Characterization and Reactivity of Di-μ-chloro-tetrahydridotetrakis-(triarylphosphine)diruthenium(III) Complexes, $Ru_2H_4Cl_2(PR_3)_4$

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Abstract

The chloride-bridged, dimeric ruthenium(III) complexes $[RuH_2Cl(PR_3)_2]_2$ (PR_3 = PPh_3, and tri-p-tolylphosphine, $Ptol_3$) have been isolated by H_2-reduction of the corresponding $RuCl_3(PR_3)_2$ complexes. The dimers have been fully characterized by spectroscopy, their chemical reactivity and, in the case of the p-tolyl derivative, preliminary X-ray crystallographic data; in a tentative assignment of the hydride ligands, one is considered to be bridging, two are terminal on one Ru, and one is terminal on the other Ru. Kinetic data on the reaction of $[RuH_2Cl(Ptol_3)_2]_2$ with $Ptol_3$, which generates $RuHCl(Ptol_3)_3$ via loss of H_2, suggest the highly reactive intermediate $[RuHCl(Ptol_3)_2]_2$, the key type of species that probably effects catalytic hydrogenation of olefins using precursor $RuHCl(PR_3)_3$ complexes.

Introduction

The mechanisms involved in the catalytic hydrogenation of olefins and acetylenes, and other unsaturated moieties such as ketonic and nitro-groups, using the well-known $RuHCl(PPh_3)_3$ complex are generally considered to involve the bis-phosphine species $RuHCl(PPh_3)_2$ [1–3]. Detailed studies on the mechanism of olefin hydrogenation with this Ru system and related ones, including incorporation of chiral phosphines, have been on-going in this laboratory for many years [4–8], but a reasonably comprehensive picture of the contribution of the various reaction pathways to the overall catalysis for any single substrate has yet to be published. Pathways via orthometallation, reaction of metal alkyl and H_2, reaction of metal alkyl and metal hydride, and via active $RuH_2(PPh_3)_3$ species, have all been demonstrated or suggested [1, 3]. The scientific story resembles in many ways developments in the elucidation of details of hydrogenation of olefins catalyzed by $RhCl(PPh_3)_3$, where at least two even more fundamental questions were the role of bis-phosphine species and the contribution of dimeric species [1, 3]. The same problems are encountered in the Ru system.

Several years ago, a communication from this laboratory [9] described isolation and spectroscopic characterization of $[RuHCl(PPh_3)_2]_2$, **1**, while the structure of the supposed tri-p-tolylphosphine derivative **2** was subsequently determined and reported at a Conference [10]. Complexes **1** and **2** were synthesized from the reaction of H_2 with the Ru(III) precursors $RuCl_3(PR_3)_2$ [6, 7, 11] in the presence of a strong base such as Proton Sponge†. Some chemical evidence for formulation of **1** was demonstration of the stoichiometries of reactions (1) and (2) [9], together with isolation of '$RuCl_2(PPh_3)_2$' as a dimer [12, 13]:

$$2RuCl_3(PPh_3)_2 + H_2 \longrightarrow 2'RuCl_2(PPh_3)_2' + 2HCl \quad (1)$$

$$'RuCl_2(PPh_3)_2' + H_2 \xrightarrow{base} RuHCl(PPh_3)_2 + base\cdot HCl \quad (2)$$

We now find that the $[RuCl_2(PPh_3)_2]_2$ dimer does indeed react quite rapidly with 1 mol H_2 per Ru, but that a slower subsequent reaction occurs in which a further half mol of H_2 per Ru is absorbed. Similarly, the Ru(III) precursor eventually absorbs a total of 2 H_2 per Ru. Both these stoichiometries correspond to formation of a '$RuH_2Cl(PPh_3)_2$' species. This complex and particularly the more soluble p-tolyl analogue have been now fully characterized as the dimeric moieties. The structure **2** referred to above [10] is now considered to be $[RuH_2Cl(Ptol_3)_2]_2$ and not $[RuHCl(Ptol_3)_2]_2$.

Experimental

Solvents used were spectroscopic grade; toluene was distilled from sodium benzophenone prior to

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†Proton Sponge is 1,8-bis(dimethylamino)naphthalene; dma = N,N'-dimethylacetamide.

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use, while dma was stirred over CaH_2 for at least 24 h and vacuum-distilled. Alcohols were dried by distilling from the corresponding Mg alkoxide. Pre-purified H_2 was obtained from Matheson and passed through an Englehard Deoxo catalytic purifier to remove traces of O_2. Purified CO (Matheson) was used without further purification. Phosphines (Strem Chemicals) were used as supplied for syntheses, while $Ptol_3$ for use in kinetic studies was recrystallized from ethanol–diethyl ether. Proton Sponge (Aldrich) was purified by column chromatography (dry-packed alumina, petroleum ether (30–60 °C) eluent) to give a white solid, mp 47–50 °C, lit. [14] 47–48 °C. Norbornadiene (nbd), an Eastman product, was purified by passage through a column of activated alumina (MCB, A X 612 Chromatographic Grade, 80–200 mesh).

The primary ruthenium source was $RuCl_3 \cdot 3H_2O$ obtained from Johnson, Matthey Ltd. All synthetic reactions were carried out under Ar using Schlenk techniques. Elemental analyses were performed by Mr. P. Borda of this department.

