

Synthesis and Characterization of New Water-Soluble Hydrides of Ru^{II}: A Step towards Dinitrogen Activation?

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Dedicated to Professor *André E. Merbach* on the occasion of his 65th birthday, in recognition of his fundamental contribution to the coordination chemistry of the lanthanide and transition-metal ions

The basic aqueous coordination chemistry of Ru^{II} has been studied using the catalytically important TPPTS phosphine (TPPTS = trisodium salt of 3,3',3''-phosphinetriylbenzenesulfonic acid) and small gas molecules (H₂, CO, N₂) as ligands. As a result, new water-soluble ruthenium mixed hydride complexes, presumably key species in many industrial catalytic processes, have been formed and identified. The Ru^{II} mixed hydrides were synthesized, and their formation was followed *in situ* by multinuclear NMR spectroscopy, pressurizing aqueous Ru^{II}–TPPTS systems with H₂ and CO gas in sapphire NMR tubes. The formation equilibrium of these complexes is highly dependant on the temperature and the gas pressures. Under 50 atm of N₂, the unique [RuH(CO)(N₂)(TPPTS)₂(H₂O)]⁺ complex has been identified, which could be the first step toward dinitrogen activation.

Introduction. – Interest in the chemistry water-soluble complexes of Ru^{II} has increased over the past few years due to potential applications in catalysis [1] and medicine [2]. Ru^{II} aqua ions show an ideal compromise between ‘softness and acidity’ of coordinated H₂O and back-bonding into π* orbitals of carbon π ligands [3]. Moreover, as H₂O is a ‘weak’ ligand in these aqua ions, it can easily be replaced by many other ligands, which introduce modifications in the coordination chemistry at the Ru^{II} center.

Aebischer et al. [4] reported that pressurizing the [Ru(H₂O)₆]²⁺ solution with H₂ results the formation of the dihydrogen pentaqua Ru^{II} complex. They also showed that, in presence of D₂O, an exchange between the D of the solvent and the coordinated H of the dihydrogen complex occurs. *Merbach* and co-workers [5] characterized two H₂O-soluble dinitrogen complexes of the Ru^{II} by multinuclear NMR spectroscopy. Indeed, pressurizing a solution of [Ru(H₂O)₆]²⁺ with N₂ leads to the formation of the dinitrogen pentaqua complex and to the [Ru(H₂O)₅(N₂)Ru(H₂O)₅]⁴⁺ dimer. As N₂ is known for its inertness, these results showed a promising step towards the further functionalization or activation pathways. In presence of CO [6], the Ru^{II} aqua ion can be transformed into the monocarbonyl, *cis*-dicarbonyl (as the *trans*-complex is strongly disfavored by the π-acceptor properties of CO) and *fac*-tricarbonyl complexes.

Several reports have been published concerning the catalytic properties of [Ru(H₂O)₆]²⁺ in reactions with olefins as well. Under ethylene pressure [7] of [Ru(H₂O)₆]²⁺, ethylene dimerization occurred, and several isomers of butene (except the isobutene) have been isolated.

The coordination properties of Ru^{II} can be modified with different phosphine ligands. However, only few phosphines are found among the ligands studied in substitution reactions with [Ru(H₂O)₆]²⁺, despite the important role of some H₂O-soluble tertiary phosphines in catalytic industrial application. With the TPPTS ligand (TPPTS = the trisodium salt of 3,3',3''-phosphinetriylbenzenesulfonic acid, 'trisodium salt of tris(*meta*)monosulfonated)triphenylphosphine'), [Ru(TPPTS)₂(H₂O)₄]²⁺ [8], [Ru(H)₂(TPPTS)₄] [9], and [HRuCl(CO)(TPPTS)₃] [10] have been isolated and characterized.

