Aqueous Organometallic Chemistry. Synthesis and Solution Equilibria of Trisodium Carbonylchlorotris[3-(diphenylphosphino-κ*P*)benzenesulfonato]-hydridoruthenate(3−) ([RuH(Cl)(CO){*m*-(Ph_2P)−C_6H_4−SO_3Na}$_3$]) and Trisodium Aquacarbonyltris[3-(diphenylphosphino-κ*P*)benzenesulfonato]-hydridoruthenate(2−) Tetrafluoroborate(1−) ([RuH(CO)(H_2O)-{*m*-(Ph_2P)−C_6H_4−SO_3Na}$_3$] [BF_4])

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Dedicated to Professor *André E. Merbach* on the occasion of his 65th birthday, in recognition of his fundamental contributions to inorganic and coordination chemistry and catalysis

An improved procedure for the preparation of the known H_2O-soluble hydrogenation and hydroformylation catalyst, [RuH(Cl)(CO)(*m*tppms)$_3$] (*m*tppms = *meta*-monosulfonated triphenylphosphine) was developed. In contrast to the methods reported earlier, this synthesis yields the complex free of *m*tppms impurities. ^{1}H- and ^{31}P{H}-NMR measurements revealed that in aqueous solution, [RuH(Cl)(CO)(*m*tppms)$_3$] reversibly dissociated to give [RuH(CO)(H_2O)(*m*tppms)$_3$]$^+$ (*Scheme*). The equilibrium constant of this dissociation was determined as $9.8 \cdot 10^{-2}$ M at 293 K. Such a dissociation was not observed in MeOH but took place to varying degrees in MeOH/H_2O mixtures of varying composition. [RuH(CO)(H_2O)(*m*tppms)$_3$][BF_4] was also obtained on an independent synthetic route: by ligand exchange in [RuH(CO)($NCMe$)$_2$(PPh_3)$_2$][BF_4] (*Scheme*). The results may help the understanding of the mechanisms of reactions catalyzed by [RuH(Cl)-(CO)(*m*tppms)$_3$] in aqueous solutions or in aqueous–organic biphasic systems.

Introduction. – Aqueous organometallic chemistry and catalysis have shown impressive progress over the last three decades [1]. A major recent impetus of this progress originates from the aim of developing green chemical processes by replacing organic solvents with H_2O. The study of organometallic compounds in H_2O often involves the synthesis of H_2O-soluble analogs of known H_2O-insoluble organometallic complexes. For example, the exchange of the triphenylphosphine ligands in [RhCl(PPh_3)$_3$] for *m*tppms (= *m*-(Ph_2P)−C_6H_4−SO_3Na), *i.e.*, *meta*-monosulfonated triphenylphosphine, furnishes [RhCl(*m*tppms)$_3$], a hydrosoluble variant of *Wilkinson*'s catalyst [2a]. Other H_2O-soluble tertiary phosphines such as *m*tppts (3,3′,3″-phosphinidynetris[benzenesulfonic acid], *i.e.*, *meta*-trisulfonated triphenylphosphine) [2b], pta (1,3,5-triaza-7-phosphatricyclo-[3.3.1.1^{3,7}]decane, 1,3,5-triaza-7-phosphaadamantane) [2c], and the like can be used for the same purpose. However, even in the case of a strict structural analogy between the organosoluble and hydrosoluble complexes, the change of solvent for H_2O may bring about significant changes in the molecular state [3] and chemical properties – this aspect is often overlooked.

The catalytic properties of [RuH(Cl)(CO)(PPh_3)$_3$] were studied extensively by *Sánchez-Delgado* and co-workers [4]. The complex was highly active for the homogeneous hydrogenation of aldehydes and ketones. Interestingly, addition of a small amount of H_2O *accelerated* these hydrogenations. The syntheses of the cationic complexes, [RuH(CO)(H_2O)(PPh_3)$_3$][BF_4] [5] and [RuH(CO)(NCMe)$_2$(PPh_3)$_2$]-[BF_4] [6] and the catalytic properties of the latter in hydrogenation and hydroformylation reactions have also been reported.

