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Synthesis and properties of the 16-electron complex $[(C_5Me_5)RuCl(PMe^iPr_2)]$ and of half-sandwich ruthenium hydrido complexes containing bulky monodentate phosphine ligands

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Abstract

The 16-electron complex $[(C_5Me_5)RuCl(PMe^iPr_2)]$ (**1**) was obtained by reaction of $[\{(C_5Me_5)RuCl\}_4]$ with PMe^iPr_2 in petroleum. This compound appears to be in equilibrium with the dimer $[\{(C_5Me_5)Ru(PMe^iPr_2)\}_2(\mu\text{-}Cl)_2]$ as inferred from low-temperature NMR studies. The 18-electron complex $[(C_5Me_5)RuCl(PMe^iPr_2)_2]$ was formed upon addition of PMe^iPr_2 to **1**. The related species $[(C_5H_5)RuCl(PMe^iPr_2)_2]$ (**2**) was obtained by reaction of $[(C_5H_5)RuCl(PMe^iPr_2)(PPh_3)]$ with PMe^iPr_2, followed by column chromatography. A range of Ru^{IV} dihydrides $[(C_5R_5)RuH_2(PR_3)_2][BPh_4]$ ($R = Me$, H; $PR_3 = PMe^iPr_2$, PEt_3) have been prepared and characterised. The corresponding monohydrido complexes $[(C_5R_5)RuH(PR_3)_2]$ were obtained by deprotonation of the cationic dihydrides. Protonation at low temperature of either of these monohydrido complexes yielded back the corresponding dihydrido derivative, except in the case of $[(C_5Me_5)RuH(PEt_3)_2]$, for which the metastable cationic dihydrogen complex $[(C_5Me_5)Ru(H_2)(PEt_3)_2]^+$ was obtained and characterised by NMR spectroscopy. This compound rearranges to its dihydrido tautomer as the temperature is raised, and a kinetic study of such process was accomplished. Interestingly, the only isolable dinitrogen adduct of the type $[(C_5R_5)Ru(N_2)(PR_3)_2][BPh_4]$ among all possible combinations of phosphines and cyclopentadienyl ring substituents was $[(C_5Me_5)Ru(N_2)(PEt_3)_2][BPh_4]$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Half-sandwich complexes; Hydrido complexes; Dihydrogen complexes; Dinitrogen complexes

1. Introduction

Half-sandwich ruthenium derivatives of the type $[(C_5R_5)Ru(H_2)P_2]^+$ ($R = Me$, H; $P_2 =$ two monodentate phosphine ligands, or one bidentate phosphine ligand) constitute one of the most important classes of known dihydrogen/dihydrido complexes [1–4]. We have previously studied in detail the dihydrogen to dihydrido tautomerisation process for the systems $[(C_5R_5)Ru(H_2)(dippe)]^+$ ($R = H$, Me; dippe = 1,2-bis(diisopropylphosphino)ethane) [5] as part of our studies on the activation and binding of small molecules by transition metal complexes containing bulky phosphine ligands. We were able to prepare as well the half-sandwich dinitrogen complexes $[(C_5R_5)Ru(N_2)(dippe)]^+$ ($R = H$, Me). This allowed us to establish a correlation between the value found for $\nu(N_2)$ and the observed stability of the dihydrogen adducts. The work was extended to systems containing hydrotris(pyrazolyl)borate-(1-) ({HB(pz)$_3$}) and both bidentate [6] and monodentate bulky phosphines [7] as ligands. The complexes $[\{HB(pz)_3\}Ru(H_2)(dippe)]^+$ [6] and $[\{HB(pz)_3\}Ru(H_2)(PR_3)_2]^+$ ($PR_3 = PMe^iPr_2$, PEt_3) [7] were all found to be stable species which do not rearrange to their dihydrido tautomers, at variance with what occurs for the $[(C_5R_5)Ru(dippe)]^+$ ($R = H$, Me) systems [5]. Stable {HB(pz)$_3$}Ru dinitrogen complexes were also prepared and characterised. In order to complete this study, we have focused our attention on the C_5Me_5 and C_5H_5 ruthenium systems containing bulky monodentate phosphines, particularly PMe^iPr_2, which can be considered as a monodentate equivalent of the bulky, strong electron releasing phosphine dippe [7].

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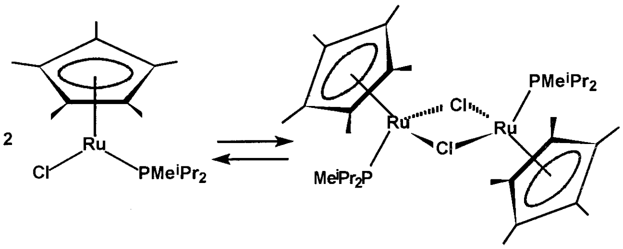
The steric and electronic properties of PMe^iPr_2 have also allowed the isolation of the 16-electron complex $[(C_5Me_5)RuCl(PMe^iPr_2)]$, which belongs to a family of stable, yet reactive coordinatively unsaturated derivatives of the type $[(C_5Me_5)RuX(PR_3)]$ (X = halide, OR, $OSiR_3$, NHPh; $PR_3 = P^iPr_3$, PCy_3, PPh^iPr_2) [8–10]. Only phosphines having large cone angles allow the isolation of such species. However, from our studies PMe^iPr_2 could be exceptional in the sense that complexes containing two of these ligands attached to the same metal centre, e.g. $[(C_5Me_5)RuCl(PMe^iPr_2)_2]$, are also accessible. In this work we describe the synthesis and properties of $[(C_5Me_5)RuCl(PMe^iPr_2)]$ and related compounds, as well as the study of C_5Me_5 and C_5H_5 ruthenium dihydrido/dihydrogen complexes containing bulky monodentate phosphine ligands.

