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Ruthenium Dihydrogen Complexes with Wide Bite Angle Diphosphines

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The wide bite angle diphosphines homoxantphos (10,11-dihydro-4,5,-bis(diphenylphosphino)dibenzo[b,f]oxepine), sixantphos (4,6-bis(diphenylphosphino)-10,10-dimethylphenoxasilin), and thixantphos (2,8-dimethyl-4,6-bis(diphenylphosphino)phenoxathiin) were used to prepare *cis*[MH_2(diphosphine)$_2$] complexes (**1a**–**f**) by reaction of [Ru(cod)(cot)] (cod = cyclo-octa-1,5-diene, cot = cyclo-octa-1,3,5-triene) with 2 equiv of the diphosphine under dihydrogen pressure. The electronic properties of the thixantphos ligand were varied. Complexes **1a**–**f** can be protonated with HBF_4 or CF_3COOH to yield hydrido(dihydrogen) complexes *cis*[$MH(H_2)$(diphosphine)$_2$]$^+$ (**2a**–**f**), which were characterized by VT (variable temperature) NMR and T_1 measurements. These complexes show fast hydrogen atom exchange between the η^2-H_2 and the terminal hydride at all temperatures studied. They are thermally unstable toward dihydrogen loss yielding the cationic monohydride complexes *cis*[MH(diphosphine)$_2$]$^+$ (**3a**–**f**). Coordination of the η^2-H_2 is dominated by $\sigma \rightarrow$ d donation, and hence, the H–H distance is hardly influenced by the electronic properties of the ligands.

Introduction

In the past decade, much experimental[1] and theoretical[2] research has been devoted to the chemistry of dihydrogen complexes. The η^2-coordination of a dihydrogen molecule to a transition metal results from a subtle balance between σ-donation from the H−H bond and π-back-bonding from the metal center. The electronic and steric properties of the ancillary ligands have thus a dramatic influence on the structure and reactivity of the dihydrogen ligand. Crabtree and co-workers[3] have studied a series of rhenium polyhydride complexes [ReH_7{P(C_6H_4-*p*-X)$_3$}$_2$] in which the electron-donating ability of the X substituent was varied (X= CH_3, H, F, CF_3, OCH_3). All complexes were shown to contain an elongated η^2-H_2 ligand in which the H−H distance increased from 1.24 to 1.42 Å on going from X = CF_3 to X = OCH_3. This lengthening on increasing the electron-donating ability of the phosphine shows that for these complexes π-back-bonding is the dominant process involved in the stabilization of the η^2-H_2 ligand. On the other hand, Morris and co-workers[4,5] have investigated the influence of the substituents R on the acidity of the dihydrogen ligand in iron, ruthenium, and osmium complexes, [$M(H_2)H${$PR_2(CH_2-CH_2)PR_2$}$_2$]. They reported that on going from R = 4-$C_6H_4CF_3$ to R = 4-$C_6H_4OCH_3$ the pK_a of the corresponding dihydrogen complexes increased by more than 7 units, but the H−H bond length did not change significantly, except for the osmium

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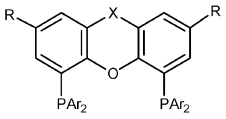

	X	R	Ar	Bite Angle(°)[a]
a Homoxantphos	CH_2-CH_2	H	Ph	102.0 [b]
b Sixantphos	$Si(CH_3)_2$	H	Ph	106.2
c Thixantphos-OCH_3	S	CH_3	$C_6H_4OCH_3$	106.9
d Thixantphos-CH_3	S	CH_3	$C_6H_4CH_3$	106.7
e Thixantphos	S	CH_3	Ph	106.4
f Thixantphos-CF_3	S	CH_3	$C_6H_4CF_3$	109.3

Figure 1. Xantphos-type ligands used. (a) Natural bite angles taken from ref 24. (b) From ref 22b.

complexes. The increased acidity of the dihydrogen ligand in complexes containing electron-poor diphosphines reflects the fact that in this case σ-donation is dominant, and therefore, the H−H distance is hardly affected.

When chelating diphosphines are used, their steric properties have a large influence on the geometry of the complexes, and thus, the combination of steric and electronic factors will determine the stability and reactivity of the dihydrogen ligand. Most of the known $[MH(H_2)(PP)_2]^+$ complexes with chelating diphosphines have a strong preference for the trans geometry.[6−14] Theoretical studies have shown that, for M = Ru, the trans geometry corresponds to the global energy minimum of the system and the dihydrogen ligand prefers to coordinate trans to a ligand of high trans influence (hydride, in this case).[2b,15] Ab initio calculations by Morokuma and co-workers[15] showed that when the bite angle of the diphosphine is increased, the most favored geometry changes from octahedral with the hydride trans to the dihydrogen molecule, to a very distorted cis complex. For intermediate bite angles, an equilibrium with the classical trihydride species is observed. Usually, complexes containing cis hydride and dihydrogen ligands exhibit fast hydrogen atom exchange, even at low temperature. This is the case for the cis isomer of $[MH(H_2)(PR_3)_4]^+$ (M = Fe, Ru; R = Me, Et) prepared by Berke et al.[16] and for the complexes $[RuH(H_2)(PP)_2]PF_6$ (PP = dppb, diop) reported by Saburi and co-workers.[6,7] A remarkable exception are the complexes $[\{P(CH_2CH_2PR_2)_3\}M(H)(H_2)]$ containing tetradentate ligands, which show decoalescence of the hydride and dihydrogen signals in the ^{1}H NMR spectra at ambient temperature.[17,18] Caulton, Eisenstein, and co-workers[19] have carried out a detailed experimental and theoretical study on $Fe(H)_2(\eta^2$-$H_2)(PEtPh_2)_3$, in which they showed the existence of a "cis effect" between a η^2-H_2 ligand and the adjacent hydrides. A similar interaction occurs in $RuH(H_2)I(PCy_3)_2$.[20] This interaction opposes the effect of d → σ* back-donation and is held responsible for the fast intramolecular hydride−dihydrogen exchange already described. Further theoretical investigations on the mechanism of this exchange have been carried out on *cis*$[FeH(H_2)(PR_3)]^+$ by Maseras et al.[21]

In our research group, several diphosphines based on xanthene-like backbones have been developed.[22] The wide bite angles enforced by these ligands in combination with the rigidity of the backbone impose geometrical constraints that have an important influence on the structure and catalytic activity of several Rh and Pd complexes.[23] Recently, a number of xanthene-based ligands in which the electronic properties of the phosphorus were varied without significant changes in the bite angle were prepared in our research group.[24] In a previous communication,[25] we have reported the synthesis of ruthenium(II) hydrido−dihydrogen complexes using sixantphos (**b**) and thixantphos (**c**) as chelating ligands (Figure 1). In this paper, we present the synthesis and characterization of ruthenium dihydride complexes with different xantphos-type ligands, their reaction with acids to yield hydrido-dihydrogen complexes, as well as the charac-

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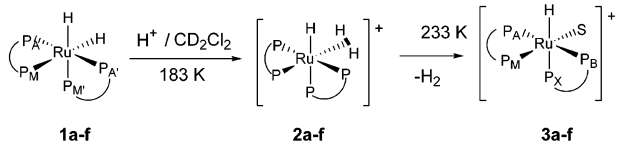
Scheme 1. Protonation of Neutral Dihydrides To Give Dihydrogen Complexes and Loss of Dihydrogen



terization of the monohydrides arising from the thermal loss of the dihydrogen ligand. The influence of the bite angle and the electronic properties of the diphosphines on the hydrido−dihydrogen complexes will be discussed.