Infrared spectra were recorded as KBr discs on a Perkin Elmer 598; optical spectra were recorded on a Perkin Elmer 552A, fitted with thermostatted cell compartments, using specially designed, quartz anaerobic spectral cells of 1.0 cm or 1.0 mm pathlength [15]. The ^1H NMR spectra were recorded on Bruker WP-80 or WH-400 spectrometers with $SiMe_4$ as standard; ^{31}P NMR, measured on the WP-80 or Varian XL-100 machines, are referenced with respect to 85% H_3PO_4, downfield shifts being positive.

Evolved H_2 from solution reactions was identified using a Carle 311 GC instrument (thermal conductivity mode) with a 14 ft hand-packed Porapak Q column (Waters Associates, 80–100 mesh); use of a He carrier gas at 20 p.s.i. at 30 °C gave good separation of H_2 (retention time 195 ± 5 s) from other gases.

The constant pressure gas-uptake apparatus used for determining gas stoichiometries (absorption and evolution, ±5%) has been described previously [16]; the complexes were added from a glass bucket suspended by a side-arm of the reaction vessel, following presaturation of the solvent with any desired gas (H_2, CO, Ar) at pressures up to 1 atm.

Ruthenium Complexes

The following Ru complexes were prepared from $RuCl_3 \cdot 3H_2O$ according to literature procedures, the reference being given in parentheses: $RuX_2(PR_3)_3$, $RuX_3(PR_3)_2$, $RuCl_3(AsPh_3)_2$, X = Cl, Br, R = Ph, Ptol [11, 17, 18]; $RuX_2(O_2CPh)(PPh_3)_2$, X = Cl, Br [19]; $RuHCl(nbd)(PPh_3)_2$ [20, 21]; $RuHCl(PPh_3)_3$ [20, 22]. The Ru(III) complexes were isolated either as methanol solvates [11], or dma solvates if the syntheses were carried out in dma solvent [6, 7]. The synthesis and characterization of $[RuCl_2(PPh_3)_2]_2$ have been reported previously [12]. The p-tolyl analogue was prepared in a corresponding manner by stirring $RuCl_3(Ptol_3)_2$dma (2.0 g, 2.2 mmol) in dma (10 ml) under H_2 (1 atm) for 24 h; reduction of the volume of the resulting brown solution to a few ml, followed by addition of methanol (75 ml), yielded an orange-brown solid that was filtered off, washed with methanol, and vacuum-dried (yield, 65%). The elemental analyses were somewhat variable due to the presence of some dma impurity (seen as nitrogen content, for example, *Anal.* Calcd. for $C_{42}H_{42}Cl_2P_2Ru$: C, 64.61; H, 5.42. Found: C, 62.8; H, 5.4; N, 0.87%); however, the single $^{31}P\{^1H\}$NMR AB pattern in toluene-d_8 at −40° (δ_A = 60.1, δ_B = 52.5 ppm, J_{AB} = 42 Hz) is consistent with the presence of a single chloro-bridged dimer with two square pyramids sharing a basal edge [12, 13, 23].

$RuHCl(Ptol_3)_3$

The best route for synthesis of the p-tolyl analogue of the well-known $RuHCl(PPh_3)_3$ complex [20, 22] was found to be via reaction of the hydride dimer $[RuH_2Cl(Ptol_3)_2]_2$ (2, see below) with $Ptol_3$. Benzene (10 ml) was added to a mixutre of 2 (1.7 g, 1.13 mmol) and recrystallized $Ptol_3$ (0.66 g, 2.17 mmol), and the mixture heated to 60°; the colour changed from red to violet within 5 min, when the gas above the solution was then recharged with Ar to remove evolved H_2 (see eqn. 7 later). After 30 min at 60 °C, the atmosphere was again replaced by fresh Ar, and the mixture then stirred at 20 °C for 18 h. The volume was reduced to ~2 ml to give a violet paste; pet. ether (30–60 °C) (80 ml) was then added and the red solution allowed to stand for 24 h, when violet crystals formed. These were filtered, washed with pet. ether, and vacuum-dried (yield 0.3 g, 15%). *Anal.* Calcd. for $C_{63}H_{64}ClP_3Ru$: C, 72.02; H, 6.14. Found: C, 72.4; H, 6.1%; ν_{Ru-H} 2020 cm; $\delta_{C_6D_6}^{30\,°C}$, 7.70 (m, H_o), 6.80 (d, 8 Hz, H_m), 2.00 (s, $-CH_3$), −16.84 (q, J_{PH} = 26 Hz, Ru–H).