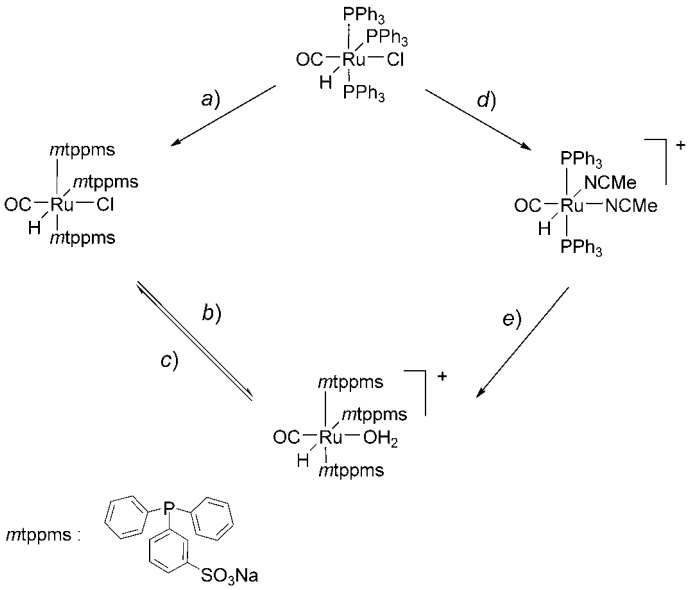
As early as in 1980, [RuH(Cl)(CO)(*m*tppms)$_3$] was prepared [7] by the prolonged reflux of a solution of $RuCl_3 \cdot$ aq and *m*tppms in 2-methoxyethanol (the method was originally disclosed by *Vaska* and *Di Luzio* for the synthesis of [RuH(Cl)(CO)(PPh_3)$_3$] [8]), however, the properties of this complex were not studied in detail. Later, it was shown by *Andriollo et al.* [9] that this synthesis afforded a mixture of compounds difficult to separate. They could obtain [RuH(Cl)(CO)(*m*tppms)$_3$] from the well-characterized [RuH(Cl)(CO)(PPh_3)$_3$] by ligand exchange in a toluene/H_2O biphasic system, and the resulting complex was used as catalyst for the hydrogenation of alkenes and unsaturated aldehydes [10]. Very recently, *Baricelli et al.* reported the synthesis of [RuH(CO)(NCMe)(*m*tppms)$_3$][BF_4] and its use as an alkene hydrogenation catalyst in aqueous-organic biphasic systems [11].

Based on our earlier observations [3][12], it seemed to us conceivable that, in aqueous solution, the neutral [RuH(Cl)(CO)(*m*tppms)$_3$] and cationic [RuH(CO)-(H_2O)(*m*tppms)$_3$]$^+$ complexes are in a mobile equilibrium which may be shifted by changes in the ligand concentration, the solution pH, and temperature. This may have an important effect on the catalytic properties observed with the same catalyst precursor [RuH(Cl)(CO)(*m*tppms)$_3$]; however, this aspect was not considered in the earlier investigations. Here, we report the synthesis of [RuH(CO)(H_2O)-(*m*tppms)$_3$][BF_4], and an improved procedure for the preparation of [RuH(Cl)-(CO)(*m*tppms)$_3$]. Results of the study on their equilibrium properties in aqueous solutions are also presented.

Results and Discussion. – Our efforts to prepare [RuH(Cl)(CO)(*m*tppms)$_3$] by the modification of known syntheses [8][13] of [RuH(Cl)(CO)(PPh_3)$_3$] proved unsuccessful. The reaction of $RuCl_3 \cdot$ aq and *m*tppms in refluxing 2-methoxyethanol [7] yielded a mixture of carbonyl(phosphine)ruthenium complexes [9]. *Ahmad et al.* prepared [RuH(Cl)(CO)(PPh_3)$_3$] by reducing $RuCl_3 \cdot$ aq with aqueous HCHO solution in the presence of PPh_3 in boiling 2-methoxyethanol [13]; the product precipitated from the reaction mixture as cream-white microcrystals. We found, however, that this method is not suitable for an efficient synthesis of [RuH(Cl)(CO)(*m*tppms)$_3$] since this compound is well soluble in the resulting 50% (*v*/*v*) H_2O/2-methoxyethanol mixture and can be isolated and purified only by a tedious workup. Another approach is the PPh_3 *vs.* *m*tppms phosphine exchange in [RuH(Cl)(CO)(PPh_3)$_3$]. The procedure of *Andriollo et al.* is based on extraction of a toluene solution of [RuH(Cl)(CO)(PPh_3)$_3$] with 6 equiv. of *m*tppms dissolved in H_2O [9][10]. Ligand exchange requires 4 h stirring at reflux temperature, during which [RuH(Cl)(CO)(*m*tppms)$_3$] transfers to the aqueous phase, from which it is isolated by the evaporation of the solvent. This method is not completely satisfying either since the excess of *m*tppms remains in the H_2O phase and is found in the product after evaporation of the aqueous phase to dryness.

