# Molecular Hydrogen Complexes: The Effect of Steric Factors on the Protonation of the Monohydrides $[(\eta^5\text{-}C_5H_5)Ru(Ph_2P(CH_2)_nPPh_2)H]$ ($n$ = 1—3)

**Fiona M. Conroy-Lewis and Stephen J. Simpson***

*Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.*

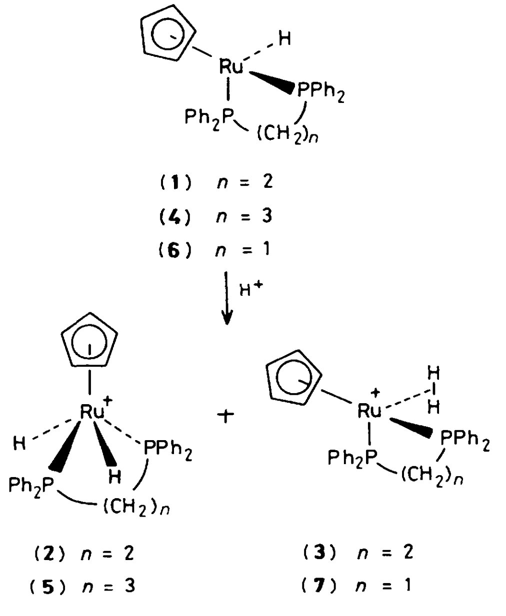
Protonation of the title complexes leads to either ($\eta^2$-$H_2$) or *trans*-dihydride monocations depending on the length of the chain connecting the two phosphine atoms; $T_1$ and $J_{HD}$ measurements are used to support these structures.

We reported recently[1] that protonation of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(Bu^tNC)H]$ gave the ($\eta^2$-$H_2$) cation, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(Bu^tNC)(H_2)]^+$. The most likely product, a dihydride cation, is not seen at all in this reaction, but extension of this reaction to related systems gave either an ($\eta^2$-$H_2$) or ($\sigma$-H)$_2$ product and in one case a mixture of both products. We now present these results and show how n.m.r. measurements support the assignments made.

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)H]$ (**1**)[2] with $HPF_6$ gave a white microcrystalline solid which $^1H$, $^{31}P\{^1H\}$, and $^1H\{^{31}P\}$ n.m.r. data showed to be a 2 : 1 mixture of the dihydride cation (**2**) and the molecular dihydrogen cation (**3**). In particular the high field $^1H$ n.m.r. spectrum of (**2**) contains a triplet ($\delta$ −8.60, $J_{PH}$ 28 Hz), while that of (**3**) is a broad peak ($\delta$ −9.02, $w_{\frac{1}{2}}$ 14 Hz). Figure 1 shows the results of the determination of $T_1$ for the mixtures of (**2**) and (**3**) by the inversion–recovery method at 298 K. The values of 1.3 s for (**2**) and 0.03 s for (**3**) provide the first internal comparison for an isomer mixture of this type in the absence of exchange processes. Saturation transfer experiments on the mixture demonstrated that the exchange (**2**) ⟷ (**3**) was not occurring on the n.m.r. timescale; also the ratio of (**2**) to (**3**) is invariant with time.

Treatment of (**1**) with the fluorinated carbon acid $(CF_3SO_2)_2C(Ph)D$ gave a mixture of isotopomers of (**2**) and (**3**). Analysis of the n.m.r. spectrum of the mixture prepared *in situ* revealed values for $J_{HD}$ of <1 Hz for (**2**) and 24.9 Hz for (**3**). These values of $J_{HD}$ and the $T_1$ data above fully support the proposed structures of (**2**) and (**3**), since they reflect trends reported by Crabtree,[3] Morris,[4] and Kubas.[5] In addition the spectrum due to $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)(\eta^2\text{-}HD)]^+$ shows a value for $J_{PH}$ of 2.0 Hz. This is the first reported value of $J_{PH}$ for an ($\eta^2$-$H_2$) complex derived by direct observation, since normally the linewidth of the ($\eta^2$-$H_2$) resonance precludes this measurement even when the $^1H\{^{31}P\}$ spectrum is obtained, whereas the decreased linewidth in the ($\eta^2$-HD) complex allows resolution. Morris has recently reported a value for $^2J_{PH}$ of 5.8 Hz for $[Os(\eta^2\text{-}H_2)H(Et_2PCH_2CH_2PEt_2)_2]^+$, obtained from spectral simulation. In this case, even for the ($\eta^2$-HD) isotopomer, the coupling was not resolvable at low temperature.[4]

Treatment of $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2CH_2PPh_2)H]$ (**4**) with $HPF_6$ gave exclusively the dihydride cation $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2CH_2PPh_2)(H)_2]PF_6$ (**5**) which exhibits a high field triplet in the $^1H$ n.m.r. spectrum ($\delta$ −8.62, $J_{PH}$ 28 Hz). Inversion–recovery experiments gave a $T_1$ value of 1.15 s for (**5**) at 298 K. In contrast, protonation of $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2PPh_2)H]$ (**6**),[6] containing the smaller chelating diphosphine, gave exclusively the molecular dihydrogen cation (**7**) whose $^1H$ n.m.r. spectrum contained a broad signal at $\delta$ −6.98, $w_{\frac{1}{2}}$ 10 Hz. The ($\eta^2$-HD) isotopomer of (**7**) showed that $J_{HD}$ was 21.9 Hz confirming the intact nature of the HD bond in (**7**).