2. Results and discussion

2.1. Synthesis and properties of $[(C_5Me_5)RuCl(PMe^iPr_2)]$ and related compounds

The 16-electron complex $[(C_5Me_5)RuCl(PMe^iPr_2)]$ (**1**) was obtained by treatment of the tetramer $[\{(C_5Me_5)RuCl\}_4]$ [11] with the stoichiometric amount of the corresponding phosphine in petroleum ether, a procedure which has been successfully used for the preparation of other related species of the type $[(C_5Me_5)RuCl(PR_3)]$ ($PR_3 = PCy_3$, P^iPr_3, PPh^iPr_2) [8–10]. Other synthetic procedures, such as the reduction of $[\{(C_5Me_5)RuCl_2\}_2]$ with zinc dust in THF in the presence of PMe^iPr_2, have proven to be less effective in the isolation of the desired pure complex. As its congeners containing bulkier phosphines, **1** is a blue, crystalline material, very soluble in non-polar solvents and extremely air-sensitive both in the solid state and in solution. Thus, exposure to air of solutions of **1** results in rapid colour change to red–brown, and formation of phophine oxide plus paramagnetic species as inferred from NMR spectroscopy. The observed colour change is consistent with the possible formation of paramagnetic oligomeric oxoruthenium(III) complexes of the type $[\{((C_5Me_5)RuCl_x)(\mu\text{-}O)\}_n]$, very much like $[((C_5Me_5)RuCl_2)_2(\mu\text{-}O)]$, already described in the literature [12]. The spectral properties for **1** are consistent with those reported for other $[(C_5Me_5)RuCl(PR_3)]$ complexes. Thus, the ^{1}H-NMR spectrum of **1** in toluene-d_8 at room temperature shows one singlet at 1.39 ppm attributable to the methyl resonances of the C_5Me_5 ring, whereas its $^{31}P\{^1H\}$-NMR spectrum displays one sharp singlet at δ 31.7 ppm. These features are consistent with a 'two-legged' piano stool structure for this complex, analogous to that found by single crystal X-ray diffraction for $[(C_5Me_5)RuCl(P^iPr_3)]$ [8]. When the temperature is lowered at 180 K, the $^{31}P\{^1H\}$-NMR resonance broadens and shifts to 32.6 ppm (ca. 1 ppm downfield), and a new, broad resonance arises at 33.4 ppm (Fig. 1). The original spectrum is restored when the temperature is raised. We have interpreted this behaviour in terms of a monomer–dimer equilibrium, as shown.



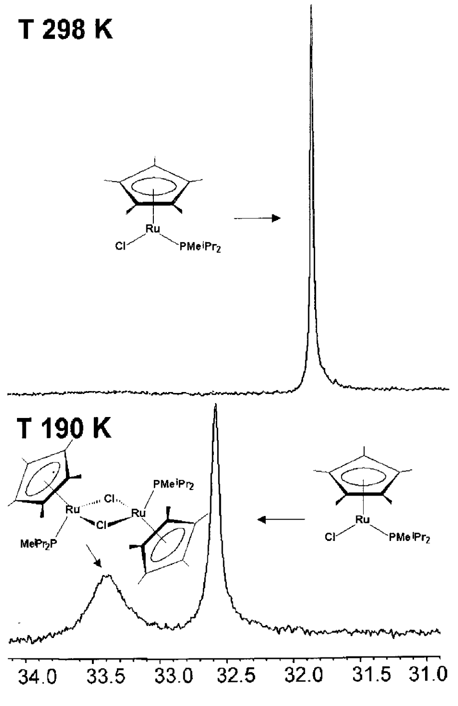


Fig. 1. $^{31}P\{^1H\}$-NMR spectra of $[(C_5Me_5)RuCl(PMe^iPr_2)]$ in toluene-d_8.

The new, broad resonance observed at 33.4 ppm should therefore correspond to the dimeric species. The amount of dimeric product observed is significative only at very low temperatures, since higher temperatures favour the monomer **1** within this equilibrium for entropical reasons. In fact, only the monomer appears to be present at room temperature, and hence the proposed monomer–dimer equilibrium (which should be rapid on the NMR time scale) only starts at already very low temperatures. This is a possible explanation for the observed downfield shift of the $^{31}P\{^1H\}$-NMR resonance of **1** as the temperature is lowered, although it could be also interpreted just in terms of the chemical shift dependence on the temperature over an expanded

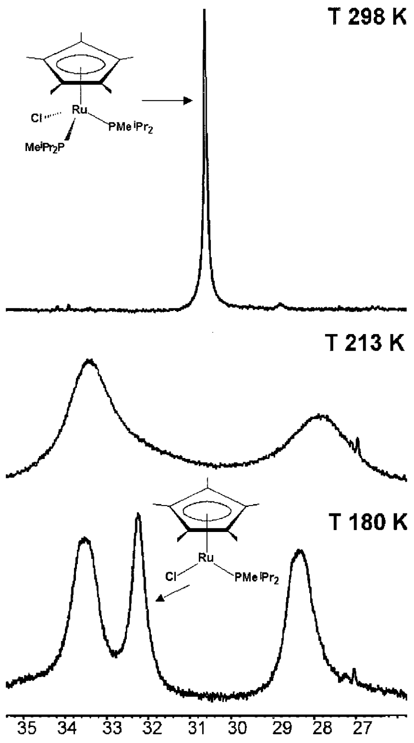
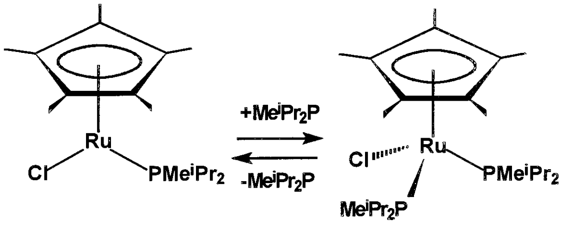


Fig. 2. ^{31}P{^{1}H}-NMR spectra (toluene-d_8) of [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)] with added PMe^{i}Pr$_2$.

range of ca. 100 K. We have found no precedent for this behaviour for other compounds of the type [(C$_5$Me$_5$)RuCl(PR$_3$)]. The coordinative unsaturation in such species is partially mitigated by π-electron donation from the lone pairs of the halide ligand, helping therefore in their stabilisation [10]. The other way for achieving 18-electron configuration if by halide-bridging dimerisation, a process which is entropically disfavoured. However, if the dimer is more stable than the monomer on enthalpy basis, an equilibrium between the two species should occur in more or less extent at low temperature, when ΔG becomes close to zero, and this is apparently what happens in our system, at variance with other ones containing bulkier phosphines.