As stated above, [Ru(H₂O)₆]²⁺ showed the abilities to coordinate small molecules and acted as a catalyst in the dimerization reaction of olefins. So, it has been decided to focus on the study of the abilities of the Ru^{II} aqua complex to activate small molecules such as H₂, CO, or N₂. We report here the synthesis and characterization of new H₂O-soluble hydride Ru^{II} species, including a complex having both dinitrogen and hydride ligands present in the first coordination sphere.

Result and Discussion. – *Preliminary Tests.* The dihydrogen aqua Ru^{II} complex, [Ru(H₂)(H₂O)₅]²⁺, is readily prepared, detected, and characterized under a H₂ pressure of [Ru(H₂O)₆]²⁺, using NMR sapphire-tube techniques. Pressurizing with N₂ gas, the dihydrogen aqua Ru^{II} complex showed no reaction between nitrogen and the dihydrogen aqua complex, as monitored by multinuclear (¹H, ¹⁷O, and ¹⁵N) NMR spectroscopy. When the reverse experiment is carried out, dihydrogen can substitute the nitrogen in [Ru(N₂)(H₂O)₅]²⁺, and finally the dihydrogen aqua complex formed. This was predicted by *Aebischer et al.* reporting the weakness of the Ru–N₂ bond in Ru^{II} aqua complexes. Pressurizing a solution of *cis*- and *trans*-[Ru(TPPTS)₂(H₂O)₄]²⁺ with N₂ gas shows no observable reaction. Aware of these facts, we started to investigate modified Ru^{II} aqua complexes, which must be able to coordinate both N₂ and H₂.

Synthesis and Study of [RuH(TPPTS)₂(H₂O)₃]⁺. A solution of [Ru(TPPTS)₂(H₂O)₄]²⁺ is pressurized overnight with H₂ at 100 atm at room temperature in a sapphire NMR tube. The initial deep orange color became pale. The reaction was followed by ¹H-NMR spectroscopy. In aqueous solution, in the presence or absence of excess TPPTS, only two *triplet* signals appeared at –9.7 and –9.6 ppm in the ¹H-NMR spectra (*Fig. 1*) after 8 h. These two signals correspond to two isomers of the complex [RuH(TPPTS)₂(H₂O)₃]⁺, as confirmed by ³¹P-NMR. As shown in *Fig. 2*, the two TPPTS ligands can be in *trans* (*OC-6-12*) [11] or in *cis* (*OC-6-22*) position to each other in the complex. It is not surprising that the ²*J*(H,P) in both complexes are 38 Hz, as in both complexes the two TPPTS ligands are in *cis*-position relative to the hydride. No dihydride or dihydrogen complexes could be detected. The activation of H₂ is heterolytic *via* an *edge-on* mode and produces a proton and a hydride. A 2D-NMR-HETCORR ¹H/³¹P spectrum was recorded, and the hydride signals at –9.6 and –9.7 ppm in the ¹H-NMR spectra correspond to the 55-ppm and 51-ppm ³¹P signals in 161-MHz ³¹P-NMR, respectively. According to the literature [12], it is obvious that *OC-6-12* and *OC-6-22* [RuH(TPPTS)₂(H₂O)₃]⁺ correspond to –9.6 and –9.7 ppm in ¹H-NMR spectra, respectively. At room temperature, the ratio between *OC-6-22* and *OC-6-12* is 75:25 (*Fig. 1*), and at 343 K ratio between them evolves to 60:40. Even when *OC-6-22* is the major isomer, the complex behaves like [Ru(TPPTS)₂(H₂O)₄]²⁺ [8], with the temperature the concentration of the *OC-6-12* isomer increases.