Results and Discussion

Synthesis and Characterization of Ruthenium Dihydrides. Ruthenium dihydride bis(diphosphine) complexes *cis*[$RuH_2(PP)_2$] (**1a**−**f**) were prepared by hydrogenation of Ru(cod)(cot) in the presence of the diphosphine ligands using the method reported by Chaudret et al.[26] These dihydrides were convenient precursors for the synthesis of cationic hydrido−dihydrogen complexes. In our study, six diphosphine ligands having wide bite angle were used (Figure 1, **a**−**f**). Ligands were prepared as reported by van Leeuwen and co-workers.[22,24]

Reaction of Ru(cod)(cot) with 2 equiv of the diphosphine under 3 bar of dihydrogen gas in THF afforded the desired product as olive green or light brown solids in 40−65% yield. A temperature of 150 °C and long reaction time (16 h) are required to obtain acceptable conversions. At a higher pressure of dihydrogen (10−20 bar), mainly colloidal ruthenium was formed, even at room temperature. The products were characterized by ^{1}H and ^{31}P NMR spectroscopy in C_6D_6. The proton and phosphorus NMR spectra of all complexes are very similar, with the exception of complex **1a** carrying the homoxantphos ligand that will be discussed separately.

The high field region of the ^{1}H NMR spectrum of **1b**−**f** shows a pseudodoublet of triplets at around −8 ppm. This signal corresponds to the XX′ part of an AA′MM′XX′ spin system where AA′MM′ are the four phosphorus atoms. A similar signal has been observed for the complexes *cis*[RuH_2-$(dppe)_2$][8] and *cis*[$RuH_2(dppf)_2$][5] indicating a cis arrangement of the diphosphines. For complexes **1b**−**f**, two clearly distinct singlets are observed for the methyl groups of the ligand backbone (Figure 1). Additionally, the spectra of compounds bearing ligands **c** and **d** show three different signals for the methyl groups, between 3.2 and 3.4 ppm for the anisyl substituent and between 1.8 and 2.1 ppm for the tolyl substituent.

The ^{31}P{^{1}H} NMR spectra of all complexes are virtually identical and show an A_2X_2 spin system, the chemical shifts of which are between 30 and 38 ppm. The P−P coupling constants are close to 18 Hz, in agreement with a cis geometry having two magnetically inequivalent phosphorus atoms, those trans to one another (P_A) and those trans to the hydride ligand (P_X) (Scheme 1).

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Table 1. T_1 Data and H−H Distances for Dihydrogen Complexes **2a**−**f**[a]

ligand	β_n (deg)[b]	σ Hammet parameter	T_{1min} (ms)	T of min (K)	T_1 MH[c] (ms)	d(H−H) (Å)[d] fast rot	d(H−H) (Å)[d] slow rot
a	102.0[e]		18	233	166	0.87	1.10
b	106.2		24	203	622	0.90	1.14
c	106.9	−0.27	25	243	274	0.92	1.15
d	106.7	−0.17	29	233	318	0.94	1.18
e	106.4	0.0	19	243	242	0.87	1.10
f	109.3	0.54	27	233	296	0.93	1.17

[a] All spectra were measured in CD_2Cl_2 at 300 MHz. [b] Natural bite angles taken from ref 24. [c] T_1 of the corresponding monohydride at the temperature of the minimum. [d] H−H distance considering fast and slow rotation of the η^2-H_2 ligand. [e] From ref 22b.

The dihydride complex **1a** with the more flexible homoxantphos ligand shows a different spectroscopic behavior. As expected, all four ethylenic protons of the backbone are inequivalent, giving rise to a complex pattern consisting of two apparent triplets (3.1 and 3.4 ppm) and two broad apparent doublets (2.30 and 2.88 ppm). The signal for the two hydrides is very similar to that observed for complexes **1b**−**f**. The ^{31}P{^{1}H} spectrum of **1a** consists of only one singlet at 40.7 ppm. As the shape of the hydride signal in the ^{1}H NMR spectrum excludes a structure with four equivalent or rapidly exchanging phosphorus atoms, we carried out variable temperature experiments. No change was observed in the ^{1}H or ^{31}P NMR spectra on cooling to 193 K. This suggests that the A and X signals display fortuitously the same chemical shift.

Hydrido−Dihydrogen Complexes. Protonation of the dihydride complexes **1a**−**f** using HBF_4·OEt_2 or CF_3COOH at 183 K led to the formation of hydrido−dihydrogen complexes (**2a**−**f**). Complexes **1a**−**f** were dissolved in CD_2-Cl_2 in an NMR tube, and the solution was frozen in liquid N_2. After addition of the acid, the tube was shaken to melt the solvent and immediately introduced into the NMR probe precooled at 193 K. The ^{1}H and ^{31}P NMR spectra, as well as relaxation times T_1, were recorded at 193 K and then at 20 K intervals up to 298 K. Both ^{1}H and ^{31}P spectra showed the disappearance of the signals from the precursor dihydride, and signals of a new product were observed. The high field region of the ^{1}H spectrum shows a broad signal at −6.5 ppm, while the ^{31}P{^{1}H} spectrum exhibits two apparent triplets between 20 and 35 ppm with a splitting around 24 Hz. The average minimum relaxation time T_{1min} of the 3 hydrogen nuclei was observed between 203 and 243 K and in all cases was found to be shorter than 25 ms (for T_1 data for all complexes, see Table 1 and next section). This short relaxation time is characteristic of the presence of a dihydrogen ligand. We therefore assign the new species to a hydrido−dihydrogen complex *cis*[$Ru(H)(H_2)(PP)_2$]$^+$. The hydride and dihydrogen ligands are in fast exchange, and no decoalescence is observed even at 193 K.

