z* (rel%): 465 (86, M^+), 422 (38), 339 (47), 257 (100). $[\alpha]_\lambda^{20}$: +64.0 (589 nm), +77.4 (578 nm), +163 (546 nm), (*c* = 0.5, $CHCl_3$). ^1H NMR (300 MHz, chloroform-*d*): δ 4.10, 4.01, 3.99, 3.94, 3.92, 3.87, 3.85 (s, 1H, *Cp*Fe), 2.90 (pq, 1H, $H^{2''ax}$), 2.2 (s, 6H, $N(CH_3)_2$), 2.60−0.92 (m, Cy + protons of the interannular chain). $^{31}P\{^1H\}$ NMR (121 MHz, chloroform-*d*): δ −1.16 (s).

Preparation of (S_c,S_p)-1-Diisopropylphosphino-2,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene, (S_c,S_p)-P^{ip}APF. In a 150 mL Schlenk tube was dissolved under argon 1.4 g (5.22 mmol) of (*S*)-1,1′-[1-(*N*,*N*-dimethylamino)-1,3-propanediyl]-ferrocene[8b] ($[\alpha]_D^{20}$ =

(37) Bruce, M. I.; Hameister, C.; Swinger, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.

−32°, (c = 1, MeOH)) in 35 mL of dry diethyl ether. To the degassed solution was added dropwise 4.1 mL of *n*-butyllithium (6.56 mmol, 1.6 M in hexane). After stirring for 16 h at room temperature 1.2 mL (7.54 mmol) of chlorodiisopropylphosphine was added dropwise at 0 °C and the mixture was stirred for additional 24 h at room temperature. The reaction mixture was quenched at 0 °C with 30 mL of saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with diethyl ether (4 × 30 mL). The combined organic layers were washed with 60 mL of brine and dried with $MgSO_4$, the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (40−63 μm, eluent: $CHCl_3/CH_3OH$ 8/2) followed by a chromatography on alumina under argon (eluent: petroleum ether/Et_2NH 99/1). Yield. 1.065 g (2.77 mmol, 53%). Anal. Calcd for $C_{21}H_{32}FeNP$: C, 65.46; H, 8.37; N, 3.64. Found: C, 69.89; H, 8.67; N, 3.60. MS (EI 60 °C) *m/z* (rel%): 385 (99, M^+), 342 (62), 299 (99), 257 (80). $[\alpha]_\lambda^{20}$: +63.9 (589 nm), +77.9 (578 nm), +169 (546 nm), (c = 0.5, $CHCl_3$). ^1H NMR (300 MHz, chloroform-*d*): δ 4.10, 4.02, 4.00, 3.97, 3.95 (s, 1H, *Cp*Fe), 3.90 (s, 2H, *Cp*Fe), 3.05 (pq, 1H, $H^{2''ax}$), 2.61 (dd, 1H, $H^{1''ax}$), 2.30 (m, 1H, $H^{2''eq}$), 2.30 (dd, 1H, $H^{3''eq}$), 1.85 (pt, 1H, $H^{3''ax}$), 2.15 (s, 6H, N(CH_3)$_2$), 2.20−2.10 (m, 2H, C*H*(CH_3)$_2$), 1.40 (dd, 3H, CH(CH_3)$_2$), 1.20−1.10 (m, 6H, CH(CH_3)$_2$), 0.95 (m, 3H, CH(CH_3)$_2$). ^{31}P {^1H} NMR (121 MHz, chloroform-*d*): δ −1.12 (s).