Bulky phosphines in [(C$_5$Me$_5$)RuCl(PR$_3$)] (PR$_3$ = P^{i}Pr$_3$, PCy$_3$, PPh^{i}Pr$_2$) complexes are substitutionally labile, being readily replaced by phosphines like PEt$_3$ or PMe$_3$, and phosphites like P(OMe)$_3$, both having smaller cone angles, furnishing the corresponding 18-electron complexes [(C$_5$Me$_5$)RuCl(PR$_3$)$_2$] (PR$_3$ = PEt$_3$ or PMe$_3$) and [(C$_5$Me$_5$)RuCl(P(OMe)$_3$)$_2$], respectively [13]. In no case has been detected the formation of [(C$_5$Me$_5$)RuCl(PR$_3$)$_2$] for bulky phosphines such as P^{i}Pr$_3$ or PCy$_3$, this being attributed to steric reasons [8]. We have observed that addition of an excess of PMe^{i}Pr$_2$ to a toluene-d_8 solution of [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)] causes a colour change to orange–brown. A new singlet resonance is observed at 30.5 ppm in the ^{31}P{^{1}H}-NMR spectrum, which splits in two signals when the temperature is lowered, corresponding to an unresolved AB pattern (Fig. 2). This indicates clearly the presence of two phosphine ligands attached to ruthenium despite the bulkiness of PMe^{i}Pr$_2$, suggesting the formation of the 18-electron complex [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)$_2$].



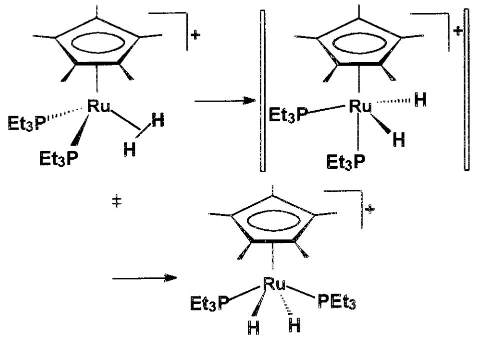
The inequivalence of the phosphorus atoms within this complex arises from freezing out conformers around single Ru–P and P–C bonds, very much as it has been recently observed for the even more sterically crowded compound [{HB(pz)$_3$}RuCl(PMe^{i}Pr$_2$)$_2$] [7]. At 180 K, one minor signal attributable to [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)] is also present in the ^{31}P{^{1}H}-NMR spectrum, indicating its co-existence with the coordinatively saturated species [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)]. The fact that both [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)] and [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)$_2$] can be generated clearly indicates that the stabilisation of this sort of coordinatively unsaturated species (at least for PMe^{i}Pr$_2$) is solely attributed to electronic, rather than steric reasons. Furthermore, in the case of the {HB(pz)$_3$} ligand, more sterically demanding than C$_5$Me$_5$, the 16-electron species [{HB(pz)$_3$}RuCl(PMe^{i}Pr$_2$)] has not yet been detected. It appears that the steric and electronic properties of PMe^{i}Pr$_2$ trace a line between those of bulkier phoshines like P^{i}Pr$_3$, PPh^{i}Pr$_2$ or PCy$_3$, and those of smaller phosphines like PEt$_3$ or PMe$_3$. [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)$_2$] was not isolated pure in solid form. All efforts to isolate it as a solid always yielded a brown oil, contaminated with substantial amounts of free PMe^{i}Pr$_2$. In relation to this, we had previously found that displacement of two PPh$_3$ ligands by PMe^{i}Pr$_2$ in [(C$_5$H$_5$)RuCl(PPh$_3$)$_2$] did not take place, and the only isolated complex upon prolonged heating at 120°C with excess of PMe^{i}Pr$_2$ was the mixed phosphine complex [(C$_5$H$_5$)RuCl(PMe^{i}Pr$_2$)(PPh$_3$)] [14]. We initially attributed this to the fact that due to the steric hindrance, the derivative [(C$_5$H$_5$)RuCl(PMe^{i}Pr$_2$)$_2$] was possibly an unstable species. However, upon isolation of complexes such as [{HB(pz)$_3$}RuCl(PMe^{i}Pr$_2$)$_2$] [7] and the detection of [(C$_5$Me$_5$)RuCl(PMe^{i}Pr$_2$)$_2$], we suspected that [(C$_5$H$_5$)RuCl(PMe^{i}Pr$_2$)$_2$] (**2**) should be stable. We prepared **2** by reaction of [(C$_5$H$_5$)RuCl(PMe^{i}Pr$_2$)(PPh$_3$)] with an excess of PMe^{i}Pr$_2$ in refluxing toluene, and it was isolated in the form of orange crystals upon purification by column chromatography on silica gel. The presence in the reaction mixture of free PPh_3 released from $[(C_5H_5)RuCl(PPh_3)_2]$ had initially prevented the substitution of the second PPh_3 by PMe^iPr_2. This problem was eventually solved by making the overall substitution in two separate steps, leading to the isolation of the desired complex **2**. This compound exhibits all the typical spectral features expected for half-sandwich complexes of the type $[(C_5H_5)RuCl(PR_3)_2]$, i.e. one singlet for the C_5H_5 protons in the ^1H-NMR spectrum, and one singlet in the $^{31}P\{^1H\}$-NMR spectrum. At variance which what was observed for the system $[(C_5Me_5)RuCl(PMe^iPr_2)_2]$, in the case of **2** no decoalescence was observed at low temperature for the resonance in the $^{31}P\{^1H\}$-NMR spectrum, suggesting that the rotation barrier around Ru–P and P–C bonds is lower in energy as expected, given the decrease in steric hindrance when substituting the ligand C_5Me_5 with C_5H_5.