With the exception of complex **1e** carrying the thixantphos ligand, protonation of **1a**−**f** yields the dihydrogen complexes **2a**−**f** together with the new species **3a**−**f**. These species display a sharp and symmetric multiplet centered at −4 ppm in the ^{1}H NMR spectrum and an ABMX pattern in the ^{31}P-{^{1}H} spectrum. They were identified[25] as the monohydride

complexes $[RuH(diphosphine)_2]^+$ resulting from H_2 loss from the dihydrogen complexes **2a**−**f**. Their properties will be discussed further in the next section. As the temperature was slowly raised, the signals for the monohydride complexes **3a**−**f** increased in intensity at the expense of the signals for the hydrido−dihydrogen species. At 263 K, only the signals for **3a**−**f** were detected. The dihydrogen complexes **2b**−**e** could be prepared by protonation of **1b**−**e** using either $HBF_4 \cdot OEt_2$ or CF_3COOH. Protonation of **1a** or **1f** using $HBF_4 \cdot OEt_2$ led to the immediate formation of the corresponding monohydride complexes **3a** and **3f**. Complex **2a** (homoxantphos) could be formed by protonation of **1a** with 1 equiv of CF_3COOH. Nevertheless, 3 or more equiv of TFA was required for quantitative protonation of complex **1f** containing the thix-CF_3 ligand. In a separate experiment, **1f** was protonated with a 1:1 mixture of CF_3COOH and $HBF_4 \cdot OEt_2$, giving rise to the same hydrido−dihydrogen complex obtained by using pure trifluoroacetic acid. We propose that for these two complexes the CF_3COO^- counterion provides additional stabilization of the η^2-H_2 ligand via hydrogen bonding. It is remarkable that the two ligands in the extremes of the scale, that is, the one with the smallest bite angle (homoxantphos) and the one with the widest bite angle and the strongest π-acceptor (thixantphos-CF_3), exhibit this special behavior.

Upon protonation of complex **1b**, carrying the sixantphos ligand, three different products are observed by ^1H and ^{31}P NMR. In particular, the high field region of the ^1H NMR spectrum shows one sharp multiplet centered at −5.6 ppm and two broad signals at −6.6 ppm (minor) and −6.9 ppm (major). As discussed in a previous communication,[25] the two broad signals are assigned to isomeric dihydrogen complexes *cis*$[Ru(H)(H_2)(PP)_2]^+$ (**2b**/**b′**) in a 1:4 ratio, the third signal corresponding to the monohydride **3b**. Increasing the temperature results in a decrease in the intensity of **2b**/**b′** and an increase of the signal for **3b**, which is the only species present at 213 K. In order to investigate the nature of these isomers, the possible geometries of the $[(diphosphine)_2Ru(H)(H_2)]^+$ complexes were studied using molecular mechanics. We found that two relative orientations of the diphosphines are possible, which will give rise to two types of complexes (Figure 2). Although complexes of type A have favorable π-stacking interactions, this geometry is hindered by the methyl groups of the backbone in the thixantphos-type ligands, and only complexes of type B are observed for the latter ligands.

Attempts to regenerate the dihydrogen complex from the cationic monohydride were made using complex **3c** with the thix-OMe ligand. Once the signals for **2c** were no longer observable by NMR (263 K), the tube was cooled to 193 K, and H_2 was bubbled through the solution for 5 min, after which the NMR spectrum was recorded at the later temperature. Surprisingly, both the ^1H and the ^{31}P spectra were identical to those recorded at 263 K, indicating that the loss of H_2 is irreversible. Further attempts were made by using a high pressure NMR tube. The tube was charged with pure **3c**, 1.5 mL of CD_2Cl_2 was added, and the tube was pressurized to 5 bar of H_2. The reaction was followed by ^1H and ^{31}P VT (variable temperature) NMR for 16 h, but no reaction was observed at 233 K.

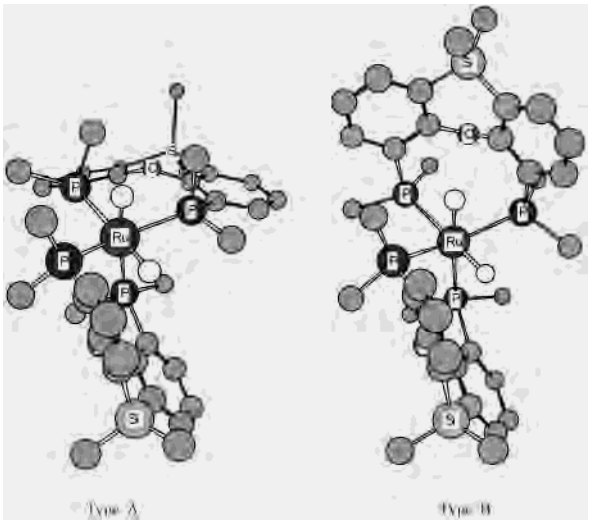

Figure 2. Possible isomers for *cis*$[MH(H_2)(Sixantphos)_2]^+$ (**2b**).

The low thermal stability of dihydrogen complexes **2** may be explained by insufficient d → σ^* back-donation required to stabilize the η^2-H_2 ligand. INDO/1 calculations[25] show that the wide bite angle of the ligands induces a distortion from the octahedral geometry that can lead to poor orbital overlap. Most hydrido−dihydrogen complexes with chelating diphosphines adopt a trans geometry (see Introduction), but if the steric bulk of the diphosphine is increased, as for dppf and dcpe (bis(dicyclohexylphosphino)ethane), the classical trihydride $[M(H)_3(PP)_2]^+$ becomes the preferred isomer. Gusev et al.[16] observed that while $[Ru(H)(H_2)(PMe_3)_4]^+$ exists as the cis isomer only, the analogous complex with the more bulky phosphine PEt_3 coexists in equilibrium with its trihydride isomer. In some cases, the geometric constraints imposed by the ancillary ligands can force the complex to adopt a cis conformation, as for example in the complexes with tetradentate ligands $[\{P(CH_2CH_2PR_2)_3\}M(H)(H_2)]$.[17,18] This is also the case for complexes **2a**−**f**, in which the wide bite angle and the rigidity of the xantphos-type ligands prevent their coordination trans to one another. These complexes may find additional stabilization via the attractive "cis effect" between the dihydrogen and the hydride ligands as proposed by Caulton and Eisenstein.[19]

As already mentioned, the dihydrogen ligand and the terminal hydride are in rapid exchange as indicated by the broad signal observed in the ^1H NMR spectrum. Many theoretical studies have been devoted to the investigation of the nature of this type of intramolecular atom exchange. To date, the most favored mechanism is the single-step transfer of a hydrogen atom between the two ligands (open direct transfer), which has a very low energy barrier and requires minimum rearrangement of the phosphine ligands. Fast scrambling of the η^2-H_2 and the hydride ligands is commonly observed for ruthenium complexes with chelating diphosphines (both cis and trans), although most trans complexes

show coalescence of the hydride and dihydrogen resonances at higher temperatures only.[4,6,8,11−14,27−30]

^{1}H NMR T_1 Measurements and H−H Distances. A common method to characterize η^2-H_2 complexes is the measurement of the minimum relaxation time of the dihydrogen ligand.[12,27,31] It is generally assumed that dipole−dipole relaxation (R_{dd}) is the main relaxation mechanism in dihydrogen complexes. Several authors have pointed out that the protons of the ancillary ligands and other nuclei make a significant contribution to the observed relaxation rate of the dihydrogen ligand.[31−33] Halpern et al.[33] described a method to calculate the contribution of the rest of the molecule to the dipolar relaxation of the η^2-H_2 moiety. For complexes of the general formula $MH(H_2)L_4$, the contribution of the rest of the molecule can be estimated by measuring the relaxation rate of the terminal hydride in the corresponding MHL_4 complex, which does not contain a dihydrogen ligand (at the same temperature, solvent, and magnetic field strength). In this case, the overall relaxation rate of the dihydrogen ligand is

$$R_{HH} = R_{dd} + R^2_{obs} \quad (1)$$

R_{HH} is the observed relaxation rate of the dihydrogen ligand *only*, R_{dd} is the dipole−dipole relaxation, and R^2_{obs} is the observed relaxation rate of the classical hydride in MHL_4.