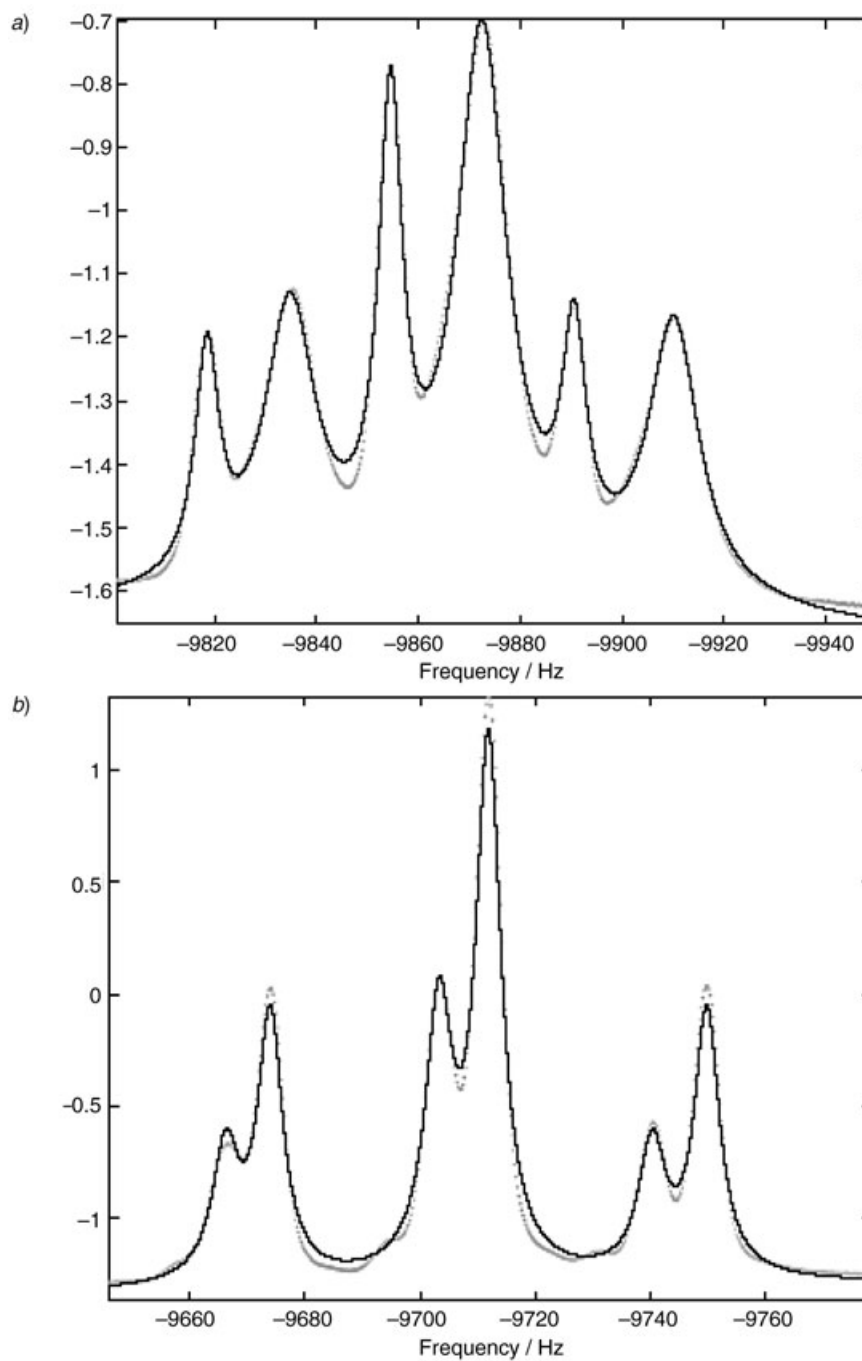


Fig. 1. Measured (dotted, grey) and calculated (black) 400-MHz $^1\text{H-NMR}$ spectra of OC-6-22 and OC-6-12 $[\text{RuH}(\text{H}_2\text{O})_3(\text{TPPTS})_2]^+$ in the hydride signal region ($\delta = -9.7$ and -9.6 ppm, triplets) at 298 K [ratio 75:25] (a) and 343 K [ratio 60:40] (b). $^2J(\text{H,P}) = 38$ Hz for both complexes.

