Spectroscopic Evidence of the First Example of an Isomer with the Hydride Ligand in the Equatorial Plane in the $HRh(CO)_{4-x}(PR_3)_x$ Family: $HRh(CO)_2(PR_3)_2$ (PR_3 = 1,2,5-Triphenyl-1*H*-phosphole, TPP)

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A variable-temperature multinuclear NMR study using enriched ^{13}CO shows that the $HRh(CO)_2(TPP)_2$ (TPP = 1,2,5-triphenyl-1*H*-phosphole) complex, the resting state of the catalytic system for the hydroformylation of styrene by the Rh/TPP mixture, exists in solution as two stereoisomers in equilibrium. The minor isomer (10%) exhibits a geometry where the hydride ligand occupies an equatorial position, a unique case within the $HRh(CO)_{4-x}(PR_3)_x$ family.

Introduction

Earlier studies from our laboratory have shown that rhodium complexes of 1,2,5-triphenyl-1*H*-phosphole (TPP) are prone to catalyze the hydroformylation of a broad range of substrates such as 1-hexene,[1] styrene,[2] and ethyl acrylate[3] under milder conditions and with higher efficiency than related triphenylphosphine systems. An analysis of the influence of the TPP/Rh ratio revealed the existence of a unique active species, tentatively formulated as $HRh(CO)_x(TPP)_2$,[4] in contrast to the case of the PPh_3/Rh system, where several species are involved. With the aim of gaining more insight into the mechanism of this catalytic reaction, we were prompted to carry out a kinetic study of the hydroformylation of styrene[5,6] with concomitant in situ monitoring by infrared and NMR spectroscopy. We report here an account of the results of spectroscopic studies on $HRh(CO)_2(TPP)_2$, previously identified as the catalyst's resting state.

Results and Discussion

Preliminary NMR experiments were done in a heavy-walled 5 mm o.d. NMR tube (fitted with a valve) under experimental conditions analogous with those used earlier in a typical catalytic run,[5] albeit with a different styrene/rhodium ratio (dichloromethane solution; [styrene]/[$RhCl(CO)(TPP)_2$] = 2; 2 equiv of NEt_3; 5 bar of CO and 5 bar of H_2). While allowing the detection of both the expected organic products resulting from the hydroformylation of styrene and the triethylammonium hydrochloride salt (resulting from the trapping of hydrogen chloride liberated during the formation of the active rhodium hydride species), these experiments also revealed a hydride resonance arising as a triplet centered at −9.92 ppm. Relevant spectra obtained from similar experiments carried out in the absence of styrene exhibited the same pattern in the hydride region, thereby confirming the existence of the same organometallic species. Consequently, further studies of these species were conducted in the absence of olefinic substrate.

Variable-temperature ^1H and ^{31}P NMR studies were conducted under 5 bar of CO and 5 bar of H_2 in dichloromethane solution. $^{31}P\{^1H\}$ NMR spectra are displayed in Figure 1. The spectrum recorded at 193 K shows three resonances: namely, a doublet at 33.6 ppm (J_{Rh-P} = 133 Hz), a broad doublet at 28.2 ppm (J_{Rh-P} = 140 Hz), and a sharp singlet at 1.6 ppm. Upon selective decoupling of the phenyl protons (Figure 2), the doublet at 33.6 ppm is converted into a doublet of doublets (J_{PH} = 15 Hz; J_{Rh-P} = 133 Hz), showing that this signal is characteristic of the complex **1**, containing one hydride ligand. Increasing the temperature to 298 K causes only a slight shift of the 33.6 ppm doublet to 34.1 ppm (J_{Rh-P} = 122 Hz). In contrast, the 28.2 ppm doublet changes to a second-order figure at 233 K and tends to fade into the baseline as the temperature reaches 298 K. Simultaneously, the sharp resonance at 1.6 ppm broadens and finally shifts to 5 ppm, the characteristic chemical shift of the free TPP (Figure 1). These observations are consistent with the existence of a nonhydridic species **2**, which would reversibly uptake and release free TTP. Indeed, in a separate experiment, addition of TPP (1 equiv) was found to cause both an enhancement of the 1.6 ppm signal and a shift of the 28.2 ppm doublet to 25.7 ppm. In contrast, saturation of the free TPP resonance did not affect the resonance figure of the hydride species **1**, thereby indicating the absence of exchange between this complex and free TPP.