2.2. Hydrido complexes

Despite its coordinatively unsaturated character, **1** does not react with hydrogen at room temperature in toluene or petroleum ether. However, it reacts with H_2 and $NaBPh_4$ in MeOH in the presence of an excess of PMe^iPr_2 affording the Ru^{IV} dihydride $[(C_5Me_5)RuH_2(PMe^iPr_2)_2][BPh_4]$ (**3a**). Likewise, the dihydrido derivatives $[(C_5R_5)RuH_2(PR_3)_2][BPh_4]$ ($R = Me$, $PR_3 = PEt_3$ (**3b**); $R = H$, $PR_3 = PMe^iPr_2$ (**4a**), PEt_3 (**4b**)) were all obtained by reaction of the corresponding chloro complex $[(C_5R_5)RuCl(PR_3)_2]$ with H_2 and $NaBPh_4$ in MeOH. The mixed-phosphine dihydride $[(C_5H_5)RuH_2(PMe^iPr_2)(PPh_3)][BPh_4]$ (**4c**) was also obtained in analogous fashion starting from $[(C_5H_5)RuCl(PMe^iPr_2)(PPh_3)]$. All these compounds are crystalline solids, which display one high-field triplet in their ^1H-NMR spectra for the hydrido ligands, which are equivalent. The $^{31}P\{^1H\}$-NMR spectra consist of one singlet for all compounds except **4c**, for which a two-doublet pattern corresponding to an AX spin system is observed. In this particular case, the triplet for the hydrido resonance arises from the accidental coincidence of the values of the two coupling constants $^2J_{HP}$ and $^2J_{HP'}$ within the complex. The long minimum longitudinal relaxation times $(T_1)_{min}$ for these hydrides, along with the null value of the coupling constant J_{HD} for the corresponding isotopomers is fully consistent with the formulation as Ru^{IV} dihydrides for these species. A transoid four-legged piano-stool structure, analogous to that found by X-ray crystallography for $[(C_5Me_5)RuH_2(dippe)][BPh_4]$ [5], $[(C_5Me_5)RuH_2(PMe_3)_2][BF_4]$ [4a], or $[(C_5Me_5)RuH_2(dppm)][BF_4]$ (dppm = 1,1-bis(diphenylphosphino)methane) [4b], is hence proposed on spectral grounds. No dihydride–dihydrogen equilibrium has been observed when lowering the temperature for any of these hydrido complexes. Only in the case of **3a**, a broadening in the $^{31}P\{^1H\}$-NMR resonance is observed, which is again attributed to the freezing of conformers around Ru–P and P–C as consequence of the bulkiness of the PMe^iPr_2 ligand and the steric repulsion within the formally seven-coordinate complex.

All dihydrides are readily deprotonated by a strong base such as $KOBu^t$ furnishing the corresponding neutral monohydrido complexes $[(C_5Me_5)RuH(PR_3)_2]$ ($PR_3 = PMe^iPr_2$ (**5a**), PEt_3 (**5b**)), $[(C_5H_5)RuH(PR_3)_2]$ ($PR_3 = PMe^iPr_2$ (**6a**), PEt_3 (**6b**)) and $[(C_5H_5)RuH(PMe^iPr_2)(PPh_3)]$ (**6c**). All these compounds are highly air sensitive, and they were isolated as oils in several instances. All of them display one high-field triplet for the hydrido ligand in their ^1H-NMR spectra, and one singlet in the $^{31}P\{^1H\}$-NMR spectra (except for **6c**, which shows two doublets as expected). Besides, a strong IR absorption is present at ca. 1950 cm^{-1}, attributed to the stretching $\nu(RuH)$. Our main interest in these monohydrido complexes was to study their protonation reaction at low temperature, in an effort to obtain cationic dihydrogen adducts of the type $[(C_5R_5)Ru(H_2)(PR_3)_2]^+$ ($R = Me$, H). We carried out the protonation reaction of the monohydrido complexes in an NMR tube in CD_2Cl_2 at 193 K using $HBF_4 \cdot OEt_2$ as acid (excess). Immediately, the sample was inserted in the pre-cooled probe and the ^1H- and $^{31}P\{^1H\}$-NMR spectra were recorded. We had previously used this procedure for the study of the metastable dihydrogen complexes $[(C_5R_5)Ru(H_2)(dippe)]^+$ ($R = Me$, H), which rearrange to their dihydrido tautomers as the temperature is raised [5]. Rather surprisingly, the only products resulting from the protonation of the monohydrides **5a** and **6a**–**c** were the corresponding cationic Ru^{IV} dihydrido complexes, these being the complex cations in compounds **3a** and **4a**–**c**, respectively. Only in the case of the protonation of **3b**, the dihydrogen derivative $[(C_5Me_5)Ru(H_2)(PEt_3)_2][BF_4]$ (**7**) was quantitatively generated, as inferred from ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy. This compound exhibits one broad resonance at -9.98 ppm for the dihydrogen ligand, for which a minimum longitudinal relaxation time $(T_1)_{min}$ of 17.5 ms was measured. A value of 21.5 Hz was obtained for the coupling constant $^1J_{HD}$ in the isotopomer $[(C_5Me_5)Ru(HD)(PEt_3)_2][BF_4]$ (prepared by reaction of **3b** with DBF_4, generated from a mixture $HBF_4 \cdot OEt_2/D_2O$ 1:3). Both $(T_1)_{min}$ and $^1J_{HD}$ are consistent with a 'non-classical' formulation for compound **7**. As temperature is raised, **7** undergoes irreversible tautomerisation to its dihydride form **3b**. At room temperature, the conversion into **3b** is quantitative. We studied the kinetics of this tautomerisation process by following the dissappearace of the phosphorus resonance for **7** in its $^{31}P\{^1H\}$-NMR spectrum, as we previously did with the related dippe complexes.