$[RuH_2Cl(PPh_3)_2]_2$ and Analogues

The bis(dma) solvate of the title dimer was readily synthesized by stirring $RuCl_3(PPh_3)_2$dma (1.0 g, 1.2 mmol) and Proton Sponge (1.0 g, 4.7 mmol) under 1 atm H_2 in dma (30 ml) for 24 h, during which time a red solid deposited. This was filtered, washed with dma, hexane and vacuum-dried (yield, 60%). *Anal.* Calcd. for $C_{40}H_{41}ONClP_2Ru$: C, 64.04; H, 5.51; N, 1.87; Cl, 4.73. Found: C, 63.9; H, 5.6; N, 1.8; Cl, 4.6%. The corresponding $[RuH_2Cl_2(AsPh_3)_2] \cdot 2$dma violet complex was prepared analogously in about 50% yield from the $AsPh_3$ precursor. *Anal.* Calcd. for $C_{40}H_{41}ONClAs_2Ru$: C, 57.32; H, 4.93; N, 1.67; Cl, 4.23. Found: C, 57.1; H, 5.0; N, 1.5; Cl, 4.1%. The procedure for synthesiz-

ing the corresponding bromo analogues $[RuH_2Br(PPh_3)_2]_2 \cdot 2dma$, and $[RuH_2Br(AsPh_3)_2]_2 \cdot 2dma$, from the tribromoruthenium(III) precursors was similar but the reactant solutions did not deposit solids. The solution volumes were thus reduced to ~10 ml and methanol (50 ml) added; the resulting violet solids (~50% yield) were filtered, washed with methanol and vacuum-dried. *Anal.* Calcd. for $C_{40}H_{41}ONBrP_2Ru$: C, 60.46; H, 5.20; N, 1.76. Found: C, 62.4; H, 5.3; N, 1.4%. *Anal.* Calcd. for $C_{40}H_{41}ONBrAs_2Ru$: C, 54.44; H, 4.68; N, 1.59. Found: C, 55.5; H, 4.5; N, 1.2%.

The dma-free $[RuH_2Cl(PPh_3)_2]_2$ dimer was best prepared by stirring $[RuCl_2(PPh_3)_2]_2$ (0.8 g, 1.1 mmol) and Proton Sponge (1.0 g, 4.7 mmol) in toluene (20 ml) under 1 atm H_2 for 24 h. During this time, the solution became red and deposited Proton Sponge hydrochloride. Dry ethanol (30 ml) was added and the mixture stirred for 30 min; filtration, followed by washing with dry ethanol, diethyl ether, and hexane, and vacuum-drying, yielded the required complex in 80% yield. *Anal.* Calcd. for $C_{36}H_{32}ClP_2Ru$: C, 65.21; H, 4.86. Found: C, 65.5; H, 4.9%. The $[RuH_2Cl(Ptol_3)_2]_2$ complex (2) was made by stirring $RuCl_3(Ptol_3)_2dma$ (2.0 g, 2.4 mmol) and Proton Sponge (1.5 g, 7.0 mmol) in benzene (50 ml) under 1 atm H_2 for 24 h. The resulting red-brown suspension was filtered through Celite to give a dark red solution. Dry ethanol (40 ml) was added and crystallization allowed to occur over several hours. The red solid was obtained in 60% yield following filtration, washing with dry ethanol and hexane, and vacuum-drying. *Anal.* Calcd. for $C_{42}H_{44}ClP_2Ru$: C, 67.51; H, 5.94. Found: C, 68.4; H, 6.3%.

The characterization of the tetrahydrido dimers is discussed below.

Results and Discussion

The $[RuH_2XL_2]_2$ complexes were prepared by stirring an appropriate Ru(III) or Ru(II) precursor with Proton Sponge in dma, toluene, or benzene under H_2 for 1 day. The bromo complexes were difficult to prepare analytically pure, and this is probably due to the presence of some $RuBr_2L_3$ impurity in the precursor $RuBr_3L_2$ complexes [8]; the excess L ligand (*e.g.* PPh_3) leads, via the reaction with H_2, to formation of $RuHBrL_3$ which was detected in the $^{31}P\{^1H\}$NMR [13]. Because of this problem, emphasis was placed on the chloro complexes. The elemental analyses and IR of the $[RuH_2XL_2]_2$ complexes isolated from dma solutions showed the presence of one dma molecule per Ru; an IR band at 1640 cm^{-1} in all cases suggests the dma is present as a solvate [24, 25]. The slightly high carbon analyses found for complexes isolated from benzene solutions by adding ethanol resulted from a tendency to trap benzene. The higher solubility of the $[RuH_2Cl(Ptol_3)_2]_2$ complex (2) allowed for isolation of a crystal suitable for X-ray analysis (see below); a cryoscopic measurement in benzene under Ar was consistent with the dimeric formulation (M. wt. 1300, calcd. 1495). Complex 2 and the PPh_3 analogue (3) obeyed Beer's Law over the concentration range from (1.0–120) $\times 10^{-4}$ M in dma (λ_{max} 495 nm) and toluene (λ_{max} 500 nm) under H_2, ϵ being 1500 M^{-1} cm^{-1} in both solvents.

The IR spectra were of little value in assigning terminal versus bridging hydride ligands: broad peaks in the 2050 ± 50 cm^{-1} region were sometimes comparable to triaryl-phosphine and -arsine overtone bands, while the region around 1100 cm^{-1} was cluttered by undefined bands of the Group V ligands.

Attempts to prepare carboxylate analogues by comparable routes were unsuccessful. The products of hydrogenating $RuX_2(O_2CPh)(PPh_3)_2$ in the presence of base showed no carboxylate in the IR and were identified as $[RuH_2X(PPh_3)_2]$ by visible spectroscopy.