The variable-temperature ^1H NMR spectrum in the hydride region is presented in Figure 3. The doublet of triplets observed at 273 K (δ −9.92 ppm, J_{PH} = 7.5 Hz, J_{RhH} = 2 Hz) is seen to broaden when the temperature

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[1] (a) Neibecker, D.; Réau, R. *J. Mol. Catal.* **1989**, *53*, 219. (b) Neibecker, D.; Réau, R. *J. Mol. Catal.* **1989**, *57*, 153.

[2] Neibecker, D.; Réau, R.; Lecolier, S. *J. Org. Chem.* **1989**, *54*, 5208.

[3] Neibecker, D.; Réau, R. *New J. Chem.* **1991**, *15*, 279.

[4] Bergounhou, C.; Neibecker, D.; Réau, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1370.

[5] Bergounhou, C.; Neibecker, D.; Réau, R. *Bull. Soc. Chim. Fr.* **1995**, *132*, 818.

[6] Bergounhou, C.; Neibecker, D.; Mathieu, R. Submitted for publication.

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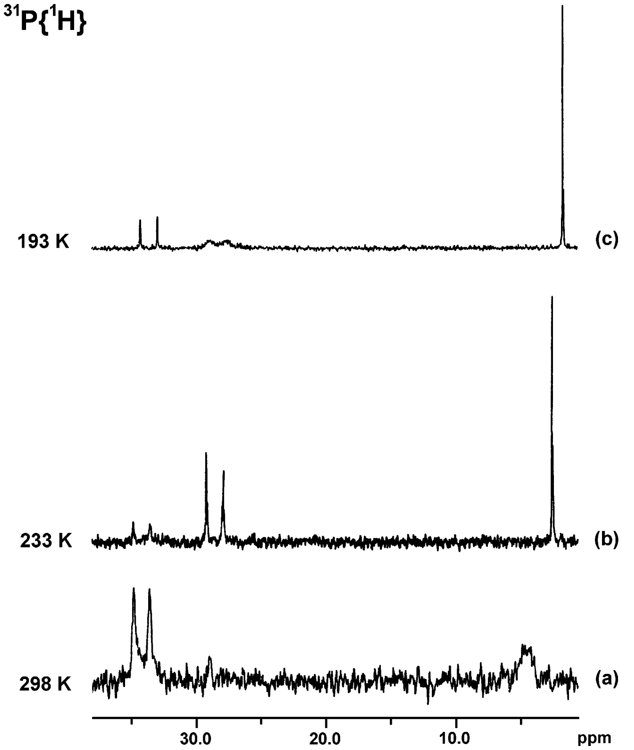

Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra (Bruker WM250; CD_2Cl_2) of the reaction mixture without styrene after 20 min at 40 °C. Conditions: H_2, 5 bar; CO, 5 bar; RhCl(CO)(TPP)$_2$, 10 mg (1.2×10^{-5} mol); Et_3N, 3 μL (2.2×10^{-5} mol); CD_2Cl_2, 1 mL.

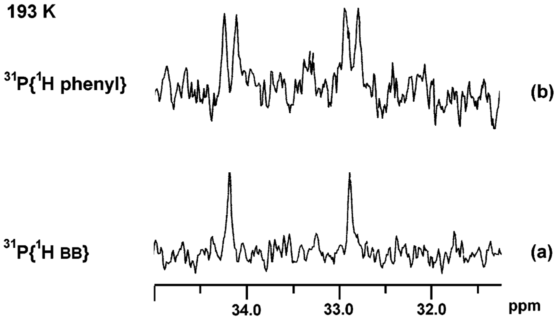

Figure 2. ^{31}P{^{1}H BB} and ^{31}P{^{1}H phenyl} NMR spectra at 193 K (Bruker WM250; CD_2Cl_2): δ 33.6 ppm; $J_{P-H} = 15.0 \pm 1.0$ Hz; $J_{P-Rh} = 133 \pm 1$ Hz.

is lowered down to 193 K, where it then arises as a triplet (δ −10.16 ppm, $J_{PH} = 15.5$ Hz). This indicates that complex **1** contains two TPP ligands, whereas the evolution of chemical shifts and coupling constants with temperature suggests the occurrence of an equilibrium between two or more isomers, one being in major proportion.