After screening several solvents and solvent mixtures, we found that both $[RuH(Cl)(CO)(PPh_3)_3]$ and *m*tppms are sufficiently soluble in a THF/$CHCl_3$ 1:1 mixture, while $[RuH(Cl)(CO)(mtppms)_3]$ precipitates from this solvent. With this solvent mixture, the ligand exchange takes place in a homogeneous solution and, consequently, low temperature (40°) and less sulfonated phosphine are sufficient to make the reaction complete (see *Scheme*). Due to the suitable solubilities, the excess of *m*tppms remains in solution, and the product is virtually free of excess phosphine and phosphine oxide.

Scheme 1. *Synthetic Routes for the Preparation of* $[RuH(CO)(H_2O)(mtppms)_3]^+$



a) *m*tppms, THF/$CHCl_3$ 1:1 (*v*/*v*), 40°. *b*) H_2O, r.t. *c*) NaCl, r.t. *d*) MeCN, Na[BF_4], reflux. *e*) *m*tppms, H_2O, THF/$CHCl_3$ 2:1 (*v*/*v*), 40°.

The ^1H- and $^{31}P\{H\}$-NMR spectra of $[RuH(Cl)(CO)(mtppms)_3]$, recorded in CD_3OD solution, are in accord with the earlier data of *Andriollo et al.* The high-field resonance of the Ru–H proton appears at $\delta(H)$ −7.20 as a *dt* ($^2J(H,P_a) = 24.1$ Hz, $^2J(H,P_b) = 105.0$ Hz), while the ^{31}P signals are observed at $\delta(P)$ 40.5 (*d*), and 14.5 (*t*) ($^2J(P,P) = 14.5$ Hz). These data unambiguously show that the complex has an octahedral geometry with two P-atoms (P_a) *cis* to the hydrido ligand and with one (P_b) in the *trans* position.

Interestingly, the NMR chemical shifts change drastically in H_2O, however, the pattern of the signals remain the same as before. The hydrido ligand now resonates at $\delta(H)$ −7.89 (*dt*), the P-signals appear at $\delta(P)$ 41.0 (*d*) and 22.5 (*t*), while the signals at $\delta(P)$ 40.5 and 14.5 can hardly be distinguished from the baseline. At room temperature, both the ^1H and the ^{31}P resonances are remarkably sharp showing the lack of exchange processes. In H_2O/CD_3OD mixtures of *increasing* H_2O concentration, the ^{31}P signals at $\delta(P)$ 40.5 and 14.5 are gradually replaced by the ones at $\delta(P)$ 41.0 and 22.5, and in H_2O/