Preparation of (S_c,S_p)-1-Dicyclohexylphosphino-2,1'-(1-diphenylphosphino propanediyl)-ferrocene, (S_c,S_p)-$P^{Cy}P^{Ph}$PF. To a degassed solution of (+)-(S_c,S_p)-aminophosphine P^{Cy}APF (0.650 g, 1.40 mmol) in freshly distilled acetic acid (12 mL) was added diphenylphosphine (0.35 mL, 2 mmol). The solution was stirred at 100 °C for 16 h. The reaction mixture was cooled to room temperature and CH_2Cl_2 (15 mL) and saturated $NaHCO_3$ solution (20 mL) were added (vigorous evolution of CO_2). The organic layer was separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed until neutral with saturated $NaHCO_3$ solution and water and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by chromatography on alumina (eluent: petroleum ether followed by petroleum ether/$CHCl_3$ 8/2). Yield: 0.348 g (0.57 mmol, 41%). Anal. Calcd for $C_{37}H_{44}FeP_2$: C, 73.27; H, 7.31. Found: C, 73.38; H, 7.20. MS (EI 140 °C) *m/z* (rel%): 606 (100, M^+), 523 (68), 440 (10), 255 (19). $[\alpha]_\lambda^{20}$: −105 (589 nm), −87.8 (578 nm), +22.2 (546 nm), (c = 0.5, $CHCl_3$). ^1H NMR (300 MHz, chloroform-*d*): δ 7.62−7.10 (m, 10H, Ph), 3.98 (s, 2H, *Cp*Fe), 4.05, 4.01, 3.95, 3.90, 3.80 (s, 1H, *Cp*Fe), 2.90 (pq, 1H, $H^{2''ax}$), 2.65 (dd, 1H, $H^{1''ax}$), 2.40 (m, 1H, $H^{2''eq}$), 2.35 (dd, 1H, $H^{3''eq}$), 2.00−0.85 (m, 23H, Cy + $H^{3''ax}$). ^{31}P {^1H} NMR (121 MHz, chloroform-*d*): δ −5.54, −6.25 (AB, J_{PP} = 43.1 Hz).

Preparation of (S_c,S_p)-1-Diisopropylphosphino-2,1'-(1-diphenylphosphino propanediyl)-ferrocene, (S_c,S_p)-$P^{ip}P^{Ph}$PF. The preparation procedure followed exactly that of diphosphine (S_c,S_p)-$P^{Cy}P^{Ph}$PF. The following amounts were used: (+)-(S_c,S_p)-aminophosphine, P^{ip}-APF, (0.673 g, 1.75 mmol), acetic acid (15 mL), diphenylphosphine (0.4 mL, 2.3 mmol). Yield: 0.471 g (0.89 mmol, 51%). Anal. Calcd for $C_{31}H_{36}FeP_2$: C, 70.73; H, 6.89. Found: C, 70.56; H, 6.65. MS (EI 140 °C) *m/z* (rel%): 526 (5, M^+), 483 (100), 440 (47), 255 (63). $[\alpha]_\lambda^{20}$:−43.9 (589 nm), −33.0 (578 nm), +40.1 (546 nm), (c = 0.5, $CHCl_3$). ^1H NMR (300 MHz, chloroform-*d*): δ 7.6−7.1 (m, 10H, Ph), 4.03, 4.01, 3.95, 3.92, 3.89, 3.87, 3.86 (s, 1H, *Cp*Fe), 2.95 (pq, 1H, $H^{2''ax}$), 2.60 (dd, 1H, $H^{1''ax}$), 2.30 and 2.05 (m, 1H, $H^{3''eq}$ and $H^{2''eq}$), 1.60 (pt, 1H, $H^{3''ax}$), 1.5 (dd, 3H, CH(CH_3)$_2$, 1.45−1.23 (m, 6H, CH(CH_3)$_2$), 1.60 (m, 2H, C*H*(CH_3)$_2$), 0.85 (pt, 3H, CH(CH_3)$_2$). ^{31}P {^1H} NMR (121 MHz, chloroform-*d*): δ −5.15 (d, J_{PP} = 45.7 Hz, *P*Ph$_2$), −13.6 (d, P^iPr_2).