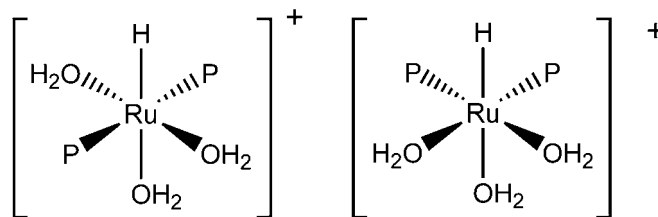


Fig. 2. OC-6-12 (left) and OC-6-22 (right) $[RuH(H_2O)_3(TPPTS)_2]^+$ isomers

Furthermore, as the solvent was D_2O , an exchange between D of the water and the hydride occurred. Unfortunately, as in the case of $[Ru(TPPTS)_2(H_2O)_4]^{2+}$, pressurizing the solution of $[RuH(TPPTS)_2(H_2O)_3]^+$ with N_2 gas showed no reaction.

Synthesis and Study of $[RuH(CO)(TPPTS)_2(H_2O)_2]^+$. Even though CO has a very poor dipolar moment (0.112 D) and is not considered as a strong base, it forms strong bonds with the transition metals. This is due to the capacity of CO to be a good σ -donor and π -acceptor ligand. A solution of $[RuH(TPPTS)_2(H_2O)_3]^{2+}$ was pressurized overnight with CO and H_2 (1:1; total pressure is 100 atm) at room temperature in a sapphire NMR tube, the previously orange solution turned in a very pale yellow one. 1H -NMR Spectra showed deshielding of the -9.6 and -9.7 ppm hydride signals to -6.44 and -6.45 ppm, respectively (Fig. 3). No other hydride complexes were found,

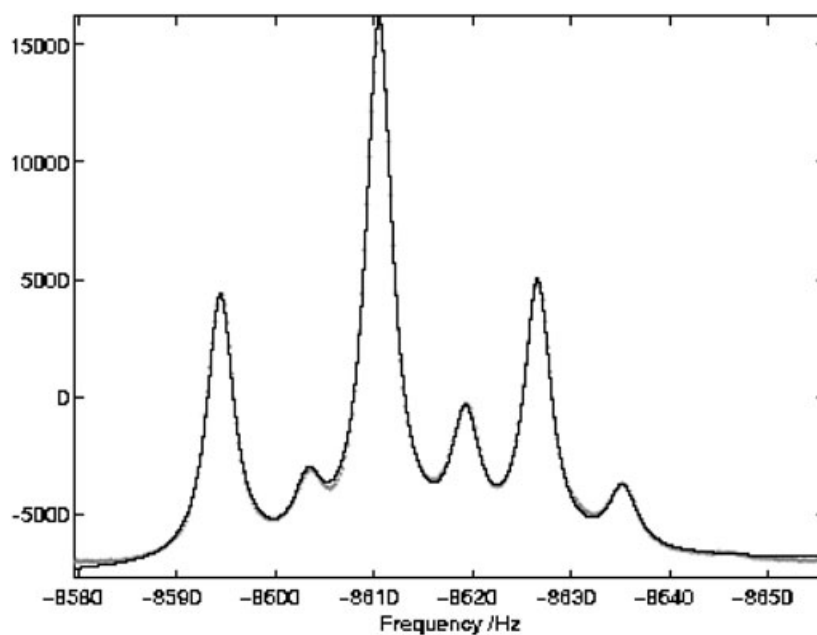


Fig. 3. Measured (dotted, grey) and calculated (black) 400-MHz 1H -NMR spectra of OC-6-23 and OC-6-13 $[RuH(CO)(TPPTS)_2(H_2O)_2]^+$ in the hydride signal region ($\delta = -6.44$ and -6.45 ppm, triplets) at 298 K [ratio 20:80]