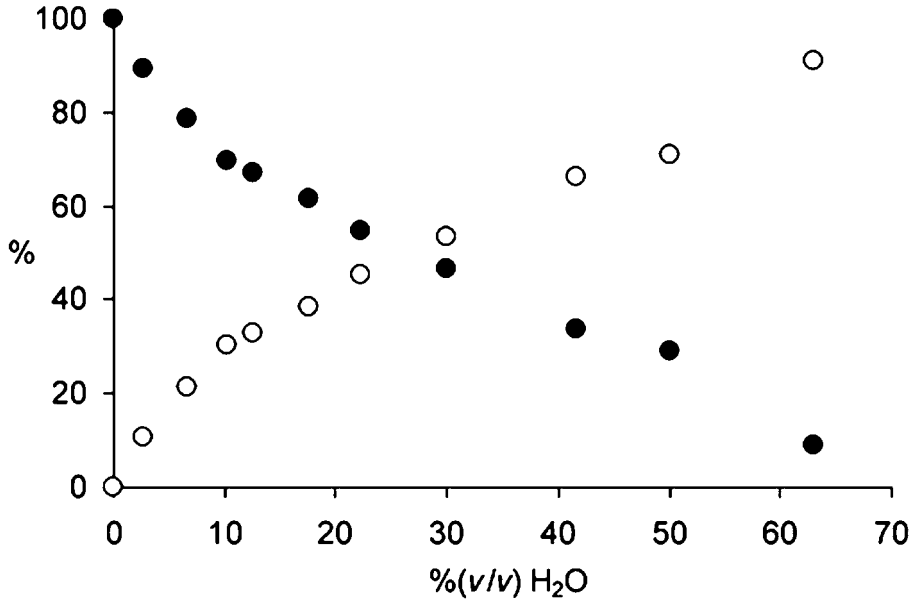


Fig. 1. *Dissociation of [RuH(Cl)(CO)(*m*tppms)$_3$] in CD_3OD/H_2O mixtures as a function of the H_2O concentration.* [RuH(Cl)(CO)(*m*tppms)$_3$], ●; [RuH(CO)(H_2O)(*m*tppms)$_3$]$^+$, ○; [Ru] = $2.21 \cdot 10^{-5}$ M, 25.0°.

CD_3OD 1:1, only 30% of their original intensity can be detected (*Fig. 1*). This phenomenon has not been reported earlier.

It seemed reasonable to us that the spectral changes can be caused by the electrolytic dissociation of the original complex, as shown in the *Scheme* (*Step b*).

It was found, accordingly, that addition of Cl^- to aqueous solutions of [RuH(Cl)(CO)(*m*tppms)$_3$] led to the reappearance of the original spectrum of this neutral species (*Step c*). The spectra were recorded at various Cl^- concentrations, and the relative amounts of [RuH(Cl)(CO)(*m*tppms)$_3$] and [RuH(CO)(H_2O)(mtppms)$_3$]$^+$ were calculated from the integrated intensities of the $^{31}P\{H\}$-NMR signals. The data are shown on *Fig. 2*. These measurements allowed the calculation of the dissociation constant as $9.8 \cdot 10^{-2}$ M at 293 K. It is to be noted that in these experiments, the ionic strength varied with the increasing Cl^- concentration; nevertheless, this dissociation constant gives a fairly good description of the distribution of [RuH(Cl)(CO)(*m*tppms)$_3$] and [RuH(CO)(H_2O)(*m*tppms)$_3$]$^+$ in Cl^--containing aqueous solutions. It is also remarkable that, in contrast to the general observations on triphenylphosphine complexes in organic solvents, in this case, it is the Cl^- and not one of the phosphine ligands which dissociates and leaves behind a coordination site occupied by a loosely bound solvent molecule.

[RuH(Cl)(CO)(*m*tppms)$_3$] was applied [10] for the hydrogenation of *trans*-cinnamaldehyde; however, the complex showed reasonable activities only at elevated temperatures (80–120°). Therefore, we examined the temperature dependence of the dissociation equilibrium by variable temperature NMR measurements. For this purpose, we choose H_2O/CD_3OD 1:4 (*v*/*v*) as solvent in which the relative amount

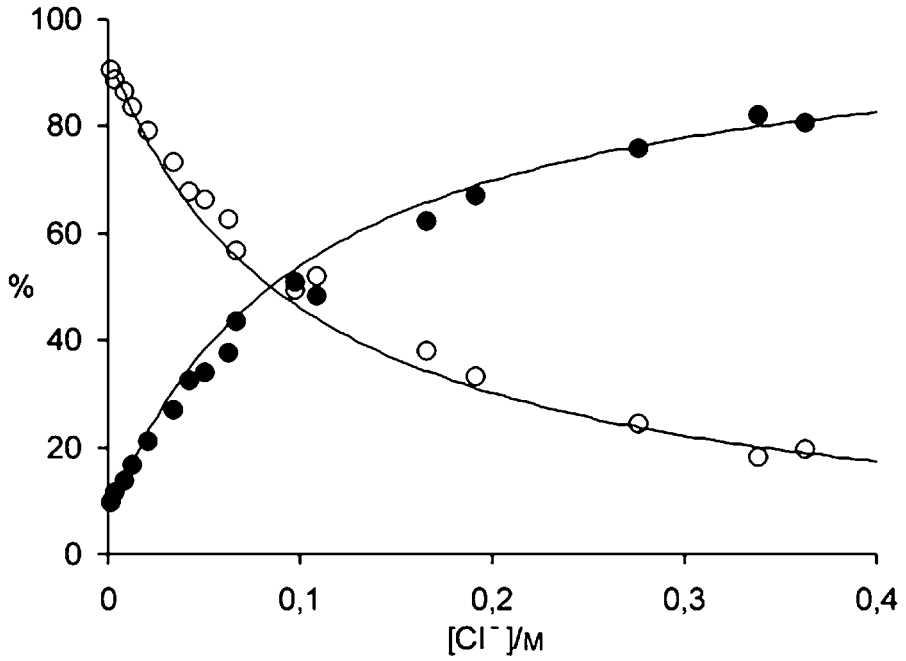


Fig. 2. *Relative concentrations of [RuH(Cl)(CO)(*mtppms*)$_3$]* (●) *and [RuH(CO)(H$_2$O)(*mtppms*)$_3$]$^+$* (○) *as a function of the concentration of* added *chloride.* [Ru] = $2.05 \cdot 10^{-5}$ M, H_2O/CD_3OD 6:1 (*v*/*v*), 25.0°.