Preparation of CpRuCl(PP^{Ph}PF) 1, CpRuCl((S_c,S_p)-$P^{Cy}P^{Ph}$PF) 2 and CpRuCl((S_c,S_p)-$P^{ip}P^{Ph}$PF) 3. Complexes **1**−**3** were prepared following a similar method. As a representative example, complex **1** was prepared as follows: a sample of CpRuCl(PPh_3)$_2$ (72.5 mg, 0.1 mmol) was dissolved in 12 mL of toluene. Another solution of PP^{Ph}PF (65.3 mg, 0.11 mmol) in 8 mL of toluene was added to the first solution. The reaction mixture was heated at 95−105 °C with continuous stirring for 13 h. The solution was evaporated to dryness and the resulting solid was passed through a chromatography column filled with alumina. Toluene was used as the first eluent and PPh_3 was removed as a colorless solution. An orange solution of complex **1** was obtained when THF was used as eluent. The solvent was evaporated to dryness and **1** was isolated as an orange powder. Yield: 67.7 mg (0.085 mmol, 88%. For **2**, the amounts were as follows: CpRuCl(PPh_3)$_2$ (435 mg, 0.59 mmol), (S_c,S_p)-$P^{Cy}P^{Ph}$PF (350 mg, 0.60 mmol). An orange product was obtained. Yield: 391 mg (0.48 mmol, 82%). For **3**, the amounts were as follows: CpRuCl(PPh_3)$_2$ (536 mg, 0.74 mmol), (S_c,S_p)-$P^{ip}P^{Ph}$PF (450 mg, 0.78 mmol). An orange product was obtained. Yield: 458 mg (0.63 mg, 85%). **1**: Anal. Calcd for $C_{42}H_{37}ClFeP_2Ru$: C, 63.55; H, 4.52. Found: C, 63.59; H, 4.63. IR (cm^{-1}) 286 (w, ν(Ru−Cl)). ^1H NMR (300 MHz, chloroform-*d*): δ 8.8−6.7 (m, 20H, Ph), ortho protons assigned: 8.15 (m, 2H, P_APh_{down}), 8.15 (m, 2H, P_APh_{up}), 8.75 (m, 2H, P_BPh_{down}), 6.78 (m, 2H, P_BPh_{up}), 3.98 (s, 5H, *Cp*Ru), 4.43 (s, 1H, *Cp*Fe), 4.35 (s, 1H, *Cp*Fe), 4.31 (s, 1H, *Cp*Fe), 3.99 (s, 1H, *Cp*Fe), 3.87 (s, 1H, *Cp*Fe), 3.17 (s, 1H, *Cp*Fe), 2.21 (s, 1H, *Cp*Fe-$H^{5'}$), 3.15 (t, J_{HP} = 6 Hz, $H^{1''}$), 2.46 (pq, $H^{2''ax}$), 2.20 (m, $H^{2''ec}$), 1.45 (t, $H^{3''ax}$), 1.85 (dd, $H^{3''ec}$). ^{31}P {^1H} (121 MHz, chloroform-*d*): 65.21 (d, J_{PP} = 56.8 Hz, P_APh_2), 35.52 (d, P_BPh_2). **2**: Anal. Calcd for $C_{42}H_{49}ClFeP_2Ru$: C, 62.49; H, 5.95. Found: C, 62.32; H, 5.98. IR (cm^{-1}) 275 (w, ν(Ru−Cl)). ^1H NMR (300 MHz, chloroform-*d*): δ 8.2−7.0 (m, 10H, Ph), ortho protons assigned: 8.16 (m, 2H, P_APh_{down}), 4.52 (s, 5H, *Cp*Ru), 4.43 (m, 2H, *Cp*Fe), 4.29 (m, 2H, *Cp*Fe), 4.07 (m, 2H, *Cp*Fe), 4.04 (s, 1H, *Cp*Fe), 3.15−2.0 (m, 5H, interanular chain), 3.15−0.84 (m, 22H, *Cy*). ^{31}P {^1H} (121 MHz, chloroform-*d*): 62.05 (d, J_{PP} = 54.2 Hz, P_APh_2), 46.28 (d, P_BCy_2). **3**: Anal. Calcd for $C_{36}H_{41}ClFeP_2Ru$: C, 59.46; H, 5.50. Found: C, 59.47; H, 5.46. IR (cm^{-1}) 273 (w, ν(Ru−Cl)). ^1H NMR (300 MHz, chloroform-*d*): δ 8.2−7.0 (m, 10H, Ph), ortho protons assigned: 8.10 (m, 2H, P_APh_{down}), 6.99 (m, 2H, P_APh_{up}), 4.39 (s, 5H, *Cp*Ru), 4.38 (s, 1H, *Cp*Fe), 4.22 (m, 3H, *Cp*Fe), 3.97 (m, 2H, *Cp*Fe), 3.94 (s, 1H, *Cp*Fe), 3.02 (ddd, J_{HP} = 6 Hz, $H^{1''}$), 2.80 (m, 2H, J_{HH} = 7 Hz, C*H*CH_3), 2.70 (m, $H^{2''ax}$), 2.20 (dd, $H^{3''ax}$), 1.35 (m, $H^{2''ec}$), 1.32 (pt, $H^{3''ec}$), 1.66 (dd, J_{H-PB} = 17.0 Hz, 3H, CHCH_3), 1.63 (dd, J_{H-PB} = 17.8 Hz, 3H, CHCH_3), 1.13 (dd, J_{H-PB} = 14,1 Hz, 3H, CHCH_3), 0.34 (dd, J_{H-PB} = 15.1 Hz, 3H, CHCH_3). ^{31}P {^1H} (121 MHz, chloroform-*d*): 62.86 (d, J_{PP} = 54.8 Hz, P_APh_2), 54.34 (d, $P_B{}^iPr_2$).