The process is first-order respect to the concentration of complex, the rate constants being independent of the concentration of complex and of acid. From the first-order rate constants measured at different temperatures, we obtained the activation parameters $\Delta H^{\neq} = 18 \pm 1$ kcal mol^{-1} and $\Delta S^{\neq} = -4.4 \pm 0.1$ eu using an Eyring plot (Fig. 3). These activation parameters lead to an overall value of $\Delta G^{\neq}_{298} = 19 \pm 1$ kcal mol^{-1} for the tautomerisation process. The observed kinetic and activation parameters are consistent with an intramolecular mechanism for the dihydrogen to dihydride rearrangement analogous to that proposed for other $[(C_5R_5)Ru(H_2)P_2]^+$ systems, as shown.



In this mechanism, initially postulated by Chinn and Heinekey [2], the dihydrogen complex traverses a relatively high-energy transition state along the pathway to dihydride, in which the coordination number changes from six to seven, and homolytic dihydrogen splitting takes place. The observed small and negative value for $\Delta S^{\neq}$ accounts for the lost of rotational freedom of the dihydrogen ligand when it transforms into a dihydrido complex [1,2]. This is fully consistent with literature data, and therefore unexceptional. The most intriguing feature is the fact that only for C_5Me_5 and PEt_3 as co-ligands appears feasible the kinetic stabilisation of coordinated dihydrogen at ruthenium in these systems. In all cases, the metal centre is electron rich and therefore the dihydrido tautomer resulting from oxidative addition of H_2 is always the final thermodynamic product, but in the case of **7**, the energy barrier for the rearrangement is high enough to allow its detection prior to isomerisation. It results surprising that the homologous dihydrogen complex $[(C_5Me_5)Ru(H_2)(PMe^iPr_2)_2]^+$, for which an even higher energy barrier could be anticipated, is not observed. We are currently carrying out detailed investigations on the $[(C_5Me_5)Ru(PMe^iPr_2)_2]^+$ system [15], and results will be reported in due course.

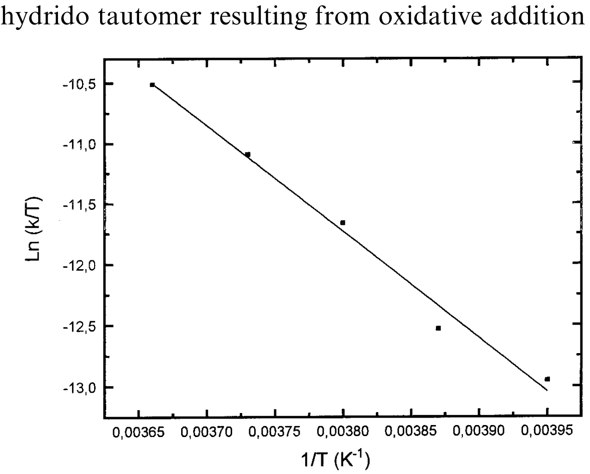


Fig. 3. Eyring plot for the tautomerisation process $[(C_5Me_5)Ru(H_2)(PEt_3)_2]^+$ (**7**) → $[(C_5Me_5)RuH_2(PEt_3)_2]^+$ (**3b**) in CD_2Cl_2.

The combination of C_5Me_5 and PEt_3 is also exceptional among the series of studied compounds because it allowed the isolation of the dinitrogen compound $[(C_5Me_5)Ru(N_2)(PEt_3)_2][BPh_4]$ (**8**) as a yellow microcrystalline material, just by reaction of $[(C_5Me_5)RuCl(PEt_3)_2]$ with N_2 and $NaBPh_4$ in MeOH. This method has been successfully used in the preparation of the half-sandwich iron derivative $[(C_5H_5)Fe(N_2)(dippe)][BPh_4]$ [16], but for other ruthenium dinitrogen complexes such as $[(C_5H_5)Ru(N_2)(dippe)][BPh_4]$ [5], or $[\{HB(pz)_3\}Ru(N_2)(PEt_3)_2][BPh_4]$ [7] the addition of a silver salt as halide scavenger was found to be essential in the synthetic procedure. Compound **8** displays one strong IR $\nu(N{\equiv}N)$ band at 2134 cm^{-1}. This frequency falls in the range for which the corresponding dihydrogen adduct is expected to be stable, according to the criterion proposed by Morris and co-workers ($2160 > \nu(N{\equiv}N) > 2060$ cm^{-1}) [17]. In this work, it has not been possible to obtain dinitrogen complexes for any other combination of C_5H_5/C_5Me_5 and phosphine ligands apart from that for compound **8**. Reciprocally, for all ruthenium dinitrogen compounds prepared by our group, the corresponding dihydrogen adduct has always been observed, or even isolated and structurally characterised in some cases. From these results, and as pointed by Morris criterion, it appears to be a correspondence between the ability of a ruthenium centre for binding N_2 and the stabilisation of the ruthenium–dihydrogen bond.

All attempts to recrystallise compound **8** were unsuccessful. Dinitrogen is released, and most often, the dioxygen derivative $[(C_5Me_5)Ru(O_2)(PEt_3)_2][BPh_4]$ (**9**) was obtained. The moiety $\{[(C_5Me_5)Ru(PEt_3)_2]^+\}$ has an enormous affinity for dioxygen, as it occurs also for $\{[(C_5Me_5)Ru(dippe)]^+\}$ [5,18], leading to the irreversible formation of the dioxygen complex even at trace level concentrations of O_2. Compound **9** is therefore a very stable material, such like $[(C_5Me_5)Ru(O_2)(dippe)][BPh_4]$ [18] or $[(C_5Me_5)Ru(O_2)(dppe)][BPh_4]$ [19], which becomes a 'stability well' to be considered in most reactions in which the moiety $\{[(C_5Me_5)Ru(PEt_3)_2]^+\}$ is involved.

3. Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional

Schlenk or drybox techniques. THF, diethylether and petroleum ether (b.p. range 40–60°C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. $[\{(C_5Me_5)RuCl\}_4]$ [11], $[(C_5Me_5)RuCl(PEt_3)_2]$, $[(C_5H_5)RuCl(PEt_3)_2]$ and $[(C_5H_5)RuCl(PMe^iPr_2)(PPh_3)]$ [14] were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on Perkin–Elmer 881 or Perkin–Elmer FTIR Spectrum 1000 spectrophotometers. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz spectrophotometers. Chemical shifts are given in ppm from $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$). Microanalyses were taken by Dr Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

3.1. Preparation of $[(C_5Me_5)RuCl(PMe^iPr_2)]$ **(1)**

To a slurry of $[\{(C_5Me_5)RuCl\}_4]$ (0.54 g, 0.5 mmol) in petroleum ether, PMe^iPr_2 (0.3 ml, 2 mmol) was added. An immediate colour change to purple–blue was observed, with the concomitant dissolution of the tetrameric $[\{(C_5Me_5)RuCl\}_4]$. The mixture was stirred for 15 min. Then, the solution was filtered through Celite, concentrated and cooled to −20°C. Large dark blue, almost black, crystals were obtained. They were filtered off and dried in vacuo. Further crops could be obtained by subsequent concentration and cooling of the mother liquor. Yield: 0.53 g, 66%. Anal. Calc. for $C_{17}H_{32}ClPRu$: C, 50.6; H, 7.93. Found C, 50.3; H, 7.88%. NMR (toluene-d_8): ^1H: δ 0.65, 0.76, 0.99 (m, $PCH(CH_3)_2$), 1.13 (d, PCH_3), 1.93, 2.23 (m, $PCH(CH_3)_2$), 1.39 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$: δ 31.7 (s).

3.2. $[(C_5H_5)RuCl(PMe^iPr_2)_2]$ **(2)**

A solution of $[(C_5H_5)RuCl(PMe^iPr_2)(PPh_3)]$ (0.8 g, 1.34 mmol) in toluene was treated with an excess of PMe^iPr_2 (0.35 ml). The mixture was heated under reflux for 18 h. At the end of this time, the solvent was removed in vacuo. The resulting orange oil was dissolved in a minimum amount of petroleum ether and passed through a silica gel chromatographic column in order to remove PPh_3. This was done in the air, an inert atmosphere being not necessary at this stage. The column was eluted with petroleum–diethylether (3:1 v/v). The fraction corresponding to the orange band was collected. Removal of the solvent afforded a yellow–orange microcrystalline material. Analytically pure samples were obtained by recrystalisation from petroleum ether/diethylether. Yield: 0.46 g, 74%. Anal. Calc. for $C_{19}H_{39}ClP_2Ru$: C, 49.0; H, 8.38. Found C, 49.1; H, 8.40%. NMR (C_6D_6): ^1H: δ 1.15, 1.18 (m, $PCH(CH_3)_2$), 1.14 (d, PCH_3), 1.86 (m, $PCH(CH_3)_2$), 4.40 (s, C_5H_5). $^{31}P\{^1H\}$: δ 40.0 (s).

3.3. $[(C_5Me_5)RuH_2(PMe^iPr_2)_2][BPh_4]$ **(3a)**

To a solution of **1** (0.15 g, ca. 0.37 mmol) in MeOH, PMe^iPr_2 (0.1 ml, excess) was added. Hydrogen was bubbled through the reaction mixture, which was then treated with an excess of solid $NaBPh_4$ (0.25 g). A light brown precipitate was immediately formed. The mixture was stirred under a H_2 atmosphere for 15 min. After this time, the solids were filtered off, washed with ethanol and petroleum ether and dried in vacuo. The compound was recrystallised from acetone/ethanol as a light brown microcystalline material. Yield: 0.24 g, 80%. Anal. Calc. for $C_{48}H_{71}BP_2Ru$: C, 70.2; H, 8.65. Found C, 69.9; H, 8.73%. IR (Nujol): $\nu(RuH)$ 2016 br cm^{-1}. NMR (CD_3COCD_3): ^1H: δ −9.21 (t, $^2J_{HP} = 28.7$ Hz, RuH_2; $(T_1)_{min} = 740$ ms at 400 MHz), 2.01 (s, $C_5(CH_3)_5$), 1.19 (m, $PCH(CH_3)_2$), 1.33 (d, PCH_3), 2.07 (m, $PCH(CH_3)_2$). $^{31}P\{^1H\}$: δ 55.7 (s).

3.4. $[(C_5Me_5)RuH_2(PEt_3)_2][BPh_4]$ **(3b)**

To a solution of $[(C_5Me_5)RuCl(PEt_3)_2]$ (0.2 g, 0.39 mmol) in MeOH, solid $NaBPh_4$ (0.3 g, excess) was added while a stream of H_2 was bubbled through the reaction mixture. A white precipitate was formed. Upon stirring for 10 min, it was filtered off, washed with ethanol and petroleum ether and dried in vacuo. Recrystallisation from acetone/ethanol afforded colourless crystals of this compound, which were filtered off and dried in vacuo. Yield: 0.32 g, 95%. Anal. Calc. for $C_{46}H_{67}BP_2Ru$: C, 69.6; H, 8.52. Found: C, 69.4; H, 8.48%. IR (Nujol): $\nu(RuH)$ 1958 w, 2004 w cm^{-1}. NMR (CD_3COCD_3): ^1H: δ −9.47 (t, $^2J_{HP} = 28.4$ Hz, RuH_2; $(T_1)_{min} = 764$ ms at 400 MHz), 2.00 (s, $C_5(CH_3)_5$), 1.10 (m, PCH_2CH_3), 1.80 (m, PCH_2CH_3). $^{31}P\{^1H\}$: δ 49.9 (s).

3.5. $[(C_5H_5)RuH_2(PR_3)_2][BPh_4]$ ($PR_3 = PMe^iPr_2$ **(4a)**, PEt_3 **(4b)**)

A method analogous to that used in the preparation of **3b** was used for the synthesis of these compounds, starting either from $[(C_5H_5)RuCl(PMe^iPr_2)_2]$ (for **4a**) or from $[(C_5H_5)RuCl(PEt_3)_2]$ (for **4b**).