For fluxional molecules in which the dihydrogen ligand and the classical hydride give rise to only one signal in the ^{1}H NMR spectrum and thus R_{HH} cannot be directly measured, eq 2 can be used to calculate the relaxation rate of the η^2-H_2 moiety:

$$mR_{HH} = \{(m+n)R^1_{obs} - nR^2_{obs}\} \quad (2)$$

where R^1_{obs} is the observed relaxation rate of *all* the hydrides in $MH(H_2)L_4$, m is the number of nonclassical hydrides, and n is the number of terminal hydrides.

Combining eqs 1 and 2, the relaxation rate due to the dipole−dipole interaction is given by eq 3:

$$R_{dd} = \frac{3}{2}(R_{obs}{}^1 - R_{obs}{}^2) \quad (3)$$

Table 1 shows the measured T_{1min} for the dihydrogen and monohydride complexes, as well as the estimated H−H distances assuming a fast or a slow motion regime. The low thermal stability of complexes **2a**−**f** limited the range of temperatures in which T_1 could be measured, and thus, we cannot be sure of having found the "true minimum". Therefore, the calculated distances are only the upper limit of the H−H distance in the η^2-H_2 ligand.

Assuming a fast motion regime, distances shorter than 0.95 Å were calculated, which is in agreement with complexes carrying an unstretched dihydrogen ligand. The differences in the T_{1min} values and therefore in the calculated H−H distances fall within the limits of experimental error of the measurement. Thus, no correlation could be found between the electronic properties or the bite angle of the diphosphine and the calculated H−H distances in the η^2-H_2 ligand.

We had anticipated that an electron-rich ligand such as thix-OMe would enhance the back-bonding and hence increase the thermal stability of complexes **2** with respect to H_2 loss. At the same time, a decrease in the H−H distance was to be expected on going from thix-OMe to thix-CF_3 (ligands **c**−**f**) due to the decreased d → σ* back-donation into the η^2-H_2 ligand. Maseras et al. have suggested that for an octahedral complex the coordination of the dihydrogen will mainly be affected by the trans ligand,[34] so the influence of the phosphine should be larger in cis complexes in which the phosphorus atom is trans to the η^2-H_2. The effect of the trans ligand on the bond length of the coordinated dihydrogen was observed by Chin et al. in $[Ru(dppe)_2(H_2)X]^+$ where the calculated distance changed from 0.88 Å for X = H to 0.92 Å for X = Cl.[5] Albertin et al. observed a similar lengthening in $[Ru\{PPh(OEt)_2\}(H_2)X]^+$ for X = H, Br, and I. Nevertheless, they did not observe a change in the H−H distance for the osmium analogues when X was a halogenide or a thiolate.[35] Majumdar et al. reported recently a series of dicationic dihydrogen compounds $[Ru(H_2)(RCN)(dppe)_2]^{2+}$ for which the spectroscopic and chemical properties are hardly influenced by the steric and electronic properties of the trans nitrile.[36] These examples show that many factors influence the bonding of the dihydrogen molecule and therefore the influence of the ancillary ligands is difficult to predict.

Cationic Monohydrides $[RuH(PP)_2]^+$. In order to characterize the products resulting from H_2 loss from the hydrido−dihydrogen complexes **2a**−**f**, monohydrides **3a**−**f** were independently synthesized. These compounds were prepared by protonation of the dihydrides **1a**−**f** with 1, 2, or 3 equiv of acid (HBF_4·OEt_2 or CF_3CO_2H) at low temperature (203 K) followed by slow warming to room temperature. When protonation was performed at room temperature, a considerable amount of an unidentified product was formed, which displayed two triplets at 60 and 25.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum and no signals in the hydride region of the ^{1}H NMR spectrum.

As mentioned previously, the high field region of the ^{1}H NMR spectra of compounds **3a**−**f** exhibits a symmetric multiplet composed of 16 lines. The minimum relaxation time of this signal is longer than 150 ms, pointing clearly to

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a classical hydride. This resonance corresponds to a hydride coupling with the four nonequivalent phosphorus atoms in **3a**−**f**. The vacant site is probably occupied by an ether molecule (stemming from the acid) or by the counterion.

Simulation[37] of the hydride region for **3c** gave good agreement between the experimental and calculated spectra. The $^{31}P\{^1H\}$ spectra of complexes **3** show an ABMX splitting pattern in which the AB system corresponds to the two mutually trans phosphorus atoms, P_X is the phosphorus trans to the hydride, and P_M is the remaining phosphorus atom (Scheme 1). Broad-band ^1H-coupled ^{31}P spectra allowed us to assign the highest field signal to P_X with a $P_{trans}-H$ coupling constant of 80 Hz. Simulation of the phosphorus spectra confirmed our assignments.

Complex **3a**, carrying the homoxantphos ligand, exhibits once again a different behavior. At first glance, the hydride signal appears as a double quadruplet, as if the hydride were coupled to three equivalent cis phosphorus atoms and a trans one. However, the ^{31}P NMR spectrum indicates that all four phosphorus nuclei are inequivalent (ABMX system), so the apparent double quadruplet must arise from very similar cis J_{PH} coupling constants. Indeed, from selective phosphorus-decoupled ^1H NMR experiments, coupling constants of 29.2 Hz ($J_{P_AH} \approx J_{P_BH}$) and 25.3 Hz ($J_{P_MH}$) were calculated. Two ABMX systems were observed in the ^{31}P spectrum of **3a** at 180 K in a ratio 1:0.56. When the temperature was slowly increased, all the signals broadened, and at 240 K broad signals for just one ABMX system were observed. The chemical shift of each component was intermediate between the chemical shifts of the two systems observed at 180 K. Upon further warming, the signals sharpen, and at 280 K, all phosphorus couplings are resolved. When the sample was cooled to 180 K again, the signals for the two conformers are restored. This may indicate that, due to the relative flexibility of homoxantphos (compared with the other ligands used), a fast equilibrium between two conformers of **3a** exists on the NMR time scale, which is slow below 280 K.

Conclusions

Ruthenium hydrido−dihydrogen complexes containing diphosphines with wide bite angles can be obtained by protonation of the corresponding neutral dihydrides at low temperature. The estimated H−H distances point to the presence of an unstretched dihydrogen ligand. Complexes **2a**−**f** are thermally unstable and lose H_2 irreversibly above 233 K. The steric demands of the diphosphines force the dihydrogen complexes to adopt a cis geometry, thus facilitating intramolecular hydrogen atom exchange.