Preparation of CpRuH(PP^{Ph}PF) 4, CpRuH((S_c,S_p)$P^{Cy}P^{Ph}$PF) 5 and CpRuH((S_c,S_p)$P^{ip}P^{Ph}$PF) 6. Complexes **4**−**6** were prepared by a similar method. As a representative example, complex **4** was prepared as follows: CpRuCl(PP^{Ph}PF) (70 mg, 0.88 mmol) was dissolved in 8 mL of THF. An excess of $LiAlH_4$ (60 mg, 1.58 mmol) was then added. The reaction mixture was stirred for 4 h at room temperature and the solvent was then evaporated to dryness. The resulting solid was extracted with toluene (3 × 10 mL). Degassed water (10 mL) was added to the resulting solution. After separation of the two phases, the organic solvent was evaporated to dryness and **4** was obtained as a pale-yellow solid. Yield: 402 mg (0.528 mmol, 60%). For **5**, the amounts were as follows: CpRuCl($PP^{Cy}P^{Ph}$F) (100 mg, 0.124 mmol), $LiAlH_4$ (60 mg, 1.58 mmol). An orange-yellow product was obtained. Yield: 43 mg (0.056 mmol, 45%). For **6**, the amounts were as follows: CpRuCl-($PP^{ip}P^{Ph}$F) (100 mg, 0.17 mmol), $LiAlH_4$ (70 mg, 1.84 mmol). A pale-yellow product was obtained. Yield: 50 mg (0.071 mmol, 42%). **4**: Anal. Calcd for $C_{42}H_{38}FeP_2Ru$: C, 66.30; H, 4.80. Found: C, 66.15; H, 4.82. IR (cm^{-1}) 1961 (w, ν(Ru−H)). ^1H NMR (300 MHz, acetone-d_6): δ 8.5−6.6 (m, 20H, Ph), ortho protons assigned: 7.89 (m, 2H, P_APh_{down}), 7.78 (m, 2H, P_APh_{up}), 8.45 (m, 2H, P_BPh_{down}), 6.73 (m, 2H, P_BPh_{up}), 4.33 (s, 5H, *Cp*Ru), 4.33 (s, 1H, Cp_{up}Fe), 4.01 (s, 1H, Cp_{up}-Fe), 3.93 (s, 1H, Cp_{up}Fe), 3.92 (s, 1H, Cp_{down}Fe), 3.73 (s, 1H, Cp_{down}-Fe), 3.30 (s, 1H, Cp_{down}Fe), 3.00 (ddd, J_{HP} = 6 Hz, $H^{1''}$), 2.58 (s, 1H, Cp_{down}Fe-$H^{5'}$), 2.58 (pq, $H^{2''ax}$), 2.11 (m, $H^{2''ec}$), 1.65 (t, $H^{3''ax}$), 1.86 (dd, $H^{3''ec}$), −12.75 (dd, 1H, J_{HP} = 34.9, Ru-*H*). ^{31}P {^1H} (121 MHz, acetone-d_6): 91.46 (d, J_{PP} = 50.7 Hz, P_APh_2), 57.71 (d, P_BPh_2). **5**:

Anal. Calcd. for $C_{42}H_{50}FeP_2Ru$: C, 65.27; H, 6.30. Found: C, 64.87; H, 6.33. IR (cm^{-1}) 1989 (w, ν(Ru−H)). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.9−6.9 (m, 10H, Ph), ortho protons assigned: 7.90 (m, 2H, P_APh_{down}), 7.76 (m, 2H, P_APh_{up}), 4.97 (s, 5H, *Cp*Ru), 4.28 (s, 1H, *Cp*Fe), 4.06 (s, 1H, *Cp*Fe), 3.91 (s, 1H, *Cp*Fe), 3.86 (s, 1H, *Cp*Fe), 3.82 (s, 1H, *Cp*Fe), 3.78 (s, 1H, *Cp*Fe), 3.75 (s, 1H, *Cp*Fe), 2.21 (pt, 1H, $H^{1''}$), 2.9−0.9 (m, Cy + protons of the interannular chain), −13.40 (t, J_{HP} = 34.5 Hz, 1H, Ru−*H*). ^{31}P {^{1}H} (121 MHz, benzene-d_6): 90.60 (d, J_{PP} = 41.5 Hz, P_APh_2), 65.49 (d, P_BCy_2). **6**: Anal. Calcd for $C_{36}H_{42}FeP_2$-Ru: C, 62.40; H, 5.90. Found: C, 62.02; H, 5.89. IR (cm^{-1}) 1977 (w, ν(Ru−H)). ^{1}H NMR (300 MHz, acetone-d_6): δ, **6M** 8.2−7.1 (m, 10H, Ph), ortho protons assigned: 8.18 (m, 2H, P_APh_{down}), 7.25 (m, 2H, P_A-Ph_{up}), 4.55 (s, 1H, *Cp*Fe), 4.51 (s, 1H, *Cp*Fe), 4.48 (s, 5H, *Cp*Ru), 4.32 (s, 1H, *Cp*Fe), 4.27 (s, 1H, *Cp*Fe), 4.14 (s, 1H, *Cp*Fe), 4.04 (s, 1H, *Cp*Fe), 4.03 (s, 1H, *Cp*Fe), 2.80 (spt, J_{HH} = 7 Hz, 2H, C*H*Me_2), 2.59 (pt, J_{HP} = 9.0 Hz, $H^{1''}$), 2.56 (m, $H^{2''ax}$), 2.15 (m, $H^{3''ec}$), 1.72 (m, $H^{2''ec}$), 1.75 (dd, J_{HP} = 14 Hz, 3H, CHC*Me₂*), 1.68 (dd, J_{HP} = 14 Hz, 3H, CHC*Me₂*),1.56 (pt, $H^{3''ax}$), 1.20 (dd, J_{HP} = 14 Hz, 3H, CHC*Me₂*), 0.36 (dd, J_{HP} = 14 Hz, 3H, CHC*Me₂*), −13.57 (t, J_{HP} = 34.1 Hz, Ru−*H*). **6m**: 8.2−7.1 (m, 10H, Ph), ortho protons assigned: 7.80 (m, 2H, P_APh_{down}), 4.73 (s, 5H, *Cp*Ru), 4.40 (s, 1H, *Cp*Fe), 4.15 (s, 1H, *Cp*Fe), 4.10 (s, 1H, *Cp*Fe), 4.05 (s, 1H, *Cp*Fe), 3.94 (m, 3H, *Cp*Fe), 3.05 (m, 2H, C*H*Me_2), 1.55 (dd, J_{HP} = 14 Hz, 3H, CH*Me₂*), 1.40 (dd, J_{HP} = 14 Hz, 3H, CH*Me₂*), 0.96 (dd, J_{HP} = 14 Hz, 3H, CH*Me₂*), 0.16 (dd, J_{HP} = 14 Hz, 3H, CH*Me₂*), −14.15 (t, J_{HP} = 34.5 Hz, Ru−*H*). **6M** or **6m**: 3.25 (pt, $H^{1''}$), 2.82 (m, $H^{2''ec}$), 2.10 (dd, $H^{3''ec}$). ^{31}P {^{1}H} (121 MHz, acetone-d_6), **6M** 90.16 (d, J_{PP} = 42.8 Hz, P_APh_2), 71.80 (d, $P_B{}^iPr_2$). **6m**: 84.39 (d, J_{PP} = 42.8 Hz, P_APh_2), 71.80 (d, $P_B{}^iPr_2$).