of the undissociated complex is *ca.* 60% at room temperature. The results are shown in *Fig. 3*. Although, with this solvent mixture, the highest temperature of the measurements was only 60°, it is clearly seen that both the extent of dissociation and the rate of the phosphine exchange processes are increased considerably. With the increase in temperature, the $^{31}P\{H\}$-NMR signals of $[RuH(CO)(H_2O)(m\text{tppms})_3]^+$ become dominant and remain sharp. Conversely, the signals of $[RuH(Cl)(CO)(m\text{tppms})_3]$ loose intensity and largely broaden. It is rather safe, therefore, to say that in aqueous solutions at elevated temperatures, it is the cationic $[RuH(CO)(H_2O)(m\text{tppms})_3]^+$ complex which should be considered as the true catalyst or immediate catalyst precursor and that $[RuH(Cl)(CO)(m\text{tppms})_3]$ has no catalytic role under such conditions. In addition, it should be mentioned that the temperature effect (between these limits) is reversible as shown by the spectra of solutions cooled back to 298 K (*Fig. 3*).

To verify the assumption of Cl^- dissociation by an independent synthetic method, we prepared $[RuH(CO)(H_2O)(m\text{tppms})_3]^+$ from a halide-free precursor, too. To this end, the known cationic MeCN complex, $[RuH(CO)(NCMe)_2(PPh_3)_2][BF_4]$ [6] was treated with *m*tppms in THF/$CHCl_3$ 2:1, containing a small amount of H_2O. A slow ligand exchange took place yielding a cream-white solid. A *MeOH solution* of this product showed the same NMR features (^{1}H-NMR (CD_3OD): δ −7.89 (*dt*), $^2J(H,P_a) = 25.5$ Hz, $^2J(H,P_b) = 102.3$ Hz; $^{31}P\{H\}$-NMR (CD_3OD): δ −41.0 (*d*), 22,5 (*t*), $^2J(P,P) = 15.0$ Hz) as *H_2O solutions* of $[RuH(Cl)(CO)(m\text{tppms})_3]$. It can be

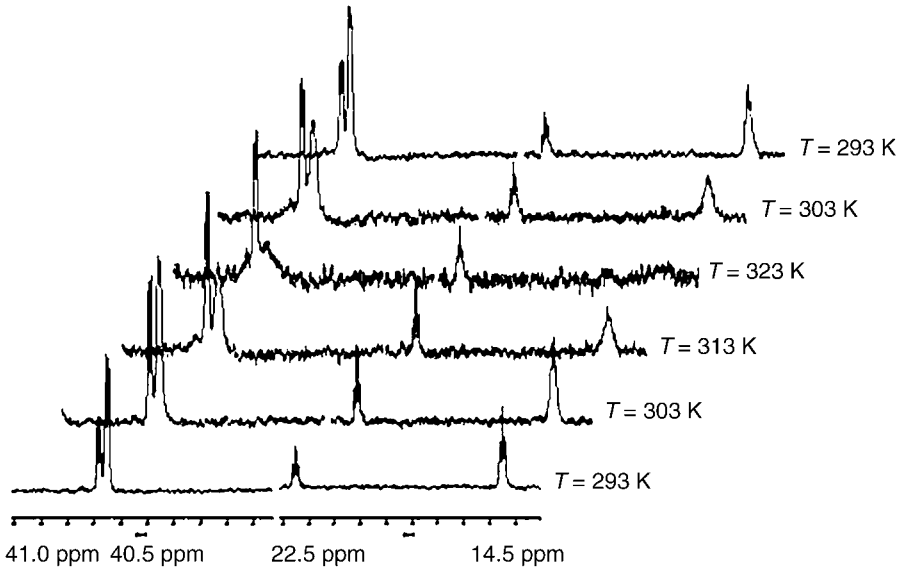


Fig. 3. *Effect of the temperature on the dissociation of [RuH(Cl)(CO)(*m*tppms)$_3$] as shown by the variable-temperature ^{31}P-NMR spectra.* [RuH(Cl)(CO)(*m*tppms)$_3$]: δ(P) 14.5 (*t*), 40.5 (*d*); [RuH(H$_2$O)(CO)(*m*tppms)$_3$]$^+$: δ(P) 22.5 (*t*), 41.0 (*d*). [Ru] = $1.84 \cdot 10^{-5}$ M, H$_2$O/CD$_3$OD 1:4 (*v*/*v*), 25.0°.