The wide bite angle of the xantphos-type ligands causes poor orbital overlap between the metal fragment and the dihydrogen ligand, leading to reduced π-back-bonding into the latter ligand. This results in the low thermal stability of the dihydrogen complex and explains why the H−H distance is almost insensitive to the electronic properties of the diphosphines.

We have presented a case in which the steric demands of the ancillary ligands outweigh the electronic factors in determining the properties of the coordinated η^2-H_2 ligand.

Experimental Section

All reactions were carried out under Ar using standard Schlenk techniques. Solvents were freshly distilled from convenient drying agents and degassed under argon prior to use.

Ru(COD)(COT),[38] homoxantphos,[22b] sixantphos,[22a] thixantphos,[22a] and thixantphos-*p*-R[24] were prepared according to reported procedures. $RuCl_3 \cdot xH_2O$ was purchased from ChemPur. High pressure reactions were carried out in homemade stainless steel autoclaves fitted with a glass liner. C_6D_6 was dried over sodium, and CD_2Cl_2 was dried over CaH_2. They were vacuum transferred, degassed by three freeze−thaw cycles, and stored over molecular sieves. NMR spectra were recorded on a Bruker AMX 300 MHz spectrometer, while variable temperature experiments and T_1 measurements were performed on a Bruker DPX 300 or Bruker DRX 300 spectrometer. Chemical shift values are reported in ppm. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer.

Computational Details. All calculations were performed using CAChe WorkSystem software[39] on an Apple Power Macintosh 950 equipped with two CAChe CXP coprocessors. The molecular mechanics calculations were performed using the MM2 force field.[40] Block-diagonal Newton−Raphson was used as optimization method. The type A and type B isomers of complex **2b** $[(sixantphos)_2Ru(H)(H_2)]^+$ were modeled using augmented MM2, with a d^2sp^3 hybridized (octahedral) Ru^{2+} atom, and Ru−P bond lengths fixed at 2.424 Å. The P−Ru−P chelate angles were fixed at 103°. The INDO/1 calculations were performed using the CAChe ZINDO-module. As input structure for the octahedral $(PH_3)_4(Ru^{2+})(H^-)$ fragment, an idealized structure was used with Ru−P bond lengths of 2.424 Å. For the distorted fragment, the P_4RuH frame from the molecular mechanics calculations already mentioned was used and modified to $[(PH_3)_4Ru(H)]^+$.

Preparation of RuH_2(homoxantphos)$_2$ (1a). Ru(COD)(COT) [225 mg (0.71 mmol)] and 802 mg (1.42 mmol) of homoxantphos were dissolved in 20 mL of THF before being transferred to an autoclave under argon. The autoclave was flushed with H_2, then pressurized to 3 bar, and heated to 150 °C for 16 h. The reaction mixture was transferred under H_2 to a Schlenk vessel, and the solvent was evaporated under vacuum. The resulting dark brown solid was washed with pentane (5 mL) and diethyl ether (2 × 5 mL) at 0 °C and then dried in vacuum to afford the pure product as an olive green powder. Yield: 520 mg (0.422 mmol), 59%. ^1H NMR (C_6D_6): 7.72 (m, 4H), 7.37 (m, 8H), 7.03−7.65 (ar, 32H), 6.46 (m, 4H), 6.30 (m, 4H), 3.22 (CH_2, 4H), 2.86 (CH_2, 2H), 2.30 (CH_2, 2H), −8.22 (apparent dt, J = 46 Hz, J = 33 Hz, hydrides, 2H). $^{31}P\{^1H\}$ NMR (C_6D_6): 41.1 ppm (s). $^{13}C\{^1H\}$ NMR (C_6D_6): 161.5 (*C*−O); 156.0, 148.9, 141.1 (*C*P); 135.2, 128.5, 117.2 (*C*, ar), 141.0, 135.2, 134.8, 134.5, 132.4, 130.3, 128.6−126.5, 123.8, 122.3 (*C*H, ar), 34.1, 30.9 (CH_2). IR (Nujol): 2050 cm^{-1} (ν_{Ru-H}). Anal. Calcd for $RuC_{76}H_{62}P_4O_2$: C 74.1%, H 5.1%. Found: C 73.8%, H 5.4%.

Preparation of RuH_2(sixantphos)$_2$ (1b). This compound was prepared as described for **1a** using 120 mg (0.381 mmol) of Ru(COD)(COT) and 453 mg (0.761 mmol) of sixantphos. Yield: 200

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mg (0.154 mmol), 49% of light brown powder. ^{1}H NMR (C_6D_6): 7.92 (m, 4H), 7.33 (apparent dd, 2H), 7.22−7.15 (ar, 6H), 6.99−6.85 (ar, 20H), 6.65−6.62 (ar, 12H), 6.46−6.40 (ar, 8H), 0.58 (s, 6H, SiCH_3), 0.13 (s, 6H, SiCH_3), −8.41 (pseudo dt, ^2J = 34.0 Hz, 48.7 Hz, 2H, hydride). ^{31}P{^{1}H} NMR: 38.1 (t, J = 18 Hz), 36.4 (t, ^2J = 18 Hz). ^{13}C{^{1}H} NMR: 164.3, 162.6 (PC*C*−O); 138.3, 131.1, 125.0 (*C*P); 136.2, 134.1, 133.9, 133.0, 126.4, 122.8 (*C*H, ar); 123.2, 121.0 (*C*−Si); 0.9 and −0.7 (Si−*C*H$_3$). IR (Nujol): 2075 cm^{-1} (ν_{Ru-H}).

Preparation of RuH$_2$(thixantphos-OMe)$_2$ (1c). This compound was prepared as described for **1a** using 181 mg (0.573 mmol) of Ru(COD)(COT) and 820 mg (1.15 mmol) of thixantphos-OMe. The product was purified by crystallization from toluene−hexane to obtain a light brown powder. Yield: 561 mg (0.365 mmol), 64%. ^{1}H NMR (C_6D_6): 7.96 (m, 4H), 7.67 (t, ^3J = 8.37 Hz, 4H), 7.49 (br, 5H), 7.05 (m, 12H), 6.8 (m, 7H), 6.57 (m, 4H), 6.34 (m, 4H), 3.40, OCH$_3$ (s, 12H), 3.33, 3.30, OCH$_3$ (s, 12H), 2.03, CH$_3$ (s, 6H), 1.61, CH$_3$ (s, 6H), −8.34, hydrides (pseudo dt, ^2J = 34.5 Hz, 48.9 Hz, 2H). ^{31}P{^{1}H} NMR: 34.1 (t, ^2J = 18.5 Hz), 31.0 (t, 18.1 Hz). ^{13}C{^{1}H} NMR: 159.8, 159.3, 159.2, 158.3 (*C*OMe), 154.0, 152.9 (t, *C*P, J_{CP} = 4 Hz); 137.2, 135.0, 134.9, 134.8, 133.9, 133.3, 132.8, 132.8, 128.7 (*C*, ar); 123.4, 122.7 (*C*S); 54.2, 53.8, 53.7 (*C*H$_3$−O), 20.6, 19.9 (*C*H$_3$). IR (Nujol): 2042 cm^{-1} (ν_{Ru-H}).