Formation of *cis*-[CpRu(η^2-H_2)(PP^{Ph}PF)]BF_4 7 and trans-[CpRuH_2-(PP^{Ph}PF)]BF_4 8. The reaction was carried out in an NMR tube at −70 °C. A solution of complex **4** (15 mg, 0.019 mmol) in 0.5 mL of acetone-d_6 was introduced into the NMR tube. The solution was cooled to −70 °C and a stoichiometric amount of a solution of HBF_4 (54% *wt*. in diethyl ether, 2.6 μL, 0.019 mmol) was added. The reaction was monitored by NMR spectroscopy by introducing the tube into the probe, which had been previously cooled to the appropriate temperature. While monitoring the reaction, the temperature was increased and the NMR recorded at 10° intervals. At −70 °C, complex **4** and two other hydride derivatives were present in the solution (see discussion). One of the reaction products is **7**. Another reaction product is **8** and this was practically the only product observed at room temperature (see discussion). The ^{1}H and ^{31}P NMR structural data for **8** are very similar to those described for **10** (see below). **7**: ^{1}H NMR (300 MHz, acetone-d_6, −70 °C): δ 8.5−6.6 (m, 20H, Ph), ortho protons assigned: 8.26 (m, 2H, P_BPh_{down}), 6.47 (m, 2H, P_BPh_{up}), 5.41 (s, 5H, *Cp*Ru), 4.79 (s, 1H, *Cp*Fe), 4.16 (s, 1H, *Cp*Fe), 3.89 (s, 1H, *Cp*Fe), 3.50 (s, 1H, *Cp*Fe), 3.08 (m, $H^{1''}$), 2.81 (s, 1H, Cp_{down}Fe−$H^{5'}$), 2.48 (m, $H^{2''ax}$), 2.05 (m, $H^{2''ec}$), 1.86 (m, $H^{3''ec}$), 1.70 (m, $H^{3''ax}$), −8.3 (bs, Ru−*H*). ^{31}P {^{1}H} (MHz, acetone-d_6, −90 °C): 74.91 (d, J_{PP} = 43.29 Hz, P_APh_2), 43.01 (d, P_BPh_2).

Deprotonation Reaction of 7 at Low Temperature. A comparable experiment to that described in the formation of **7** and **8** was carried out at −70 °C. In this way a solution of **4** (6.6 mg, 8.7 × 10^{-3} mmol) was prepared in 0.5 mL of acetone-d_6. This solution was cooled to −70 °C and a slight excess of a 0.26 M solution of HBF_4.Et_2O in acetone-d_6 (35 μL, 9.1 × 10^{-3} mmol) was added. The tube was introduced in the NMR probe previously cooled at −70 °C and monitored by ^{1}H and ^{31}P NMR. The corresponding resonances of the complexes **4**, **7**, and **8** were observed and their ratio was determined by the relative integrations of the hydride resonances (17:21:62 respectively). This tube was extracted from the NMR probe and introduced in a thermostatized bath at −70 °C. A 0.073 M CF_3CO_2Na solution (100 μL, 7.3 × 10^{-3} mmol) was added into the tube that was introduced again in the NMR probe. According with the relative integrations, the amount of **8** kept practically unchanged whereas **7** completely disappeared in favor of **9** (relative ratio of **9**:**8** = 40:60).

Formation of [CpRu(H···HO_2CCF_3)(PP^{Ph}PF)]BF_4, 9 (short dihydrogen bond). This reaction was carried out in an NMR tube at −70 °C. A solution of complex **4** (15 mg, 0.019 mmol) in 0.5 mL of acetone-d_6 was introduced into the NMR tube. The solution was cooled to −70 °C and a stoichiometric amount of CF_3CO_2H (1.4 μL, 0.019 mmol) was added. The reaction was monitored by NMR spectroscopy by introducing the tube into the probe, which had been cooled to the appropriate temperature. While monitoring the reaction, the temperature was increased and the NMR recorded at 10° intervals. The ^{1}H and ^{31}P NMR data were very similar to those of **4**. ^{1}H NMR (300 MHz, acetone-d_6, −70 °C): several resonances non overlapped with those of complex **10** could be assigned, δ 8.4−6.6 (m, 20H, Ph), ortho protons assigned: 8.35 (m, 2H, P_BPh_{down}), 6.63 (m, 2H, P_BPh_{up}), 4.33 (s, 5H, *Cp*Ru), 4.33 (s, 1H, Cp_{up}Fe), 3.98 (bs, 1H, CF_3CO_2*H*), 3.27 (s, 1H, *Cp*Fe), 3.09 (ddd, J_{HP} = 6 Hz, $H^{1''}$), 2.52 (pq, $H^{2''ax}$), 2.30 (s, 1H, Cp_{down}-Fe−$H^{5'}$), 2.05 (m, $H^{2''ec}$), 1.80 (dd, $H^{3''ec}$), 1.61 (t, $H^{3''ax}$), −12.74 (dd, 1H, J_{HP} = 34.8, Ru−*H*) ^{31}P {^{1}H} (121 MHz, acetone-d_6, −80 °C): 91.14 (d, J_{PP} = 45.2 Hz, P_APh_2), 57.40 (d, P_BPh_2).