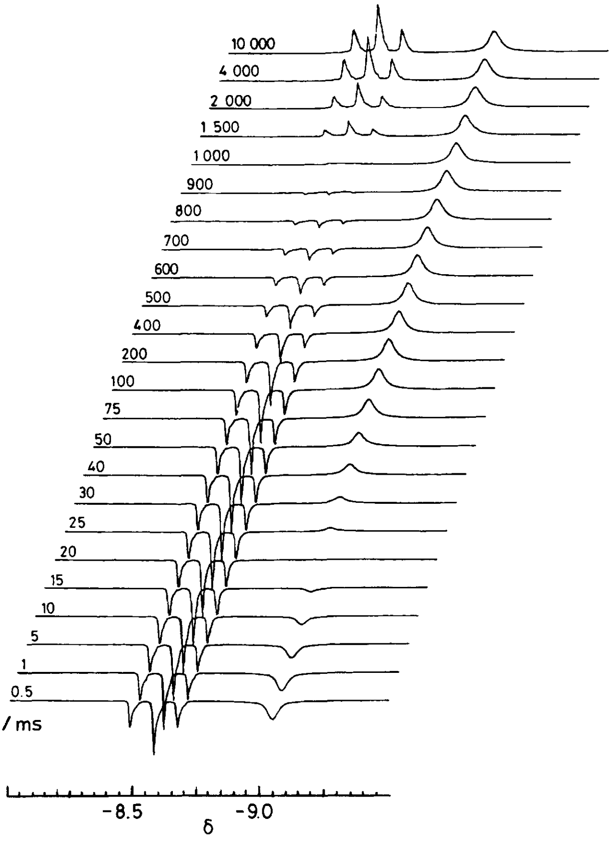
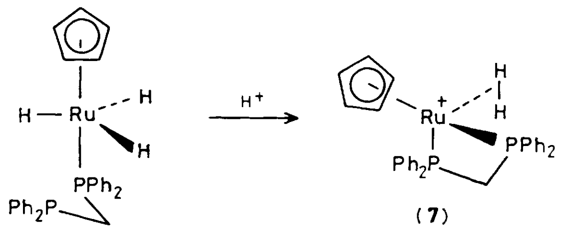


**Figure 1.** Inversion–recovery $T_1$ determination for a mixture of (**2**) and (**3**) in $CD_2Cl_2$ at 298 K, performed at 300 MHz using standard Bruker programs.



(8) (7)

$[(\eta^5\text{-}C_5H_5)RuH_3(\sigma\text{-}Ph_2PCH_2PPh_2)]$ (**8**), prepared by reaction of $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2PPh_2)Cl]$[7] with $LiAlH_4$ in tetrahydrofuran (THF),† was protonated *in situ* with $HPF_6$ and the resulting $^1H$ n.m.r. spectrum showed (**7**) to be the exclusive product, no sign of a $(\sigma\text{-}H)_2$ complex being seen.

The above results combined with the observations that the hydrides $[(\eta^5\text{-}C_5H_5)Ru(PR_3)_2H]$, ($R_3$ = $Ph_3$, $Me_3$, $MePh_2$), gave only *trans*-dihydride cations on protonation suggest the following rationalisations. (a) Electronic factors for these bisphosphine hydrides dictate that the basic $d^6$ metal centre is the site of protonation leading to *trans*-dihydride cations. The incoming proton must approach *trans* to the metal–hydride bond between the two phosphorus atoms. (b) Steric factors present in small chelate rings preventing this direction of approach force the formation of an $(\eta^2\text{-}H_2)$ complex. This can be considered as a *cis*-dihydride where the two hydrogen atoms prefer mutual bonding. We consider it likely that in this case the hydride ligand is actually protonated and not the metal centre. This rationalisation could also explain why the hydride $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(Bu^tNC)H]$ gives an $(\eta^2\text{-}H_2)$ cation on reaction; clearly in this case steric factors would predict formation of a *trans*-$(\sigma\text{-}H)_2$ complex whereas presumably the lower basicity of the metal centre in this hydride leads to attack on the hydride ligand itself. We have never seen any evidence for the formation of a classical *cis*-dihydride product in any of the systems examined.

The result of the protonation of (**8**) demonstrates the high stability of molecular dihydrogen complexes in this $Ru^{II}$ $d^6$ manifold since this is certainly a route where the dihydride cation might be the expected product. Ashworth and Singleton have previously reported the dependence on size of chelating diphosphine ligand for the isolation of trihydride cations which contained stable or labile hydrogen ligands in the system $[RuH_3(L_2)_2]^+$ ($L_2$ = chelating phosphine).[8]

We thank the S.E.R.C. for support (to F.M. C.-L.), Johnson-Matthey Chemicals Limited for a loan of ruthenium trichloride and Dr. A Siedle for a generous gift of fluorochemical acids.

*Received, 13th July 1987; Com. 996*

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† $^{31}P\{^1H\}$ n.m.r. ($C_6D_6$): δ 66.1 (d, $J_{PP}$ 108 Hz) and −25.7 (d, $J_{PP}$ 108 Hz); $^1H$ n.m.r. ($C_6D_6$): δ 4.85 (s, 5H, $C_5H_5$) and −9.89 (d, $J_{PH}$ 20.1 Hz, 3H, RuH); *cf.* $[(\eta^5\text{-}C_5H_5)RuH_3(PPh_3)]$ in ref. 2.