Compound **4a**: Yield: 70%. Anal. Calc. for $C_{43}H_{61}BP_2Ru$: C, 68.7; H, 8.12. Found C, 68.5; H, 8.22%. IR (Nujol): $\nu(RuH)$ not observed. NMR (CD_3COCD_3): ^1H: δ −9.47 (t, $^2J_{HP} = 24.9$ Hz, RuH_2; $(T_1)_{min} = 520$ ms at 400 MHz), 1.18 (d, PCH_3), 1.34–1.45 (m, $PCH(CH_3)_2$), 2.03 (m, $PCH(CH_3)_2$), 5.91 (s, C_5H_5). $^{31}P\{^1H\}$: δ 65.5 (s).

Compound **4b**: Yield: 72%. Anal. Calc. for $C_{41}H_{57}BP_2Ru$: C, 73.0; H, 7.79. Found: C, 73.1; H, 7.81%. IR (Nujol): $\nu(RuH)$ 1994 w, 2022 w cm^{-1}. NMR (CD_3COCD_3): ^1H: δ −10.09 (t, $^2J_{HP} = 25.4$ Hz,

$\mathrm{Ru}H_2$; $(T_1)_{\mathrm{min}} = 500$ ms at 400 MHz), 0.96 (m, $\mathrm{PCH_2C}H_3$), 1.43 (m, $\mathrm{PC}H_2\mathrm{CH_3}$), 4.85 (s, $\mathrm{C_5}H_5$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 54.5 (s).

3.6. *$[(C_5H_5)RuH_2(PPh_3)(PMe^iPr_2)][BPh_4]$ (**4c**)*

A procedure identical to that for **4a**–**b** was used for the preparation of this compound, starting from $[(\mathrm{C_5H_5})\mathrm{RuCl}(\mathrm{PMe}^i\mathrm{Pr_2})(\mathrm{PPh_3})]$. Yield: 60%. Anal. Calc. for $\mathrm{C_{54}H_{59}BP_2Ru}$: C, 77.9; H, 7.16. Found: C, 77.8; H, 7.21%. IR (Nujol): ν(RuH) 2008 w, 2042 w $\mathrm{cm^{-1}}$. NMR ($\mathrm{CD_3COCD_3}$): ^{1}H: δ −9.11 (t, $^2J_{\mathrm{HP}} = 24.6$ Hz, $\mathrm{Ru}H_2$; $(T_1)_{\mathrm{min}} = 320$ ms at 400 MHz), 0.94, 1.11 (m, $\mathrm{PCH(C}H_3)_2$), 1.25 (d, $\mathrm{PC}H_3$), 2.05 (m, $\mathrm{PC}H(\mathrm{CH_3})_2$), 4.78 ($\mathrm{C_5}H_5$), 7.22, 7.45, 7.63 (m, $\mathrm{P(C_6}H_5)_3$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 61.1(d), 64.3 (d), $^2J_{\mathrm{PP}} = 48$ Hz.

3.7. *$[(C_5Me_5)RuH(PR_3)_2]$ ($PR_3 = PMe^iPr_2$ (**5a**), PEt_3 (**5b**))*

To a solution of either **5a** or **5b** in THF, an excess of solid KOBu^t was added. A yellow–orange colour developed immediately. The mixture was stirred for 15 min at room temperature. At the end of this time, the solvent was removed in vacuo, and the residue extracted with petroleum ether. The resulting solution was filtered through Celite. Removal of the solvent afforded a yellow oil, which was re-dissolved in a minimum amount of petroleum ether, and cooled to −20°C. Air-sensitive yellow crystals were obtained, which were isolated by removing the supernatant liquor via cannula, and dried thoroughly in vacuo.

Compound **5a**: Yield: 50%. Anal. Calc. for $\mathrm{C_{24}H_{50}P_2Ru}$: C, 57.5; H, 9.98. Found C, 57.5; H, 9.76%. IR (Nujol): ν(RuH) 1954 $\mathrm{cm^{-1}}$. NMR ($\mathrm{C_6D_6}$): ^{1}H: δ −14.57 (t, $^2J_{\mathrm{HP}} = 37$ Hz, $\mathrm{Ru}H$), 0.95 (d, $\mathrm{PC}H_3$), 0.77, 1.01, 1.12 (m, $\mathrm{PCH(C}H_3)_2$), 1.61, 1.81 (m, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.89 ($\mathrm{C_5(C}H_3)_5$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 54.3 (s).

Compound **5b**: Yield: 58%. Anal. Calc. for $\mathrm{C_{22}H_{46}P_2Ru}$: C, 55.8; H, 9.81. Found: C, 55.6; H, 9.75%. IR (Nujol): ν(RuH) 1939 $\mathrm{cm^{-1}}$. NMR ($\mathrm{C_6D_6}$): ^{1}H: δ −14.26 (t, $^2J_{\mathrm{HP}} = 36.8$ Hz, $\mathrm{Ru}H$), 1.85 (s, $\mathrm{C_5}H_5$), 0.12 (m, $\mathrm{PCH_2C}H_3$), 1.10 (m, $\mathrm{PC}H_2\mathrm{CH_3}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 46.4 (s).

3.8. *$[(C_5H_5)RuH(PR_3)_2]$ ($PR_3 = PMe^iPr_2$ (**6a**), PEt_3 (**6b**))*

These compounds were obtained by deprotonation of the corresponding dihydride **4a** or **4b** using KOBu^t, following a procedure identical to that outlined for **5a**–**b**.

Compound **6a**: This compound was obtained as an air-sensitive oil, and it was not analysed. IR (Nujol): ν(RuH) 1944 $\mathrm{cm^{-1}}$. NMR ($\mathrm{CD_3COCD_3}$): ^{1}H: δ −9.15 (t, $^2J_{\mathrm{HP}} = 24.4$ Hz, $\mathrm{Ru}H$), 1.02 (d, $\mathrm{PC}H_3$), 0.93–1.10 (m, $\mathrm{PCH(C}H_3)_2$), 1.54, 1.75 (m, $\mathrm{PC}H(\mathrm{CH_3})_2$), 4.54 ($\mathrm{C_5}H_5$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 61.7 (s).