Preparation of *trans*-[CpRuH_2(PP^{Ph}PF)]CF_3CO_2 10, *trans*-[CpRuH_2((S_c,S_p)-P^{Cy}P^{Ph}PF)]CF_3CO_2 11 and *trans*-[CpRuH_2((S_c,S_p)-P^{ip}P^{Ph}PF)]CF_3CO_2 12. These reactions were carried out in NMR tubes at −80 °C. The reactions were monitored by NMR spectroscopy by introducing the tubes into the NMR probe, which had been cooled to the appropriate temperature. While monitoring the reaction, the temperature was increased and the NMR spectra recorded at 10° intervals. As a representative example: a sample of 25 mg of **4** (0.033 mmol) was dissolved in 0.5 mL of acetone-d_6 and the solution introduced into an NMR tube, closed and introduced into a thermostatised bath at −80 °C. After several minutes this tube was introduced in a Schlenck porta-tube and then CF_3CO_2H was added (8 μL, 0.1 mmol). The tube was shaken and rapidly introduced in the NMR probe, which had been cooled to −80 °C. The corresponding products were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. **10**: ^{1}H NMR (300 MHz, acetone-d_6): δ 8.8−7.0 (m, 20H, Ph), ortho protons assigned: 8.53 (m, 2H, P_APh), 8.80 (m, 2H, P_BPh_{down}), 6.98 (m, 2H, P_BPh_{up}), 3.99 (s, 5H, CpRu), 4.54 (s, 1H, CpFe), 4.31 (s, 1H, CpFe), 4.24 (s, 1H, CpFe), 4.09 (s, 1H, CpFe), 3.92 (s, 1H, CpFe), 3.09 (s, 1H, CpFe), 3.08 (pq, $H^{2''ax}$), 2.82 (m, $H^{2''ec}$), 1.90 (m, $H^{3''ax}$), −7.75 (dd, J_{H-PA} = 29.5 Hz, J_{H-PB} = 22.0 Hz, 1H, Ru−H), −8.21 (t, J_{H-PA} = 29.5 = J_{H-PB} = 26.9 Hz, 1H, Ru−H). ^{31}P {^{1}H} (121 MHz, acetone-d_6): 73.08 (d, J_{PP} = 7.0 Hz, P_APh_2), 54.47 (d, P_BPh_2). **11**: ^{1}H NMR (300 MHz, acetone-d_6): δ 7.9−7.1 (m, 10H, Ph), ortho protons assigned: 7.84 (m, 4H, P_APh_{down} and P_APh_{up}), 5.70 (s, 5H, CpRu), 4.85 (s, 1H, CpFe), 4.58 (s, 1H, CpFe), 4.40 (s, 1H, CpFe), 4.35 (s, 1H, CpFe), 4.30 (s, 1H, CpFe), 4.19 (s, 1H, CpFe), 4.12 (t, $H^{1''}$), 3.1−0.8 (Cy), −8.87 (t, J_{H-PA} = J_{H-PB} = 26.2 Hz, 1H, Ru−H), −8.83 (t, J_{H-PA} = J_{H-PB} = 28.6 Hz, 1H, Ru−H). ^{31}P {^{1}H} (121 MHz, acetone-d_6): 74.13 (s, P_APh_2), 63.88 (s, P_BCy_2). **12**: ^{1}H NMR (300 MHz, acetone-d_6): δ 8.9−6.6 (m, 10H, Ph), ortho protons assigned: 8.04 (m, 4H, P_APh_{down} and P_APh_{up}), 5.67 (s, 5H, CpRu), 4.80 (s, 1H, CpFe), 4.71 (s, 1H, CpFe), 4.31 (s, 1H, CpFe), 4.25 (s, 1H, CpFe), 3.42 (s, 1H, CpFe), 3.89 (s, 1H, CpFe), 3.35 (t, $H^{1''}$), 2.8−2.5 (m, 2H, C*H*Me_2), 1.63 (dd, J_{HP} = 19.0 Hz, 3H, CH*Me₂*), 1.52 (dd, J_{HP} = 18.5 Hz, 3H, CH*Me₂*), 1.07 (dd, J_{HP} = 17.5 Hz, 3H, CH*Me₂*), 0.73 (dd, J_{HP} = 17.8 Hz, 3H, CH*Me₂*), −8.97 (t, J_{H-PA} = J_{H-PB} = 27.4 Hz, 1H, Ru−H), −8.82 (t, J_{H-PA} = J_{H-PB} = 28.3 Hz, 1H, Ru−H). ^{31}P {^{1}H} (121 MHz, acetone-d_6): 74.53 (s, P_APh_2), 71.64 (s, $P_B{}^iPr_2$).