As mentioned in the Introduction, earlier work from this laboratory [9] had discussed the base-promoted solution reaction of the Ru(III) phosphines and arsines with H_2 according to the overall stoichiometry of reaction (1) plus (2), for example:

$$RuCl_3(PPh_3)_2 + 1.5H_2 \longrightarrow [RuHCl(PPh_3)_2]_2 + 2HCl \quad (3)$$

More extensive studies, including longer reaction times (up to 24 h), show that in dma or toluene solution at 30 °C containing Proton Sponge, the halide-containing Ru(III) and Ru(II) precursors at ~5 $\times 10^{-3}$ M all react with H_2 at 1 atm with the final stoichiometries shown in eqns. 4 and 5, respectively, consistent with formation of the isolated products:

$$RuX_3L_2 + 2H_2 \longrightarrow \frac{1}{2}[RuH_2XL_2]_2 + 2HX \quad (4)$$

$$\frac{1}{2}[RuX_2L_2]_2 + 1.5H_2 \longrightarrow \frac{1}{2}[RuH_2XL_2] + HX \quad (5)$$

The difference in the two stoichiometries corresponds to the reduction of Ru(III) to Ru(II) by 0.5 equivalents of H_2 (eqn. 1).

The norbornadiene complex $RuHCl(nbd)(PPh_3)_2$ in toluene or dma solution absorbed H_2 in the absence of added base to a final stoichiometry of 2.5 mol gas per Ru. Norbornane was generated quantitatively as monitored by NMR, with no intermediate norbornene being detected, while the final inorganic product was $[RuH_2Cl(PPh_3)_2]_2$, (3), as evidenced by visible and NMR spectroscopy (see below), eqn. 6:

$$RuHCl(nbd)(PPh_3)_2 + 2.5H_2 \longrightarrow \frac{1}{2}[RuH_2Cl(PPh_3)_2]_2 + \text{norbornane} \quad (6)$$

Other chemical evidence for the hydrogen content of the dimer products was obtained by the reaction of complex **2** and/or **3** with excess of the appropriate phosphine (eqn. 7), CO (eqn. 8), 2,2'-dipyridyl (eqn. 9), and HCl (eqn. 10):

$$Ru_2H_4Cl_2L_4 + 2L \longrightarrow 2RuHClL_3 + H_2 \quad (7)$$

$$Ru_2H_4Cl_2(PPh_3)_4 \xrightarrow{4\,CO} 2RuHCl(CO)_2(PPh_3)_2 + H_2 \quad (8)$$

$$Ru_2H_4Cl_2(PPh_3)_4 \xrightarrow{2\,dipy} 2RuHCl(dipy)(PPh_3)_2 + H_2 \quad (9)$$

$$Ru_2H_4Cl_2(PPh_3)_4 \xrightarrow{3\,HCl} [Ru_2Cl_5(PPh_3)_4]^- + H^+ + 3H_2 \quad (10)$$

In each reaction the H_2 was detected in the final gas phase and the gas stoichiometries quantified volumetrically in dma or toluene solution. The violet $RuHClL_3$ products (eqn. 7) were readily identified by visible or NMR spectroscopy [9, 13 and Experimental], and indeed the p-tolyl complex is conveniently synthesized via reaction 7. The yellow $RuHCl(CO)_2(PPh_3)_2$ product was identified by comparison of the hydride resonance (C_6D_6, −3.86 δ, t, J_{PH} = 20 Hz) and the ^{31}P singlet (39.9 ppm) with those of an authentic sample [26]. The brown dipyridyl complex, synthesized previously [20], was similarly identified by the high-field ^1H NMR ($CDCl_3$, −12.3 δ, t, J_{PH} = 25 Hz). The product of the protonation reaction (eqn. 10) is the triply chloro-bridged anion $\{[RuCl(PPh_3)_2]_2(\mu\text{-}Cl)_3\}^-$, identified by a characteristic ^{31}P NMR spectrum in dma/toluene-d_8 (v/v = 1:1): 25 °C, s, 48.1 ppm; −70 °C, AB pattern, δ_A = 48.2, δ_B = 47.4 ppm, J_{PP} = 36.0 Hz. The full characterization of this anion, which is also the product of the reaction between Cl^- and $RuCl_2(PPh_3)_3$ [12], will be presented elsewhere [8, 27].

It should be noted that the 'correct' *net* stoichiometry for gas absorption in reaction 8 (1.5 mol gas per Ru) was observed only in toluene solution, while in dma (when H_2 is again evolved) a stoichiometry of 2.0 mol gas/Ru was measured. This latter stoichiometry had been noted earlier in the original report on isolation of $[RuHCl(PPh_3)_2]_2$ [9], and appeared consistent with reaction 11 (*cf.* eqn. 8):

$$Ru_2H_2Cl_2(PPh_3)_4 + 4CO \longrightarrow 2RuHCl(CO)_2(PPh_3)_2 \quad (11)$$

A complication in these CO reactions, however, as revealed by NMR and IR, is the formation also of small amounts of $Ru(CO)_3(PPh_3)_2$ [28] and *cis*-, *cis*-, *trans*-$RuCl_2(CO)_2(PPh_3)_2$ [26] in equimolar amounts in both hydrocarbon and dma solvents (Fig. 1). A possible source of these two extra products is via disproportionation of a transient Ru(I) intermediate, for example (L = PPh_3):

$$Ru_2H_4Cl_2L_4 \xrightarrow[-2H_2]{2CO} [RuCl(CO)L_2]_2 \xrightarrow{3CO} Ru(CO)_3L_2 + RuCl_2(CO)_2L_2 \quad (12)$$