and the *triplets* indicate the $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_2]^+$ complex. It means that the TPPTS are equivalent each other for both cases so CO is coordinated in *trans*-position to the hydride. Indeed, if CO were in *cis*-position to the hydride, TPPTS would not be equivalent ($^2J(\text{H,P}) = 18 \text{ Hz}$ for both complexes). The 2D-HETCORR $^1\text{H}/^{31}\text{P}$ -NMR correlated spectrum shows that the signals at -6.44 and -6.45 ppm in the ^1H -NMR spectra correspond to 36.4 and 26.3 ppm in ^{31}P -NMR, respectively. The hydride signal of the *trans*- $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_3]^+$ complex (OC-6-13) appears at -6.44 ppm , and the hydride signal of the *cis*-isomer, (OC-6-23) appears at -6.45 ppm . This time, it is OC-6-13 which is present in higher concentration at room temperature, the ratio between the two isomers (OC-6-23/OC-6-13) is 25 : 75.

Synthesis and Study of $[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$. Pressurizing a solution of $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_2]^+$ with N_2 gas caused the displacement of the hydride chemical shifts to lower field in the ^1H -NMR spectra. Contrary to the other complexes, only one hydride signal could be detected, only one *triplet* at -4.17 ppm was present in the ^1H -NMR spectra, showing only one complex is present in overwhelming majority. To remove any doubts over the CO isomer complexes, two experiments have been carried out. First, ^{13}C was pressurized into the solution. The ^1H -NMR spectra revealed appearance of ^{13}C satellite signals, and the signal appeared as a *pseudo-quintet*. After fitting the spectra by NMRICMA (Fig. 4), it revealed $^2J(\text{H,CO}) = 36$ and $^2J(\text{H,P}) = 18 \text{ Hz}$, and ^{13}C -NMR spectra confirmed the ^1H -NMR results. Second, the

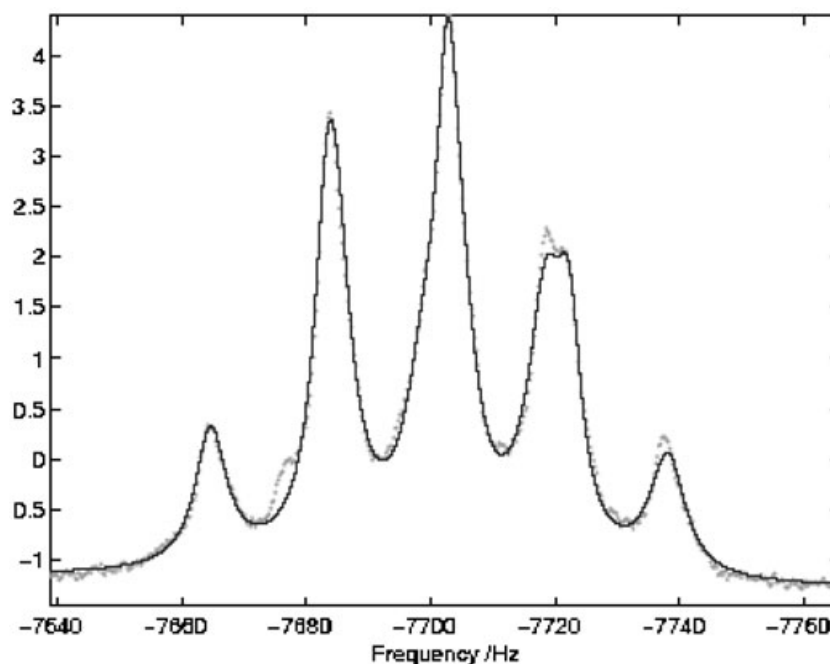


Fig. 4. Measured (dotted, grey) and calculated (black) 400-MHz ^1H -NMR spectra of OC-6-14 $[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$ in the hydride signal region at 298 K after ^{13}C exchange. $^2J(\text{H,CO}) = 36 \text{ Hz}$, $^2J(\text{H,P}) = 18 \text{ Hz}$.