Preparation of RuH$_2$(thixantphos-CH$_3$)$_2$ (1d). This compound was prepared as described for **1a** using 121 mg (0.383 mmol) of Ru(COD)(COT) and 500 mg (0.767 mmol) of thixantphos-CH$_3$. Yield: 388 mg (0.276 mmol), 72% as a light brown powder. ^{1}H NMR (C_6D_6): 6.91−6.46 (ar, 32H), 5.64 (br, 2H), 2.07 (s, CH$_3$ tolyl, 12H), 2.00 (s, CH$_3$ tolyl, 6H), 1.89 (s, CH$_3$ tolyl, 6H), 1.83 (s, CH$_3$, 6H), 1.44 (s, CH$_3$, 6H), −8.43 (pseudo dt, J = 35.4 Hz, 48.5 Hz, hydrides, 2H). ^{31}P{^{1}H} NMR: 36.0 (t, J = 18.5 Hz), 32.5 (t, J = 18.9 Hz). ^{13}C{^{1}H} NMR: 154.4, 153.3 (*C*O), 137.4, 137.2, 137.1, 136.2, 133.2 (C_{quat}), 133.1, 129.3 (PC*C*H), 123.8, 123.0 (*C*S), 21.0, 21.0, 21.1, 21.2 (*C*H$_3$). IR (Nujol): 2058 cm^{-1} (ν_{Ru-H}).

Preparation of RuH$_2$(thixantphos)$_2$ (1e). This compound was prepared as described for **1a** using 250 mg (0.792 mmol) of Ru(COD)(COT) and 949 mg (1.59 mmol) of thixantphos. Yield: 700 mg (0.540 mmol), 68% as an olive green powder. ^{1}H NMR (C_6D_6): 7.94 (m, 4H), 7.50 (apparent t, J = 8.6 Hz, 4H), 7.34 (m, 4H), 7.03−6.50 (ar, 38H), 5.65 (br, 2H), 1.92 (s, 6H, CH$_3$), 1.54 (s, 6H, CH$_3$), −8.46 (apparent dt, J = 48.6, 34.5 Hz, 2H, hydride). ^{31}P{^{1}H} NMR: 36.6 (t, ^2J = 19.0 Hz), 33.8 ppm (t, 17.6 Hz). ^{13}C{^{1}H} NMR: 154.3, 153.9 (*C*−O); 143.5, 141.0 (OC*C*P), 137.4, 134.2, 133.3 (HC*P*), 133.9, 133.6, 130.5 (*C*P), 129.6, 129.1, 128.0, 127.4, 127.1 (*C*H, ar); 124.0, 123.2 (*C*S); 20.2 (*C*H$_3$). IR (Nujol): 2064 cm^{-1} (ν_{Ru-H}). Anal. Calcd for RuC$_{76}$H$_{62}$S$_2$P$_4$O$_2$: C 70.4%, H 4.8%. Found: C 70.1%, H 4.98%.

Preparation of RuH$_2$(thixantphos-CF$_3$)$_2$ (1f). This compound was prepared as described for **1a** using 100 mg (0.317 mmol) of Ru(COD)(COT) and 868 mg (0.634 mmol) of thixantphos-CF$_3$. Yield: 379 mg (0.206 mmol), 65% as a light brown powder. ^{1}H NMR (C_6D_6): 7.47 (m, 4H), 7.2 (d, J = 8.22 Hz, 4H), 7.1−6.7 (ar, 24 H), 6.38 (pseudo d, 2H), 6.19 (t, J = 7.5 Hz, 4H), 5.61 (br, 2H), 1.82 (s, CH$_3$, 6H), 1.45 (s, CH$_3$, 6H), −9.05 (pseudo dt, J = 33.8 Hz, J = 46.56 Hz, 2H). ^{31}P{^{1}H} NMR: 28.9 (t, ^2J = 17.4 Hz), 27.7 (t, J = 18.95 Hz). ^{13}C{^{1}H} NMR: 153.3, 152.6 (*C*−O); 145.4, 145.3, 143.6, 140.0 (*C*-P); 134.9, 134.8, 134.1, 133.9, 133.0, 132.4 (PC*C*H); 131.7 (*C*CF$_3$, $^2J_{CF}$ = 32.18 Hz), 130.8, 130.6, 130.3, 130.1, 128.5, 128.4, 127.8 (C_{ar}), 130.2, 129.1, 129.1, 128.3, 127.5 (*C*H$_{ar}$), 124.5 (*C*F$_3$, $^1J_{CF}$ = 272.3 Hz), 123.6, 122.4 (*C*S), 20.8, 19.8 (*C*H$_3$). IR (Nujol) = 2062 cm^{-1} (ν_{Ru-H}). Anal. Calcd for RuC$_{84}$H$_{54}$S$_2$P$_4$O$_2$F$_{24}$: C 54.82%, H 2.96%. Found: C 54.81%, H 2.83%.

Dihydrogen Complexes. Protonation experiments were carried out in 5 mm NMR tubes equipped with a septum allowing for addition of reactants. In a typical experiment, 15−20 mg of the dihydride (**1**) was dissolved in 0.5 mL of CD_2Cl_2, and the tube was cooled to 193 K. CF_3COOH or HBF_4·OEt_2 (1 equiv) was added using a microsyringe. The tube was shaken to allow mixture of the reactants and immediately introduced into the probe at 193 K. ^{1}H and ^{31}P spectra as well as T_1 measurements were done at this temperature and then at intervals of 20 K up to 298 K.

[RuH(H$_2$)(homoxantphos)$_2$]CF$_3$COO (2a). ^{1}H NMR (upfield region): −6.49, broad. ^{31}P{^{1}H} NMR: 31.6 (pt, 24.6 Hz), 24.7 (pt).

[RuH(H$_2$)(sixantphos)$_2$]BF$_4$ (2b). Major isomer. ^{1}H NMR (upfield region): −6.9 broad. ^{31}P{^{1}H} NMR: ABMX system 32.1 (P_M, J_{MA} = 26.1 Hz, J_{MB} = 30.3 Hz, J_{MX} = 39.9 Hz); 25.4 (P_A, J_{AB} = 256.0 Hz, J_{AX} = 20.0 Hz); 8.8 (P_X, J_{BX} = 24.2 Hz); 5.3 (P_B). Minor isomer. ^{1}H NMR (upfield region): −6.6 broad. ^{31}P{^{1}H} NMR: 25.0 (pt, 24.0 Hz), 21.8 (pt).