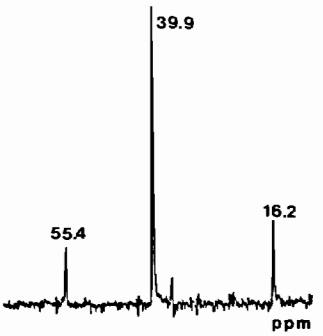


Fig. 1. $^{31}P\{^1H\}$NMR spectrum of the reaction products of $Ru_2H_4Cl_2(PPh_3)_4$ with CO in C_6D_6 or dma/C_6D_6 at 30 °C; $Ru(CO)_3(PPh)_2$, 55.4 ppm; $RuHCl(CO)_2(PPh_3)_2$, 39.9 ppm; $RuCl_2(CO)_2(PPh_3)_2$, 16.2 ppm.

Such Ru(I) complexes are known when L is a bulky phosphine like $PPh(^tBu)_2$ [29]. Of interest, reaction 12 occurs with the same net gas uptake (3 equivalents per dimer) as reaction 8, meaning that any contribution by reaction 12 is not detected in the tensiometric measurements, and so does not explain the anomalous stoichiometry observed in dma. This solvent is basic and readily forms an adduct with HCl [30], which suggests reductive elimination of HCl as a possibility, for example (L = PPh_3):

$$Ru_2H_4Cl_2L_4 \xrightarrow[dma]{4CO} RuH_2(CO)_2L_2 + RuHCl(CO)_2L_2 + dma{\cdot}HCl \quad (13)$$

Reaction 13, together with conversion of the dihydride product under CO to $Ru(CO)_3(PPh_3)_2$ with elimination of H_2 (a known reaction [28, 31]), would account for the gas stoichiometry and detection of H_2; however, the ^{31}P data are not consistent with such a product distribution ($RuH_2(CO)_2(PPh_3)_2$ has a ^{31}P shift at 57.7 ppm [8, 32]). The ^{31}P measurements in dma do require addition of C_6D_6 as a deuterium lock (dma/C_6D_6, v/v = 3:2), and so perhaps a strict comparison of the gas uptake data in neat dma and the NMR data is not justified.

A Kinetic Study of Reaction 7, L = $Ptol_3$

The reactivity of **2** with $Ptol_3$ to generate $RuHCl(Ptol_3)_3$, eqn. 7, was examined kinetically in dma

solution at 30 °C under H_2 using a standard spectrophotometric procedure (see Fig. 2). The reaction proceeded cleanly with excellent isosbestic points, and was readily monitored in the 550 nm region.

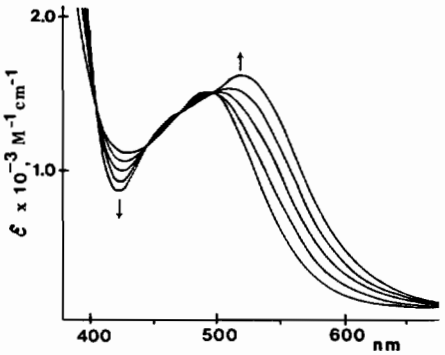


Fig. 2. Visible spectral change as a function of time accompanying the reaction of $[RuH_2Cl(Ptol_3)_2]_2$ with $Ptol_3$ in dma at 30 °C under H_2.

In the type of optical cell used (see Experimental), the concentration of H_2 in any single experiment is maintained constant, and the phosphine was also added in sufficient excess to remain effectively constant. The spectral changes then analyzed for first-order behaviour in Ru, the $\log(A_\infty - A_t)$ *vs.* time plots being linear over at least two half-lives (A_t and A_∞ are the absorbances after time t and t = ∞, respectively). The observed pseudo first-order rate constant, k_{obs}, was independent of Ru from (1.0–18.5) $\times 10^{-4}$ M, was strictly first-order in $Ptol_3$ up to 6×10^{-2} M, and was directly inversely dependent on H_2 up to 1 atm (1.6×10^{-3} M) (see Fig. 3). The data are best accommodated by a mechanism involving predissociation of H_2 to give a coordinatively unsaturated dinuclear species **4**, which then reacts with $Ptol_3$ (written as L):

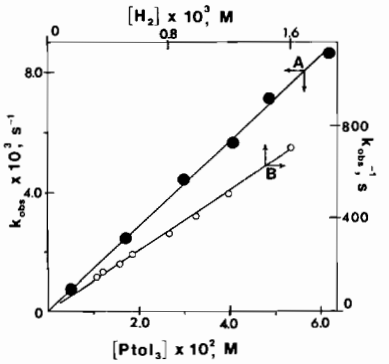


Fig. 3A. Dependence of k_{obs} on $[Ptol_3]$ for the reaction of $[RuH_2Cl(Ptol_3)_2]_2$ (3.0×10^{-4} M) with the phosphine in dma at 30 °C under 1 atm H_2 ($[H_2] = 1.6 \times 10^{-3}$ M). 3B. Plot of k_{obs}^{-1} *vs.* $[H_2]$ for the same reaction at a fixed $[Ptol_3] = 1.0 \times 10^{-2}$ M.