pressurization of $^{15}\text{N}_2$ into this system leads to the appearance of $^{15}\text{N}_2$ satellite signals in ^1H -NMR spectra (Fig. 5). The spectra simulation by gNMR 4.1 shows the satellite signals due to $^{15}\text{N}_2$ are in fact *doublets* with $^2J(\text{H,N}) = 6$ Hz. The *doublet* signals show that N_2 is coordinated to the complex through an *end-on* mode, and as the *triplet* revealed, the two TPPTS are still equivalent. Thus, N_2 is coordinated in a *cis*-position to the hydride. With all these NMR data, we propose the structure shown in Fig. 6 for $[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$. This complex contains several different types of

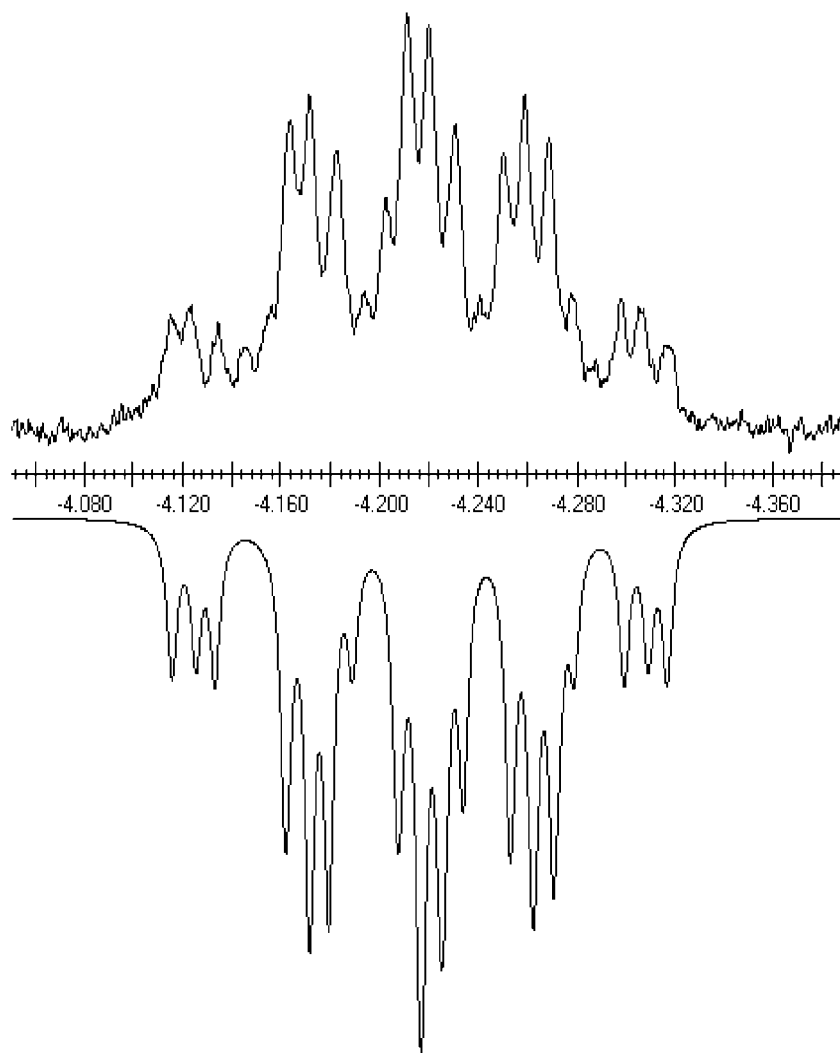


Fig. 5. Measured (top) and calculated (bottom) 400-MHz ^1H -NMR spectra of OC-6-14 $[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$ in the hydride signal region ($\delta = -4.21$ ppm, multiplet) 298 K, enriched by ^{13}CO and $^{15}\text{N}_2$. $^2J(\text{H,CO}) = 36$, $^2J(\text{H,P}) = 18$, and $^2J(\text{H,N}) = 6$ Hz.