Compound **6b**: Yield: 55%. Anal. Calc. for $\mathrm{C_{17}H_{36}P_2Ru}$: C, 57.7; H, 10.2. Found C, 57.5; H, 10.0%. IR (Nujol): ν(RuH) 1940 $\mathrm{cm^{-1}}$. NMR ($\mathrm{CD_3COCD_3}$): ^{1}H: δ −13.32 (t, $^2J_{\mathrm{HP}} = 35.6$ Hz, $\mathrm{Ru}H$), 0.91 (m, $\mathrm{PCH_2C}H_3$), 1.50 (m, $\mathrm{PC}H_2\mathrm{CH_3}$), 4.70 (s, $\mathrm{C_5}H_5$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 53.6 (s).

3.9. *$[(C_5H_5)RuH(PPh_3)(PMe^iPr_2)]$ (**6c**)*

It was obtained as described for compounds **5a**–**b** and **6a**–**b**, starting from the dihydride **4c**. Yield: 88%. Anal. Calc. for $\mathrm{C_{30}H_{38}P_2Ru}$: C, 70.4; H, 7.50. Found: C, 70.2; H, 7.43%. IR (Nujol): ν(RuH) 1944 $\mathrm{cm^{-1}}$. NMR ($\mathrm{C_6D_6}$): ^{1}H: δ −11.58 (t, $^2J_{\mathrm{HP}} = 34.4$ Hz, $\mathrm{Ru}H$), 0.38 (d, $\mathrm{PC}H_3$), 0.84, 0.97 (m, $\mathrm{PCH(C}H_3)_2$), 1.71 (m, $\mathrm{PC}H(\mathrm{CH_3})_2$), 4.58 ($\mathrm{C_5}H_5$), 5.90, 6.12 (m, $\mathrm{P(C_6}H_5)$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ 58.7 (d), 72.8 (d), $^2J_{\mathrm{PP}} = 32.8$ Hz.

3.10. *$[(C_5Me_5)Ru(H_2)(PEt_3)_2][BF_4]$ (**7**)*

Compound **7** was obtained and characterised in solution by protonation of the monohydride **5b** inside a 5 mm NMR tube in either $\mathrm{CD_3COCD_3}$ or $\mathrm{CD_2Cl_2}$ at 193 K, using a slight excess $\mathrm{HBF_4{\cdot}OEt_2}$. Yield: quantitative. NMR ($\mathrm{CD_3COCD_3}$, 203 K): ^{1}H: δ −9.98 (br, $\mathrm{Ru}(H_2)$, $(T_1)_{\mathrm{min}} = 17.5$ ms at 400 MHz, $^1J_{\mathrm{HD}} = 21.5$ Hz), 1.21 (m, $\mathrm{PCH_2C}H_3$), 2.36 (m, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.95 (s, $\mathrm{C_5(C}H_3)_5$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ (203 K) 35.0 (s).

3.11. *Kinetics of the dihydrogen to dihydride isomerisation **7**→**3b***

Samples of **7**, prepared as described above, were immersed into a liquid nitrogen/ethanol bath, in order to prevent isomerisation during transport and handling. The sample was removed and introduced into the pre-cooled probe of the Varian Unity 400 MHz spectrometer at 203 K (the NMR temperature controller was previously calibrated against a methanol sample, the reproducibility being ±5°C). Once the shims were adjusted, the probe was warmed to the desired temperature. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectra were recorded for at least three half-lives at regular intervals using the spectrometer software for accurate time control. Peak intensities were analysed from stacked plots of the $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectra. First-order rate constants were derived from the least-squares best-fit lines of the ln(intensity) versus time plots. The uncertainty in the isomerisation rate constants represents one standard deviation ($\pm\sigma$) derived from the slope of the best-fit line. Uncertainties in the activation enthalpy and entropy were calculated from the uncertainties in the slope and intercept of the best-fit lines of the Eyring plots.

3.12. *[$(C_5Me_5)Ru(N_2)(PEt_3)_2$][$BPh_4$]* (**8**)

To a solution of [$(C_5Me_5)RuCl(PEt_3)_2$] (0.25 g, ca. 0.5 mmol) in MeOH under dinitrogen, an excess of solid $NaBPh_4$ (0.3 g) was added. A yellow precipitate was formed gradually. Upon stirring for 10–15 min, the precipitate was filtered off, washed with ethanol and petroleum ether, and dried in vacuo. All attempts to recrystallise this material led to dinitrogen loss, and eventual formation of the dioxygen derivative [$(C_5Me_5)Ru(O_2)(PEt_3)_2$][$BPh_4$] (**9**), described below. As a consequence, accurate microanalysis figures could not be obtained. Yield (crude): 0.25 g, 61%. Anal. Calc. for $C_{46}H_{65}BN_2P_2Ru$: C, 67.4; H, 8.01; N, 3.4. Found C, 66.8; H, 8.11; N, 1.8%. IR (Nujol): $\nu(N_2)$ 2134 cm^{-1}. NMR (CD_2Cl_2): ^1H: δ 1.13 (m, PCH_2CH_3), 1.90 (m, PCH_2CH_3);1.75 s ($C_5(CH_3)_5$). $^{31}P\{^1H\}$: δ 22.3 s.

3.13. *[$(C_5Me_5)Ru(O_2)(PEt_3)_2$][$BPh_4$]* (**9**)

This compound was obtained following a procedure identical to that used for the dinitrogen derivative **8**, but performing the reaction under air instead of dinitrogen. Amber crystals of this compound were obtained upon recrystallisation from acetone/ethanol. Yield: 85%. Anal. Calc. for $C_{46}H_{65}BO_2P_2Ru$: C, 67.0; H, 7.97. Found C, 67.0; H, 8.10%. NMR ($CDCl_3$): ^1H: δ 1.11 (m, PCH_2CH_3), 1.74 (m, PCH_2CH_3), 1.47 s ($C_5(CH_3)_5$). $^{31}P\{^1H\}$: δ 22.2 s.

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