$$Ru_2H_4Cl_2L_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuHClL_2]_2 + H_2 \qquad (14)$$
2 **4**

$$4 + L \xrightarrow{k_2} \text{product} \left(\xrightarrow{L} 2RuHClL_3\right) \qquad (15)$$

The direct dependence on [L] requires that reaction 14 is established as a relatively rapid equilibrium ($k_1/k_{-1} = K$), and the rate-law simplifies to eqn. 16, in agreement with the experimental data (Ru_T = total Ru, expressed as dimer):

$$\text{Rate}, \frac{-d}{dt}[Ru_T] = k_{obs}[Ru_T] = \frac{Kk_2[L][Ru_T]}{[H_2] + K} \qquad (16)$$

The plots of k_{obs} *vs.* [L] and k_{obs}^{-1} *vs.* $[H_2]$ give consistent values for Kk_2 of $(2.25 \pm 0.1) \times 10^{-4}$ s^{-1}, but no definite information on the individual K and k_2 values, because the required intercept of Fig. 3B (which equals $(k_2[L])^{-1}$) is indistinguishable from zero. Nevertheless, putting an upper limit of ~10 s for this intercept gives $k_2 \geqslant 10$ M^{-1} s^{-1} and $K \leqslant 2 \times 10^{-5}$ M. Such a K value is consistent qualitatively with the stability of **2** under H_2 at 1 atm, and a noted decomposition in the absence of H_2 (see below). However, we have not been able to isolate the supposed $[RuHCl(Ptol_3)_2]$ intermediate, or the corresponding PPh_3 analogue. Our earlier reports on such complexes [9, 10] are now considered to be in error, the formulations being deficient two hydride ligands per dimer. It is almost certain, however, that the coordinatively unsaturated species such as **4** are the key intermediates in hydrogenation of olefins catalyzed by $RuHClL_3$ complexes [1, 3]. Reactivity of **2** towards olefins is currently being studied [33].

The details of reaction 15 remain unclear, but a rate-determining formation of one mol of $RuHClL_3$ product, and one mol of '$RuHClL_2$' as monomer or dimer with or without coordinated dma seems plausible; this latter species could then rapidly consume more L to give the second mol of $RuHClL_3$.

The Structure and NMR Spectroscopy of $[RuH_2Cl(Ptol_3)_2]_2$, 2

A single crystal X-ray diffraction study of the dark red, complex **2** was carried out in this department [7, 34]. Although not well refined due to crystal decomposition during data collection (final R factor of 7.7%), the structure is shown to be a chloro-bridged dimer, consistent with the solution properties. Figure 4 outlines the basic structure, and Table I lists selected bond lengths and angles. The positions of the hydride ligands could not be determined crystallographically and their positioning in Fig. 4 will be discussed following consideration of the NMR data (see below).

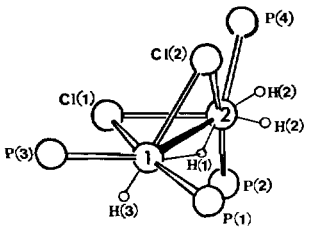


Fig. 4. Diagrammatic crystal structure of $[RuH_2Cl(Ptol_3)_2]_2$; the positions of the hydride ligands have been added following interpretation of the NMR data (see text). The Ru(1) and Ru(2) atoms are simply labelled 1 and 2, respectively.

TABLE I. Selected Bond Angles and Distances of the Structure Shown in Fig. 4.

Distance, Å		Angle, deg.	
Ru(1)–Ru(2)	2.80(0)	P(1)–Ru(1)–P(3)	97.6(5)
Ru(1)–P(1)	2.23(1)	P(1)–Ru(1)–Cl(1)	166.8(5)
Ru(1)–P(3)	2.28(1)	P(1)–Ru(1)–Cl(2)	94.4(5)
Ru(2)–P(2)	2.26(1)	P(1)–Ru(1)–Ru(2)	111.9(4)
Ru(2)–P(4)	2.39(1)	P(3)–Ru(1)–Cl(1)	95.6(5)
Ru(1)–Cl(1)	2.46(1)	P(3)–Ru(1)–Cl(2)	113.8(4)
Ru(1)–Cl(2)	2.57(1)	P(3)–Ru(1)–Ru(2)	148.4(4)
Ru(2)–Cl(1)	2.47(1)	P(2)–Ru(2)–P(4)	104.1(5)
Ru(2)–Cl(2)	2.48(1)	P(2)–Ru(2)–Cl(1)	92.1(5)
		P(2)–Ru(2)–Cl(2)	167.6(5)
		P(2)–Ru(2)–Ru(1)	110.0(4)
		P(4)–Ru(2)–Cl(1)	102.9(4)
		P(4)–Ru(2)–Cl(2)	88.0(4)
		P(4)–Ru(2)–Ru(1)	139.3(3)
		Ru(1)–Cl(1)–Ru(2)	69.3(4)
		Ru(1)–Cl(2)–Ru(2)	67.3(3)

The distance between the Ru centres (2.80 Å) coupled with the acute Ru–Cl–Ru bond angles (69.3° and 67.3°) indicates the presence of a Ru–Ru single bond, which has been found in the range 2.28–2.95 Å [35–38]. The existence of this bond between the two formally Ru(III) centres accounts for the observed diamagnetism.