concluded that replacement of the NCMe and PPh$_3$ ligands led to the formation of [RuH(CO)(H$_2$O)(*m*tppms)$_3$]$^+$, furthermore, this compound is identical to what is formed from [RuH(Cl)(CO)(*m*tppms)$_3$] in aqueous solution.

Baricelli et al. synthesized [RuH(CO)(NCMe)(*m*tppms)$_3$][BF$_4$] by refluxing [RuH(Cl)(CO)(*m*tppms)$_3$] in MeCN in the presence of Na[BF$_4$] [11]. Although no *m*tppms was added to the reaction mixture, the authors note that their starting [RuH(Cl)(CO)(*m*tppms)$_3$] complex might have contained some *m*tppms impurity due to the method of its preparation [9][10] as discussed above. This makes a noticable difference. When we repeated the published procedure with pure [RuH(Cl)-(CO)(*m*tppms)$_3$] obtained by our method (that is with no *m*tppms excess), the single product of the reaction was [RuH(CO)(NCMe)$_2$(*m*tppms)$_2$]$^+$, the H$_2$O-soluble analog of the known [6] [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]$^+$. Its ^{1}H- and ^{31}P{H}-NMR properties show the composition and the geometry of the complex unambiguously (^{1}H-NMR (CD$_3$OD): δ −12.9 (*t*), ^2J(H,P) = 16.5 Hz; ^{31}P{H}-NMR (CD$_3$OD): δ 46.4 (*s*). For comparison, the corresponding data [6] (in CDCl$_3$) for [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]$^+$ are: ^{1}H-NMR; δ −13.0 (*t*), ^2J(H,P) = 17 Hz; ^{31}P{H}-NMR; δ 44.4 (*s*). Interestingly, when the synthesis of the cationic *m*tppms complex was repeated in the presence of a three-fold excess of *m*tppms, a white solid was obtained which *did not dissolve* in H$_2$O. The NMR spectra could be taken in CD$_3$OD and showed the signals observed by *Baricelli et al.* for [RuH(CO)(NCMe)(*m*tppms)$_3$][BF$_4$]. These MeCN complexes were not studied in further details but a possible explanation of the insolubility in H$_2$O may be the (polymeric) salt formation between the large cation [RuH(CO)(NCMe)-(*m*tppms)$_3$]$^+$ and the large anion *m*-(Ph$_2$P)−C$_6$H$_4$−SO$_3^-$ (*m*tppms).

In summary, we have shown here that in aqueous solution, [RuH(Cl)(CO)(*m*tppms)$_3$] undergoes spontaneous chloride dissociation characterized by an equilibrium constant of $9.8 \cdot 10^{-2}$ M at 293 K. This means that at the usual total concentrations employed for homogeneous catalysis (0.01M [Ru] or below) the mole fraction of this compound in an aqueous solution is less than 10% at room temperature, and it is present in even lower concentrations at elevated temperatures, the major species being [RuH(CO)(H$_2$O)(*m*tppms)$_3$]$^+$. It is tempting to speculate that the pronounced effect of added H$_2$O on the catalysis of the hydrogenation of acetone by [RuH(Cl)(CO)(PPh$_3$)$_3$] as reported by *Sánchez-Delgado et al.* [4a] may be related to similar dissociation processes. The study of such effects on catalysis and the characterization of the reaction of [RuH(Cl)(CO)(*m*tppms)$_3$] with H$_2$ under various conditions affecting chloride dissociation from the complex are underway in our laboratory, and the results will be reported in due time.