Preparation of CpRu(CF_3CO_2)(PP^{Ph}PF), 13. To obtain monocrystals of complex **10**, a sample was dissolved in acetone in a Schlenk-tube. A tube containing diethyl ether was also introduced into the Schlenk tube in order to produce slow evaporation of this solvent and condensation over the acetone solution. After several days, orange monocrystals were obtained that were found to be of complex **13**. ^{1}H NMR (300 MHz, acetone-d_6, −70 °C): δ 8.5−6.8 (m, 20H, Ph), ortho protons assigned: 8.05 (m, 2H, P_APh_{down}), 8.32 (m, 2H, P_BPh_{down}), 6.80 (m, 2H, P_BPh_{up}), 4.17 (s, 5H, *Cp*Ru), 4.69 (s, 1H, *Cp*Fe), 4.33 (s, 1H, *Cp*Fe), 4.16 (s, 1H, *Cp*Fe), 4.09 (s, 1H, *Cp*Fe), 2.99 (s, 1H, Cp_{down}-Fe−$H^{5'}$), 3.53 (m, $H^{1''}$), 2.30 (m, $H^{2''ax}$), 1.95 (m, $H^{2''ec}$), 1.60 (m, $H^{3''ax}$), 1.86 (m, $H^{3''ec}$). ^{31}P {^1H} (121 MHz, acetone-d_6): 67.36 (d, J_{PP} = 57.4 Hz, P_APh_2), 38.47 (d, P_BPh_2).

X-ray Structure Determination for 4 and 13. X-ray data of suitable cystals were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) using 0.3° ω-scan frames that covered complete spheres of the reciprocal space. Data processing included a correction for absorption by the multiscan method.[38] The structures were solved with direct methods using the program SHELXS97.[39] Structure refinements on F^2 were carried out with the program SHELXL97.[39] Non-hydrogen atoms were refined anisotropically. The hydride H atom was refined in x, y, and z without restraints. All other hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Selected crystallographic and geometric data are given in Tables 1 and 2. More details are reported in the supporting.

Acknowledgment. Dedicated to Prof. Karl Schlögl on the occasion of his 80th birthday. Authors from the UCLM thank the D.G.E.S. for financial support (Grant n*o*. PB2002-00286) and the Consejería de Ciencia y Tecnología de la Junta de Comunidades de Castilla-La Mancha (Grant no. PBI-02-002).

Supporting Information Available: Tables and CIF's of X-ray structural data, including data collection parameters, positional and thermal parameters, bond distances and angles for complexes, and additional structural views of **4** and **13**. ^{13}C-{^1H} NMR information of ligands and complexes **1-6**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA031926K

(38) Bruker, Programs SMART, version 5.054; SAINT, version 6.2.9; SADABS version 2.03; XPREP, version 5.1; SHELXTL, version 5.1; Bruker AXS Inc.: Madison, WI, 2001.
(39) Sheldrick, G. M. *SHELX97*: Program System for Crystal Structure Determination; University of Göttingen: Germany, 1997.