The $[RuH_2XL_2]_2$ compounds (X = Cl, Br; L = PPh_3, $Ptol_3$, $AsPh_3$) all exhibit a broad high-field hydride resonance in the δ −12.73 to δ −13.80 region ($\nu_{1/2}$ = 60 Hz) in C_6D_6 at 25 °C. The integrated intensities of the hydrides decreased slowly with time (see reaction 14) but fresh solutions indicated ~1.5 hydrides per Ru, based on the methyl resonances in the case of 2, or the dma resonances for the dma-solvated dimers. Because of limitations in solubility, variable temperature experiments were done only with 2. In CD_2Cl_2 at 30 °C, the broad hydride resonance was detected at −13.3 δ; this broadened further on cooling to −40°, but at −95° the spectrum (Fig. 5) exhibited three discrete high-field resonances, labelled H(1), H(2), and H(3), of relative intensities of about 1:2:1 at δ −9.27 (dd, 72 Hz, 4 Hz), −11.65 ($\nu_{1/2}$ = 120 Hz), and

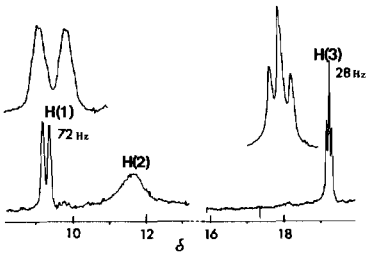


Fig. 5. High-field region ^1H NMR spectrum (400 MHz) of $[RuH_2Cl(Ptol_3)_2]_2$ in CD_2Cl_2 at −95°. Insets show the H(1) and H(3) resonances expanded.

−19.15 (t, 28 Hz). Selective irradiation of each hydride had little effect on the remaining resonances and the major couplings are assigned to J_{PH}. The broad resonance at −11.65 δ indicates rapid site exchange even at this temperature.

The $^{31}P\{^1H\}$NMR spectra of the $[RuH_2XL_2]_2$ compounds at 25–30 °C in C_6D_6, CD_2Cl_2, or toluene-d_8, are all similar; some data for complex 2 as a function of temperature are given in Figs. 6 and 7. [The 30 °C spectra on standing generate an extra resonance at ~55 ppm (see Fig. 6), that was shown, by selectively irradiating the phenyl resonances, to be due to the hydride $RuHCl(Ptol_3)_3$-(J_{PH} = 26 Hz), which must result from disproportionation of 2 following loss of H_2, *cf.* eqn. 14]. At about −50° the ^{31}P resonances of 2 broadened and coalesced and, although some resolution became apparent at −80° (Fig. 6), the limiting slow exchange could be obtained only at −95° in CD_2Cl_2

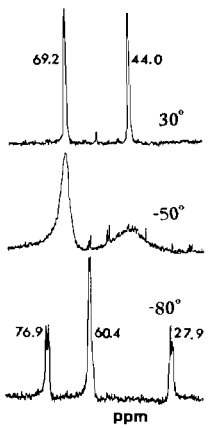


Fig. 6. $^{31}P\{^1H\}$NMR spectra (40.5 MHz) of $[RuH_2Cl(Ptol_3)_2]_2$ in toluene-d_8 as a function of temperature.

(Fig. 7): four discrete and coupled resonances centered at 74.2, 58.3, 56.3 and 33.5 ppm, labelled P(1) through P(4) are seen. The range of ^{31}P shifts is wider than expected on the basis of the crystal structure which, although slightly distorted, shows an approximate C_2 axis between Cl(1) and Cl(2), perpendicular to the Ru–Ru bond, and this approx-

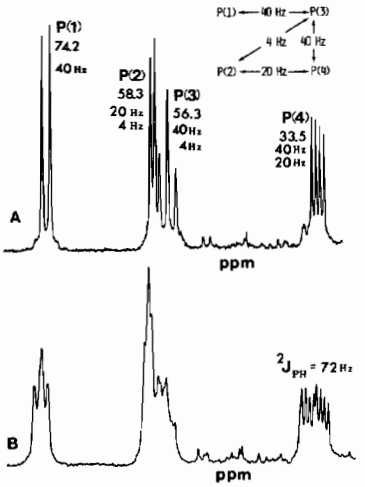
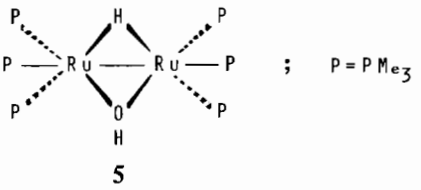


Fig. 7. ^{31}P NMR spectra (32.4 MHz) of $[RuH_2Cl(Ptol_3)_2]_2$ in CD_2Cl_2 at −95° under conditions of (A) broadband and (B) selective phenyl proton decoupling. Inset on (A) shows couplings used to simulate the spectrum.

imately transforms P(1) to P(2), and P(3) to P(4). The hydrides must thus be asymmetrically disposed to account for the disparity. The suggested positions of the hydrides at slow exchange are shown in Fig. 4, where the labels of the hydrogen and phosphorus atoms on the structural diagram are thought to correspond to those on the NMR spectra. The spectrum of Fig. 7A can be simulated exactly using the scheme shown in the inset that requires coupling between some of the phosphines on adjacent Ru centres, and which is presumably facilitated by the metal–metal bond [39, 40].