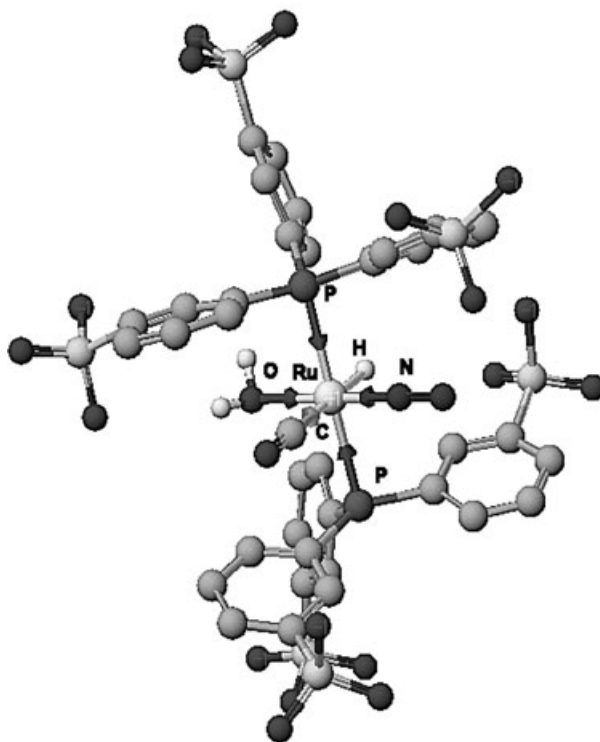


Fig. 6. Proposed structure of OC-6-14 $[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$

ligands. Although the hydride is not reactive at room temperature, it is a promising result and might provide a step to new functionalization and activation pathway of dinitrogen and other small molecules.

Conclusions. – Nitrogen gas remains non-reactive toward complexes such as $[\text{Ru}(\text{H}_2)(\text{H}_2\text{O})_5]^{2+}$ or $[\text{Ru}(\text{TPPTS})_2(\text{H}_2\text{O})_4]^{2+}$. The modification of the first coordination sphere of the Ru^{II} aqua complex allowed the coordination of both N_2 and hydride at the same time. The synthesis of new hydride Ru^{II} species can be easily carried out by the pressurization of H_2 into a solution of $[\text{Ru}(\text{TPPTS})_2(\text{H}_2\text{O})_4]^{2+}$ using simple sapphire NMR tube techniques. The mixed hydride–carbonyl complexes are synthesized by pressurizing CO/H_2 into a $[\text{Ru}(\text{TPPTS})_2(\text{H}_2\text{O})_4]^{2+}$ solution. The two isomers of the mixed carbonyl complex, OC-6-13 and OC-6-23, $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_2]^+$ have been fully characterized by NMR spectroscopy. The equilibrium between the two isomers is temperature-dependant, which is interesting in view of controlling the geometry during reaction. N_2 can replace a H_2O in $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_2]^+$, it is able to coordinate to this complex to form $[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$. Even the hydride did not show any reactivity with the ligands present in the first coordination sphere at room temperature, this might prove to be the first step to new hydrogenation,

hydroformylation, and dinitrogen catalytic activation. Further experiments are in progress.

Experimental Part

General. $[\text{Ru}(\text{H}_2\text{O})_6](\text{tos})_2$ ($\text{tos}^- = p$ -toluenesulfonate anion) was prepared according to the literature [13] and recrystallized from an aqueous solution of 1.2M TsOH. H_2 (Carbagas; 99.97%), CO (Carbagas; 99.9%), TPPTS (*m*-trisulfonated triphenylphosphine trisodium salt, Rhône-Poulenc; 96%) N_2 (Carbagas; 99.9%), ^{13}C O (99% ^{13}C , Cambridge Isotope Laboratories), and $^{15}\text{N}_2$ (99% ^{15}N , Isotec) were used without further purification. Doubly distilled water was used throughout. The ^1H (^{13}C) NMR chemicals shifts are referenced to TMS and measured with respect to the Me H-atoms (Me C-atom) of tosylate, $\delta = 2.38$ ppm (22.9 ppm). The solvent for the ^1H -, ^{13}C -, and ^{31}P -NMR characterizations was 99.95% deuterated water.