[RuH(H$_2$)(thixantphos-OMe)$_2$]BF$_4$ (2c). ^{1}H NMR (upfield region): −6.40, broad. ^{31}P{^{1}H} NMR: 34.6 (pt, 20.1 Hz), 30.9 (pt).

[RuH(H$_2$)(thixantphos-CH$_3$)$_2$]BF$_4$ (2d). ^{1}H NMR (upfield region): −6.65, broad. ^{31}P{^{1}H} NMR: 34.6 (pt, 20.1 Hz), 30.9 (pt).

[RuH(H$_2$)(thixantphos)$_2$]BF$_4$ (2e). ^{1}H NMR (upfield region): −6.7 broad. ^{31}P{^{1}H} NMR: 21.7 (pt, 23 Hz), 20.3 (pt).

[RuH(H$_2$)(thixantphos-CF$_3$)$_2$]CF$_3$COO (2f). ^{1}H NMR (upfield region): −6.90, broad. ^{31}P{^{1}H} NMR: 21.8 (pt, 24.5 Hz), 18.6 (pt).

Monohydride Complexes. During the synthesis of the monohydride complexes **3a**−**f**, we could not avoid the formation of small amounts of the dicationic complex [Ru(diphosphine)$_2$(S)$_2$]$^{2+}$ (less than 5% by NMR), which precluded our obtaining microanalytical data.

Preparation of [RuH(homoxantphos)$_2$]BF$_4$ (3a). RuH$_2$(homoxantphos)$_2$ (**1a**) [100 mg (0.081 mmol)] was dissolved in 5 mL of CH_2Cl_2, and the solution was cooled to 193 K. HBF_4·OEt_2 [20.5 μL (0.081 mmol), 54%] was added, and the reaction mixture was slowly warmed to room temperature. After 1.5 h, the solvent was evaporated under vacuum, and the resulting dark brown solid was washed with pentane (2 mL) and diethyl ether (2 × 2 mL) and dried in a vacuum. Yield: 85 mg (0.065 mmol), 80%. ^{1}H NMR (CD_2Cl_2): 8.05−5.70 (ar, 52H); 3.39−2.50 (CH$_2$, m, 8H); −4.71 (hydride, m, 1H, J_{HP_A} = 27.6 Hz, J_{HP_B} = 27.6 Hz, J_{HP_M} = 27.6 Hz, J_{HP_X} = 80.7 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): ABMX system, 63.7 (P_M, J_{MA} = 28.1 Hz, J_{MB} = 27.1 Hz, J_{MX} = 16.9 Hz); 38.8 (P_A, J_{AX} = −13.3 Hz, J_{AB} = 253.4 Hz); 34.4 (P_B, J_{BX} = −22.9 Hz); 30.4 (P_X). ^{13}C{^{1}H} NMR (CD_2Cl_2): 160.7, 160.6, 157.6, 156.3 (PC*C*O); 135.3 (P*C*); 134.9 (P*C*, J_{CP} = 3.5 Hz); 140.0−124.0 (*C*H, ar); 132.4, 132.0, 130.1, 125.4, 124.7, 124.5 (C_{quat}); 33.7, 31.6, 31.2, 26.5 (*C*H$_2$).

Preparation of [RuH(sixantphos)$_2$]CF$_3$COO (3b). This compound was prepared as described for **3a** using 100 mg (0.075 mmol) of **1b** and 11.6 μL (0.151 mmol) of CF_3COOH. Yield: 77 mg (0.055 mmol), 73% as a light green solid. ^{1}H NMR (CD_2Cl_2): 8.51−5.92 (ar, 52H); 0.57 (s, CH$_3$, 3H); 0.41 (s, CH$_3$, 3H); −0.02 (s, CH$_3$, 3H); −0.030 (s, CH$_3$, 3H); −5.52 (hydride, m, 1H, J_{HP_A} = 43.1 Hz, J_{HP_B} = 19.7 Hz, J_{HP_M} = 32.9 Hz, J_{HP_X} = 76.2 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): ABMX system, 54.0 (P_M, J_{MA} = 40.1 Hz, J_{MB} = 24.4 Hz, J_{MX} = 21.8 Hz); 37.4 (P_A, J_{AX} = −15.8 Hz, J_{AB} = 254.8 Hz); 31.0 (P_X, J_{BX} = −21.5 Hz); 37.6 (P_X). ^{13}C{^{1}H} NMR (CD_2Cl_2): 164.3, 162.6 (PC*C*O); 160.0 (q, CF$_3$*C*OO, J_{CF} = 36.3 Hz); 138.3, 131.1, 129.5, 125.0 (*C*P); 136.2−122.8 (*C*H, ar); 123.2, 122.5, 121.0, 120.8 (*C*−Si); 118.0 (*C*F$_3$COO, J_{CF} = 290.7 Hz); 0.5, −0.9 (Si−*C*H$_3$).

Preparation of [RuH(thixantphos-OMe)$_2$]CF$_3$COO (3c). This compound was prepared as described for **3a** using 250 mg (0.163

mmol) of **1c** and 12.6 μL (0.163 mmol) of CF_3COOH. Yield: 228 mg (0.136 mmol), 85% as a dark yellow powder. ^1H NMR (acetone-d_6): 7.79−5.62 (ar, 40H); 3.92 (OCH_3, s, 3H); 3.89 (OCH_3, s, 3H); 3.84 (OCH_3, s, 3H); 3.72 (OCH_3, s, 3H); 3.67 (OCH_3, s, 3H); 3.64 (OCH_3, s, 3H); 3.62 (OCH_3, s, 3H), 2.33 (CH_3, s, 3H), 2.17 (CH_3, s, 3H); 2.08(CH_3, s, 6H), −6.33 (hydride, m, 1H, $J_{HP_A} = -42$ Hz, $J_{HP_B} = 32$ Hz, $J_{HP_M} = 24$ Hz, $J_{HP_X} = 76$ Hz). $^{31}P\{^1H\}$ (acetone-d_6): ABMX system, 50.1 (P_M, $J_{MA} = 36.5$ Hz, $J_{MB} = 26.3$ Hz, $J_{MX} = 21.2$ Hz); 34.4 (P_A, $J_{AX} = -17.8$ Hz, $J_{AB} = 265.6$ Hz); 28.3 (P_X, $J_{BX} = -21.10$ Hz); 28.1 (P_B). $^{13}C\{^1H\}$ NMR (acetone-d_6): 162.0, 161.8, 161.6, 161.5, 161.0, 160.9 (C_iOCH_3); 159.8 (q, CF_3COO, $J_{CF} = 36.3$ Hz); 151.5, 150.4 (PC*C*O); 137.5, 137.1 (P*C*CO, $J_{CP} = 4$ Hz); 135.4, 135.3 (PC_{ar}, $J_{CP} = 3$ Hz); 134.9−129.4 (*C*H, ar); 117.1 (CF_3COO, $J_{CF} = 290.7$ Hz); 123.2, 122.5 (*C*S), 114.7−113.5 (*C*H, ar); 55.7, 55.5, 55.3, 55.0, 54.9, 54.5 (CH_3−OAr), 20.6, 20.3, 20.1, 19.7 (CH_3).