While attempting to confirm this hypothesis, we were faced with the problem of getting the hydrido species in higher concentration. The problem could be solved by using a different rhodium source: namely, the mixture $Rh_4(CO)_{12}$ + 8TPP under a CO + H_2 atmosphere. Moreover, increasing the H_2/CO ratio to 9 favored the concentration of **1** at the expense of **2**, suspected to be a binuclear complex resulting from the dehydrogenation of the mononuclear hydride, by analogy with previously reported similar catalytic systems.[7] Figure 4 displays the ^{31}P{^{1}H} NMR of the resulting mixture at 213 K. Clearly, the resonance of the previously detected hydrido complex now arises as the major signal, whereas two additional doublets of lower intensity are also observed at 30.8 ppm for **2** and a new compound at 36.3 ppm ($J_{RhP} = 112$ Hz). The ^{1}H NMR spectrum at room temperature is very similar to the previously studied systems and consists of a nonsymmetrical doublet of triplets (Figure 5). New features appear when the temperature is lowered down to 193 K. In addition to the previously observed triplet at −10.12 ppm ($J_{PH} = 15.5$ Hz) for **1a**, a weak doublet of

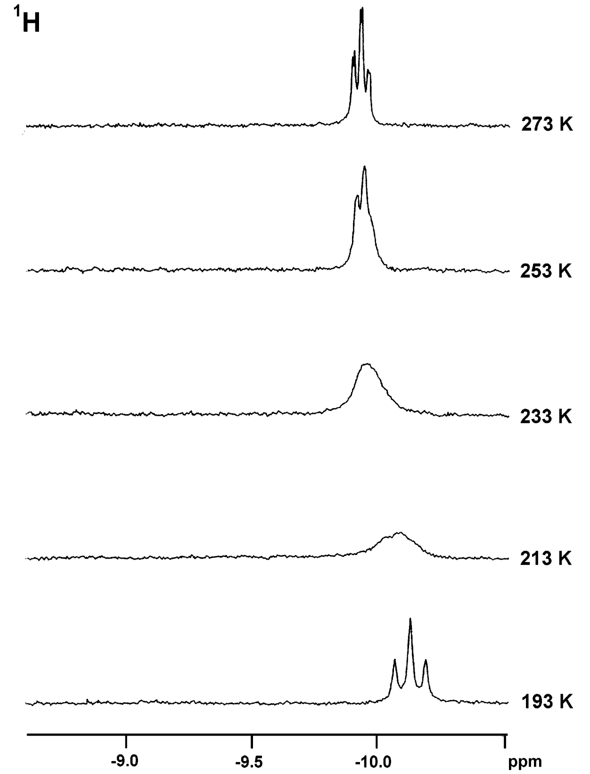

Figure 3. Variable-temperature ^{1}H NMR spectra (Bruker WM250; CD_2Cl_2) of the reaction mixture without styrene after 20 min at 40 °C. Conditions: H_2, 5 bar; CO, 5 bar; RhCl(CO)(TPP)$_2$, 10 mg (1.26×10^{-5} mol); Et_3N, 3 μL (2.17×10^{-5} mol); CD_2Cl_2, 1 mL.

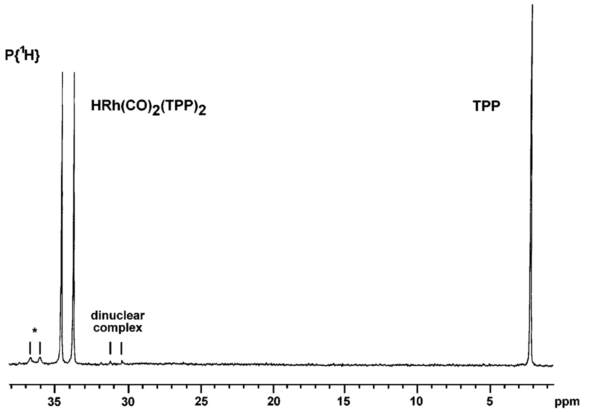

Figure 4. ^{31}P{^{1}H} NMR spectrum at 213 K (Bruker WM250; CD_2Cl_2) of the reaction mixture without styrene after 20 min at 40 °C. Conditions: H_2, 9 bar; CO, 1 bar; $Rh_4(CO)_{12}$, 10 mg (1.2×10^{-5} mol); Et_3N, 3 μL (2.2×10^{-5} mol); CD_2Cl_2, 1 mL.