$[\text{Ru}(\text{TPPTS})_2(\text{H}_2\text{O})_4]^{2+}$ (**1**), was prepared according to the procedures in [8].

$[\text{RuH}(\text{TPPTS})_2(\text{H}_2\text{O})_3]^+$ (**2**). In a sapphire NMR tube (which can support pressure up to 100 bars) [14] containing 0.5 ml of degassed D_2O , 0.1 g of $[\text{Ru}(\text{TPPTS})_2(\text{H}_2\text{O})_4](\text{tos})_2$ was dissolved. The resulting orange soln. was then pressurized under 100 bars of H_2 and shaken for 12 h at r.t. After the gas pressure was removed, the water was evaporated under vacuum, and the pale orange powder was dried under 10^{-4} bar overnight. ^1H -NMR (400 MHz, D_2O): -9.6 ppm (t , $^2J(\text{H,P}) = 38$, H of *OC*-6-12 isomer); -9.7 (t , $^2J(\text{H,P}) = 38$, H of *OC*-6-22 isomer). ^{31}P -NMR (161 MHz, D_2O): 55 (d , $^2J(\text{H,P}) = 38$, H of *OC*-6-12 isomer); 51 (d , $^2J(\text{H,P}) = 38$, H of *OC*-6-22 isomer).

$[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_2]^+$ (**3**). In a sapphire NMR tube containing 0.5 ml of degassed D_2O , 0.2 g of $[\text{RuH}(\text{TPPTS})_2(\text{H}_2\text{O})_3](\text{tos})_2$ was dissolved. The resulting pale orange soln. was then pressurized with CO/ H_2 mixture (1:1; total pressure is 100 bar) and shaken for 12 h at r.t. After the gas pressure was removed, the water was evaporated under vacuum, and the pale yellow powder was dried under 10^{-4} bar overnight. This powder contains some traces of **2**. ^1H -NMR (400 MHz, D_2O): -6.44 ppm (t , $^2J(\text{H,P}) = 17$, H of *OC*-6-13 isomer). -6.45 (t , $^2J(\text{H,P}) = 17$, H of *OC*-6-23 isomer). ^{31}P -NMR (161 MHz, D_2O): 36 (d , $^2J(\text{H,P}) = 17$, H of *OC*-6-12 isomer); 51 (d , $^2J(\text{H,P}) = 17$, H of *OC*-6-22 isomer). ^{13}C -NMR (100.62 MHz, D_2O): 189 (*m*, both isomers).

$[\text{RuH}(\text{CO})(\text{N}_2)(\text{TPPTS})_2(\text{H}_2\text{O})]^+$ (**4**). In a sapphire NMR tube containing 0.5 ml of degassed D_2O , 0.2 g of $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_3]^+$ was dissolved. The resulting pale yellow soln. was then pressurized with N_2/H_2 mixture (1:1; total pressure is 100 bar) and shaken for 12 h at r.t. After the gas pressure was removed, the water was evaporated under vacuum, and the pale yellow powder was dried under 10^{-4} bar overnight. ^1H -NMR (400 MHz, D_2O): -4.17 (*m*, $^2J(\text{H,P}) = 18$, H of *OC*-6-14 complex). ^{31}P -NMR (161 MHz, D_2O): 26 (*br. s*). ^{13}C -NMR (100.62 MHz, D_2O): 194 (*dt*, $^2J(\text{H,CO}) = 36$ $^2J(\text{P,CO}) = 12$ Hz). NMR showed the presence of some $[\text{RuH}(\text{CO})(\text{TPPTS})_2(\text{H}_2\text{O})_2]^+$ residue.

We thank the Swiss National Science Foundation and the Swiss State Secretariat for Education and Science for financial support.

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Received December 28, 2004