Preparation of RuH(thixantphos-CH_3)$_2$$CF_3OO$ (3d). This compound was prepared as described for **3a** using 100 mg (0.071 mmol) of **1d** and 17 μL (0.213 mmol) of CF_3COOH. Yield: 80 mg (0.052 mmol), 74% as a light brown solid. ^1H NMR (CD_2Cl_2): 7.75−6.22 (ar, 34 H), 5.92 (m, 2H), 6.75 (m, 2H), 6.60 (m, 2H), 2.56, 2.49, 2.45, 2.44, 2.41, 2.35, 2.32, 2.27 (s, CH_3 tolyl, 24H total), 2.20, 2.13, 2.08,2.06 (s, CH_3, 12H total); −6.39 (m, hydride, 1H, $J_{HP_A} = 22.65$ Hz, $J_{HP_B} = -48.4$ Hz, $J_{HP_M} = 35.5$ Hz, $J_{HP_X} = 79.0$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): ABMX system, 50.7 (P_M, $J_{MA} = 24.8$ Hz, $J_{MB} = 17.4$ Hz, $J_{MX} = 18.3$ Hz); 35.9 (P_A, $J_{AX} = -48.4$ Hz, $J_{AB} = 256.2$ Hz); 29.8 (P_B, $J_{BX} = -29.2$ Hz); 28.59 (P_X). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 160.7 (q, CF_3COO, $J_{CF} = 36.3$ Hz); 157.5, 154.4, 153.3, 151.5 (PC*C*O); 137.8 (P*C*, $J_{CP} = 5.3$ Hz); 137.4 (P*C*, $J_{CP} = 3.2$ Hz); 137.1 (P*C*, $J_{CP} = 3.8$ Hz); 137.4, 137.2, 137.1, 136.2, 133.2 (C_{quat}), 133.1−129.3 (*C*H, ar); 123.7, 123.0 (*C*S), 117.1 (CF_3COO, $J_{CF} = 290.7$ Hz); 21.4, 21.4, 21.2, 21.2, 21.1, 20.9, 20.8, 20.7, 20.6 (CH_3).

Preparation of [RuH(thixantphos)$_2$]CF_3COO (3e). This compound was prepared as described for **3a** using 150 mg (0.115 mmol) of **1e** and 18 μL (0.231 mmol) of CF_3COOH. Yield: 109 mg (0.076 mmol), 67% as a light green solid. ^1H NMR (acetone-d_6): 7.81 (t, $J = 8.2$ Hz, ar), 7.68 (m, ar), 7.54 (q, $J = 5.6$ Hz, ar), 7.46 (s, ar), 7.30 (t, $J = 7.2$ Hz), 7.2−7.08 (m, ar), 7.08−7.00 (m, ar), 6.95 (t, $J = 8.7$ Hz, ar), 6.91−6.83 (m, ar), 6.79−6.70 (m, ar), 5.88 (d, $J = 8.7$ Hz), 5.82 (d, $J = 6.5$ Hz), 2.33 (s,CH_3, 3H); 2.20 (s,CH_3, 3H); 2.05 (s,CH_3, 3H); 1.49 (s,CH_3, 3H); −6.14 (m, 1H, hydride, $J_{HP_A} = -43.37$ Hz, $J_{HP_B} = 32.25$ Hz, $J_{HP_M} = 20.42$ Hz, $J_{HP_X} = 76.1$ Hz). $^{31}P\{^1H\}$ NMR (acetone-d_6): ABMX system, 57.2 (P_M, $J_{MA} = 36.5$ Hz, $J_{MB} = 26.1$, Hz, $J_{MX} = 19.4$ Hz); 42.5 (P_A, $J_{AB} = 258.3$ Hz, $J_{AX} = 15.2$ Hz); 35.0 (P_B, $J_{BX} = 20.3$ Hz); 33.5 (P_X). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 160.6 (q, CF_3COO, $J_{CF} = 36.3$ Hz); 157.8 (d, PC*C*O, $J_{CP} = 17.3$ Hz); 154.5 (d, PC*C*O, $J_{CP} = 12.7$ Hz); 151.9 (d, PC*C*O, $J_{CP} = 4.1$ Hz); 150.7 (d, PC*C*O, $J_{CP} = 8.9$ Hz); 137.8 (P*C*, $J_{CP} = 5.5$ Hz); 137.6 (P*C*, $J_{CP} = 4.2$ Hz); 137.3 (P*C*, $J_{CP} = 3.8$ Hz); 137.2 (P*C*, $J_{CP} = 6.8$ Hz); 135.4 (P*C*, $J_{CP} = 7.6$ Hz); 133−128 (*C*H, ar); 131.2, 130.5, 129.4, 128.5, 128.4, 128.2 (C_{quat}), 123.6, 123.5, 122.9, 122.8 (*C*S); 116.9 (CF_3COO, $J_{CF} = 290.7$ Hz); 21.4, 21.2, 20.9, 20.6 (CH_3).

Preparation of [RuH(thixantphos-CF_3)$_2$]CF_3COO (3f). This compound was prepared as described for **3a** using 160 mg (0.087 mmol) of **1f** and 13.5 μL (0.174 mmol) of CF_3COOH. Yield: 124 mg (0.064 mmol), 73% as a light brown powder. ^1H NMR (CD_2Cl_2): 8.04−6.36 (m, ar, 37H), 5.59 (m, ar, 2H), 5.84(m, ar, ^1H) 2.46 (s,CH_3, 3H); 2.25 (s,CH_3, 3H); 2.13 (s,CH_3, 6H); −6.36 (m, hydride, 1H, $JHP_A = -43.6$ Hz, $JHP_B = 32.5$ Hz, $JHP_M = 20.2$ Hz, $JHP_X = 75.8$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): ABMX system, 52.3 (P_M, $J_{MA} = 26.3$ Hz, $J_{MB} = 36.8$ Hz, $J_{MX} = 39.9$ Hz); 36.3 (P_A, $J_{AB} = 325.6$ Hz, $J_{AX} = -48.5$ Hz); 29.3 (P_X, $J_{BX} = -22.8$ Hz); 28.8 (P_B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 160.6 (q, CF_3COO, $J_{CF} = 36.3$ Hz); 157.9, 154.5, 153.3, 152.6; 151.9 (PC*C*O); 145.4, 145.3, 143.6, 140.0 (*C*P); 134.9−127.5 (*C*H, ar); 131.0, 130.6, 130.1, 128.5, 128.4, 127.8 (C_{quat}), 125.7−124.5 (CF_3, $^1J_{CF} = 272.3$ Hz); 123.6, 122.4 (*C*S), 118.5 (CF_3COO, $^1J_{CF} = 290.3$ Hz); 21.2, 20.8, 19.8 (CH_3).

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