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(7) See for instance: van der Slot, S. C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Iggo, J. A.; Heaton, B. T. *Organometallics* **2001**, *20*, 430.

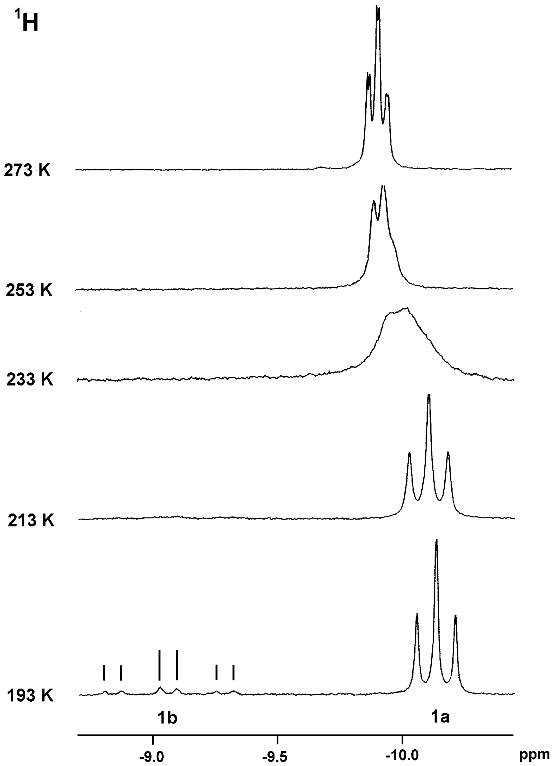
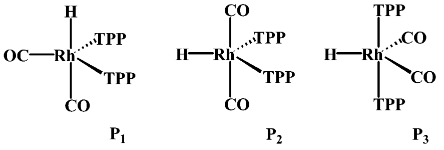


Figure 5. Variable-temperature ^1H NMR spectra (Bruker AMX400; CD_2Cl_2) of the reaction mixture without styrene after 20 min at 40 °C. Conditions: H_2, 5 bar; CO, 5 bar; $Rh_4(CO)_{12}$, 5 mg (6.8×10^{-5} mol); TPP, 17 mg (5.4×10^{-5} mol); CD_2Cl_2, 1 mL.

Chart 1



triplets is detected at −9.09 ppm ($J_{PH} = 45$ Hz, $J_{RhH} = 13$ Hz) for **1b**. Integration of signals gives a 90/10 ratio for the two isomers. The coalescence temperature of the exchange phenomenon is observed at 223 K, which is consistent with an approximate $\Delta G^{\ddagger}$ value of 43(±4) kJ mol^{-1}.

The present NMR data are consistent with a formulation of **1a** and **1b** as isomers of $HRh(CO)_2(TPP)_2$, for which three possible geometries might be considered (Chart 1). The structure referred to as $\mathbf{P_1}$, with the hydride ligand in an axial position and the two equivalent TPP ligands in the equatorial plane, can be unambiguously assigned to the major isomer. It corresponds to the general case for $HRh(CO)_2(PR_3)_2$ complexes.[8]

Two possibilities remain for the second isomer, both possessing a hydrido ligand in an equatorial position (with a very characteristic J_{RhH} coupling constant) but differing in the position of TPP ligands, being either equatorial ($\mathbf{P_2}$ geometry) or axial ($\mathbf{P_3}$ geometry). For the latter, one would expect a J_{PH} coupling constant of the same magnitude as in $\mathbf{P_1}$, which is not the case. Thus, $\mathbf{P_2}$ represents the only realistic geometry for the second (minor) isomer.