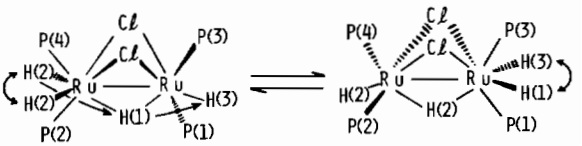
The four different phosphorus atoms, in the intensity ratio 1:1:1:1, are in the region normally found for Ru–triarylphosphine compounds [13, 18]. The simulation requires P(3) to be coupled to all other P atoms, while P(1) is coupled only to P(3); P(2) and P(4) are coupled to each other as well as to P(3). The values found for J_{PP} indicate that no phosphines are *trans* disposed, and the NMR parameters generally are consistent with the asymmetric unit described crystallographically. The coupling of P nuclei between Ru–Ru centres has been shown to be a function of the Ru–X–Ru bridge angle; larger values of $^3J_{PP}$ (80–190 Hz), that increase with X in the order halo < carboxylato < methoxo, are found for close to linear P–Ru–Ru–P moieties, and are comparable with $^2J_{PP}$ values found for mononuclear *trans* coupling [39, 40]. The asymmetric Ru(II) complex shown in 5 shows coupling constants of 2 and 46 Hz across the metal–metal bond [38], comparable to those of 4 and 40 Hz found in the present work. The upfield shift of P(4), the downfield position of H(1), and the measured $J_{H(1)P(4)}$ of 72 Hz (by ^1H and ^{31}P-{phenyl}NMR) are consistent with these ligands



5

being mutually *trans* [41, 42]. The H(1) resonance shows additional fine structure (Fig. 5), indicating a weak interaction with at least one other P atom. Because the P(2) and P(3) resonances overlap, and the values of $J_{PH(cis)}$ and J_{HH} are comparable to the line-widths (not unusual with polyhydride complexes [41]), the remaining assignments are more tentative. However, the appearance and shape of the H(3) resonance (Fig. 5) strongly indicate direct equal coupling to two P nuclei, since in no case is $J(^{31}P–^{31}P)$ large enough to introduce a deceptively simple, normal 1:2:1 triplet pattern. The magnitude of J_{PH} (28 Hz) is considered to result from coupling with P(1) and P(3); the ^{31}P-{phenyl} resonance for P(2) certainly cannot accommodate such a large value. The relatively high field shift of H(3) is consistent with its being *trans* to a ligand of low *trans* influence [41]. Further, the bond lengths of Ru(1)–Cl(2), 2.57 Å, and Ru(2)–P(4) 2.39 Å, are longer than the other corresponding Ru–Cl (2.46–2.48 Å) and Ru–P (2.23–2.28 Å) bond lengths, and this is best rationalized in terms of the *trans* influence of the hydride ligands, H(3) and H(1).

The pseudo-equivalent H(2) protons are assigned terminal positions to account for their very low exchange barrier. The slightly larger P(2)–Ru(2)–P(4) angle (104°) than P(1)–Ru(1)–P(3) (97.6°) is also consistent with there being more terminal hydrides on Ru(2). At temperatures > −40°, a single resonance is observed for the hydrides at the weighted average of the low temperature positions. Thus a second, higher energy exchange process, which interconverts all of the environment, becomes significant; the intramolecular process outlined in eqn. 17 allows for scrambling of the hydrides between the two centres, in tandem with the lower energy exchange process.



(17)

An intermolecular process with the free H_2 (*cf.* equilibrium 14) could explain interconversion of H(1) and H(3) with each other, but not H(2). As the asymmetry is decreased at the higher temperatures by the hydride scrambling, the environment of P(1) and P(2) (and P(3) and P(4)) become more equivalent; how-

ever, the $^{31}P\{^1H\}$ spectrum at 30 °C (Fig. 6), while showing fine structure, is not the simple AA'XX' pattern expected if the two sets of resonances were symmetrically coupled. Some of the distortions observed in the solid state appear to be maintained even at this temperature in solution.

Conclusions

Crystallographic, ^1H and ^{31}P NMR data, and a number of chemical reactions, confirm the existence of halide-bridged dimers of formulation $[RuH_2XL_2]_2$ (X = halide, L = tertiary-phosphine or -arsine); a tentative assignment of the hydride ligands is made. The isolated complex reported earlier to be $[RuHCl(PPh_3)_2]_2$ (**1**) is now considered to be $[RuH_2Cl(PPh_3)_2]_2$, although the catalytically active species in hydrogenation of olefins using $RuHCl(PPh_3)_3$ is almost certainly **1** (as dimer or solvated monomer).

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