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Experimental Part

General. [RuH(Cl)(CO)(PPh$_3$)$_3$] [12], [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$][BF$_4$] [6], and *m*tppms [2a] were prepared as described in the literature. RuCl$_3 \cdot 3$ H$_2$O was a loan of *Johnson Matthey*. CD$_3$OD and D$_2$O were obtained from *Cambridge Isotope Laboratories*. All other compounds were high-purity products of *Sigma-Aldrich* and were used as received. Doubly dist. H$_2$O was used throughout, and all manipulations were done under inert atmosphere. IR Spectra: *Perkin-Elmer Paragon-1000-PC* FT-IR spectrophotometer; KBr discs or nujol mulls; in cm^{-1}. ^{1}H-, ^{19}F-, and ^{31}P{H}-NMR spectra: *Bruker AV-360* spectrometer; D$_2$O or D$_2$O/CD$_3$OD solns.; δ(H) and δ(P) in ppm referenced to residual solvent peaks further referenced to external 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) sodium salt and 85% H$_3$PO$_4$, resp., δ(F) referenced to internal NaF and further referenced to CFCl$_3$; *J* in Hz.

*Trisodium Carbonylchlorotris[3-(diphenylphosphino-κP)benzenesulfonato]hydridoruthenate(3−) ([RuH(Cl)(CO)(*m*tppms)$_3$])*. A soln. of *m*tppms (251 mg, 0.628 mmol) in THF (16 ml) was added with vigorous stirring to a soln. of [RuH(Cl)(CO)(PPh$_3$)$_3$] (150 mg, 0,157 mmol) in deoxygenated CHCl$_3$ (16 ml). The mixture was warmed to 40° and stirred for 4 h while a slow Ar stream was passed through the *Schlenk* vessel. The cream-white crystalline complex started to separate after *ca.* 2.5 h. The soln. was filtered while warm, the solid product was washed with THF/CHCl$_3$ 1:1 and dried *in vacuo:* 148 mg (70% of [RuH(Cl)(CO)(*m*tppms)$_3$]). ^{1}H-NMR (CD$_3$OD): −7.89 (*dt*, ^2J(H,P$_a$) = 24.1, ^2J(H,P$_b$) = 105.0). ^{31}P{H}-NMR (CD$_3$OD): no free *m*tppms; 40.5 (*d*), 14.5 (*t*), ^2J(P,P) = 14.5. NMR data: essentially the same as those reported [10].

*Trisodium Aquacarbonyltris[3-(diphenylphosphino-κP)benzenesulfonato]hydridoruthenate(2−) Tetrafluoroborate(1−) ([RuH(CO)(H$_2$O)(*m*tppms)$_3$][BF$_4$])*. Under Ar, THF (20 ml), finely powdered *m*tppms (287 mg, 0.717 mmol), and H$_2$O (100 µl) were added quickly and successively to a soln. of [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$][BF$_4$] (220 mg, 0.161 mmol) in CHCl$_3$ (10 ml). The mixture was stirred for 48 h at 40°. The cream-white complex was isolated by filtration and dried *in vacuo:* 180 mg (78%) of [RuH(CO)(H$_2$O)(*m*tppms)$_3$][BF$_4$]. IR (Nujol): 1951 (CO). ^{1}H-NMR (CD$_3$OD): −7.89 (*dt*, ^2J(H,P$_a$) = 25.5, ^2J(H,P$_b$) = 102.3). ^{31}P{H}-NMR (CD$_3$OD): 41.0 (*d*); 22.5 (*t*); ^2J(P,P) = 15.0. ^{19}F-NMR (D$_2$O): −151.38 (br. *s*); −151.33 (br. *s*).

*Disodium Bis(acetonitrile)carbonylbis[3-(diphenylphosphino-κP)benzenesulfonato]hydridoruthenate(1−) Tetrafluoroborate(1−) [RuH(CO)(NCMe)$_2$(*m*tppms)$_2$][BF$_4$]*. To a soln. of [RuH(Cl)(CO)(*m*tppms)$_3$] (100 mg, 0.073 mmol) in dry MeCN (8 ml) was added Na[BF$_4$] (8.3 mg, 0.073 mmol), and the mixture was refluxed for 1 h. The mixture was allowed to cool to r.t., filtered, and evaporated: 20 mg (27%) of [RuH(CO)(NCMe)$_2$(*m*tppms)$_2$][BF$_4$]. Gray-white complex. ^{1}H-NMR (CH$_3$OH/CD$_3$OD): −12.9 (*t*, ^2J(H,P) = 16.5). ^{31}P{H}-NMR (CH$_3$OH/CD$_3$OD): 46.4 (*s*).

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