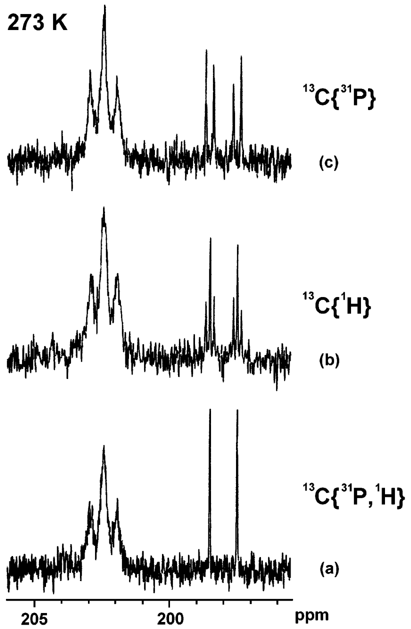


Figure 6. $^{13}C\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{13}C\{^{31}P,^1H\}$ NMR spectra at 273 K (Bruker AM250; CD_2Cl_2) of a 1/8 $Rh_4(CO)_{12}$/TPP misture after 20 min at 40 °C. Conditions: H_2, 5 bar; ^{13}CO, 5 bar; $Rh_4(CO)_{12}$, 5 mg (6.8×10^{-6} mol); TPP, 17 mg (5.4×10^{-5} mol); CD_2Cl_2, 1 mL.

The structures of **1a** and **1b** were unambiguously established by NMR using a mixture of H_2 and ^{13}CO-enriched atmosphere. The ^{13}C NMR spectrum (CO region; 273 K) of the mixture under a H_2 (5 bar) + ^{13}CO (5 bar) atmosphere is displayed in Figure 6, where various combinations of ^1H and ^{31}P decoupling experiments are shown. The broad triplet at 202.4 ppm, which is not greatly affected by ^1H and ^{31}P decoupling, is ascribed to **2**. The double doublet of triplets at 198 ppm is consistent with the $HRh(CO)_2(TPP)_2$ formulation for **1**. At 193 K the $^{13}C\{^{31}P,^1H\}$ spectrum (Figure 7) shows that the doublet at 198 ppm evolves to two main doublets of the same intensity at 200.1 ppm ($\mathbf{1a_1}$) and 198.6 ppm ($\mathbf{1a_2}$) and a weak doublet at 195.6 ppm (**1b**). At the same temperature the $^{13}C\{^{31}P\}$ spectrum shows that the doublet $\mathbf{1a_2}$ evolves to a doublet of doublets ($J_{RhC} = 50$ Hz; $J_{HC} = 18$ Hz), the other signals not being significantly affected by coupling with the hydride ligand. Finally, in the ^{13}C NMR spectrum, the signal $\mathbf{1a_1}$ now arises as a doublet of triplets ($J_{RhC} = 75$ Hz; $J_{PC} = 30$ Hz), whereas the other signals are only slightly broadened by the coupling with the phosphorus nuclei.

Considering the structures shown in Chart 1, the signals $\mathbf{1a_1}$ and $\mathbf{1a_2}$ can be attributed to the axial and equatorial CO groups of the $\mathbf{P_1}$ geometry, respectively: i.e., to the major isomer **1a**. Moreover, for the minor isomer **1b,** the fact that the two CO ligands are only weakly coupled with the TPP and hydride ligands is also in agreement with the geometry $\mathbf{P_2}$ selected on the basis of proton NMR parameters.

The study of the ^1H and ^{31}P NMR spectra on the samples with a ^{13}CO-enriched atmosphere has also allowed determining most of the NMR parameters for the two isomers at 193 and 273 K. They are collected in Table 1.

A literature survey of the $HM(CO)_xL_{4-x}$ (x = 1, 2; M = Rh, Ir) series of complexes exhibiting a trigonal-

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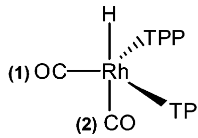
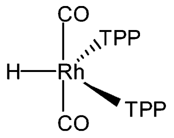
[8] *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: Weinheim, Germany, 1990.

Table 1. NMR Data for the $HRh(CO)_2(TPP)_2$ Complexes

		$HRh(CO)_2(TPP)_2$
T = 193 K	**T = 193 K**	**T = 273 K**
δ^1H = -10.16 ± 0.05 ppm	δ^1H = -9.09 ± 0.05 ppm	δ^1H = -9.92 ± 0.05 ppm
$\delta^{31}P$ = 34.2 ± 0.1 ppm	$\delta^{31}P$ = 36.3 ± 0.1 ppm	$\delta^{31}P$ = 35.3 ± 0.1 ppm
$\delta^{13}C_1$ = 200.1 ± 0.1 ppm	$\delta^{13}C$ = 195.6 ± 0.1 ppm	$\delta^{13}C$ = 198.0 ± 0.1 ppm
$\delta^{13}C_2$ = 198.6 ± 0.1 ppm		
J(H-P) = 15.5 ± 0.5 Hz	J(H-P) = 45 ± 1 Hz	J(H-P) = 7.5 ± 0.5 Hz
J(H-Rh) = 1 Hz	J(H-Rh) = 13 ± 1 Hz	J(H-Rh) = 2.0 ± 0.5 Hz
J(P-Rh) = 135 ± 1 Hz	J(P-Rh) = 112 ± 1 Hz	J(P-Rh) = 130 ± 1 Hz
$J(C_2\text{-}Rh)$ = 50 ± 1 Hz	J(C-Rh) = 70 ± 1 Hz	J(C-Rh) = 63 ± 1 Hz
$J(C_1\text{-}Rh)$ = 75 ± 1 Hz		
$J(C_2\text{-}P)$ = 1 Hz	J(C-P) = 5 Hz	J(C-P) = 9 ± 1 Hz
$J(C_1\text{-}P)$ = 30 ± 1 Hz		
$J(C_2\text{-}H)$ = 43 ± 1 Hz	J(C-H) = 1 Hz	J(C-H) = 18 ± 1 Hz
$J(C_1\text{-}H)$ = 2 Hz		

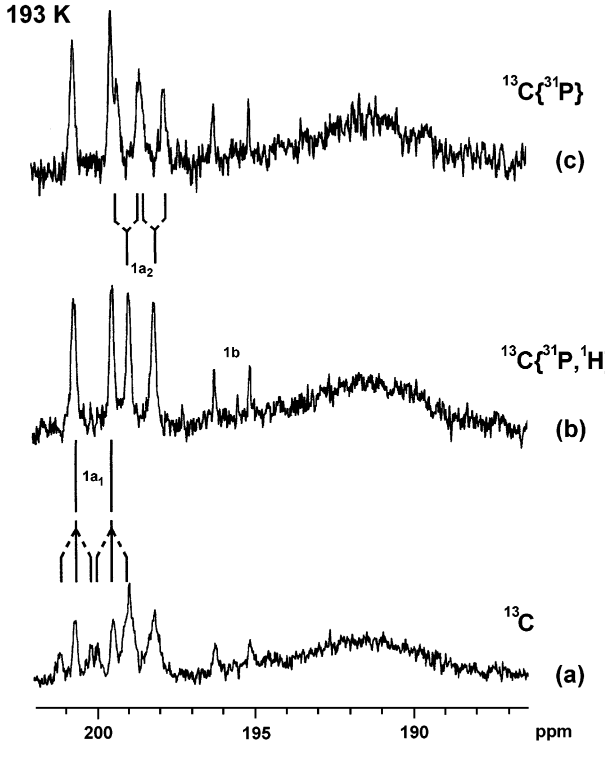


Figure 7. ^{13}C NMR spectra at 193 K (Bruker AM250 (62.896 MHz; CD_2Cl_2) of a 1/8 $Rh_4(CO)_{12}$/TPP mixture after 20 min at 40 °C. Conditions: H_2, 5 bar; ^{13}CO, bar; $Rh_4(CO)_{12}$, 5 mg (6.8×10^{-6} mol); TPP, 17 mg (5.4×10^{-5} mol); CD_2Cl_2, 1 mL.

bipyramidal arrangement[8] revealed that the present observation of a hydrido ligand in an equatorial position is unprecedented. In the case of $x = 2$ only the two structures $H_aM(CO)_{2(a,e)}L_{2(e,e)}$ and $H_aM(CO)_{2(e,e)}L_{2(a,e)}$ have been observed by spectroscopic techniques.[9-11] Moreover, the $H_aM(CO)_{2(e,e)}L_{2(a,e)}$ structure has been ascertained by an X-ray structure determination in the case where M = Ir and L = $P(p\text{-tolyl})_3$.[12] In the complex $H_aRh(CO)_{2(a,e)}(PPh_3)_{2(e,e)}$,[9] the J_{PH} value of 14 Hz compares well with the value found for **1a** (15.5 Hz), and it is noteworthy that the J_{PH} value for **1b** (45 Hz) has a value intermediate between the value observed for **1a** and the value found in the $H_aRh(CO)_{2(a,e)}(PPh_3)_{2(a,e)}$ complex for the coupling constant with the phosphorus atom in a trans position (99 Hz). This is consistent with a H−Rh−P angle value of around 120° for the complex **1b**, which supports our hypothesis about the structure of **1b** with the hydride ligand in the equatorial plane.

In both isomers, the two TPP ligands are in equatorial positions. This corresponds apparently to the highest steric crowding around the metal. Modeling studies based on theoretical calculations using the CACHE program[13] effectively indicate that the geometry with the two TPP ligands in axial positions lies at lower energy than those with the two TPP groups in the equatorial plane. In addition, we have to consider a possible stabilizing effect which is not taken into account by the program: the π stacking[14] of the phenyl and phosphole ring when the two TPP ligands are in the equatorial plane probably favors the occurrence of the two isomers we have observed.

In conclusion, the present account provides unambiguous spectroscopic evidence for the first example of a $HRh(CO)_2L_2$ isomer with the hydride ligand in the

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(9) Brown, J. M.; Canning, L. R., Kent, A. G.; Sidebottom, P. J. *J. Chem. Soc., Chem. Commun.* **1982**, 721.

(10) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1597.

(11) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5271.

(12) Ciechanowicz, M.; Skapski, A. C.; Troughton, P. G. H. *Acta Crystallogr., Sect. A* **1969**, *25*, S172.

(13) CACHE Molecular Modeling system Package 3.7.

(14) Castonguay, L. A.; Rappé, A. K.; Casewit, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 7183.

equatorial plane of the trigonal-bipyramidal structure. This type of isomer was previously considered as a possibility for the $HIr(CO)_2(PPh_3)_2$ complexes[15] but finally rejected in the case of $H_aIr(CO)_{2(e,e)}L_{2(a,e)}$ on the basis of a more comprehensive variable-temperature NMR study.[11] The authors of that study had expressed the feeling that any isomer possessing the hydride ligand in an equatorial position would be of much higher energy than those with an axial hydride ligand. Our observations now provide evidence that this is not systematically the case and that the stereoelectronic properties of the phosphorus ligand can eventually stabilize isomers with the hydride ligand in the equatorial plane.

Experimental Section

Reagents. All the gases used were of high purity from Air Liquide Co. ^{13}CO (99.37%) was furnished by Euriso-top and D_2 (99.7%) by Messer Griesheim.

All solvents were dried, distilled, and deaerated before use according to the literature procedures. They were stored under N_2 or Ar after distillation. The 1,2,5-triphenyl-1*H*-phosphole was supplied by F. Mathey[16] or synthesized according to the method of Lukas et al.[17] Triethylamine (Janssen Chimica 99%) was distilled over sodium and kept under argon. The catalytic precursor $RhCl(CO)(TPP)_2$ was prepared according to the method developed by Neibecker and Réau[1b] from bis(μ-chloro)-tetracarbonyldirhodium.[18]

Dodecacarbonyltetrarhodium, $Rh_4(CO)_{12}$, was prepared according to the method of Cattermole et al.[19] and kept under carbon monoxide at low temperature.

General Procedure. For each experiment, the precursor $RhCl(CO)(TPP)_2$ (or a 1/8 $Rh_4(CO)_{12}$/TPP mixture) was put in a Fischer−Porter reactor. After several vacuum−argon cycles, the solvent (deuterated toluene or dichloromethane) and the desired liquid reactants (styrene, triethylamine) were added (precision syringes under flushed argon). After the system was charged to the desired pressures of gaseous reactants (CO, ^{13}CO, H_2), the reaction mixture was stirred vigorously with a magnetic stirrer and heated at the required temperature in a thermostated bath. After 10 min, the mixture was cooled with an ice bath, depressurized, and transferred into the NMR tube. In the case of the NMR pressure experiments, the reaction mixture was transferred in a heavy-walled 5 mm o.d. NMR tube (fitted with a valve) and pressurized at a work pressure with the desired gaseous reactants.

NMR Spectra. The ^1H, ^{31}P, and ^{13}C spectra were recorded at different temperatures on Bruker WM250, AM250, and AMX400 spectrometers. Chemical shifts are reported in ppm (δ) relative to solvent proton (C_6D_5H, 7.27 ppm; $CHDCl_2$, 5.33 ppm) for ^1H, 85% H_3PO_4 in D_2O solution (external reference) for ^{31}P, and ^{13}C of the solvent ($^{13}CD_2Cl_2$, 53.6 ppm) for ^{13}C NMR, respectively.

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