# Some New Dicationic Dihydrogen Complexes of Ruthenium

**Kanak K. Majumdar,[a] H. V. Nanishankar,[a] and Balaji R. Jagirdar*[a]**

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A series of new dicationic dihydrogen complexes of ruthenium of the type *trans*-[(dppe)$_2$Ru($\eta^2$-H$_2$)(RCN)][BF$_4$]$_2$ [dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; R = CH$_3$, CH$_3$CH$_2$, CH$_3$CH$_2$CH$_2$, CH$_2$=CH, *p*-CH$_3$–C$_6$H$_4$–CH$_2$, C$_6$H$_5$, and (CH$_3$)$_2$N] have been prepared by the protonation reaction of the precursor hydrides, *trans*-[(dppe)$_2$Ru(H)(RCN)][BF$_4$] using HBF$_4$·OEt$_2$. The variable temperature spin-lattice relaxation times ($T_1$, ms) and the H, D coupling constants of the $\eta^2$-HD isotopomers indicate the intact nature of the H–H bond in these complexes. It was found that the spectroscopic and chemical properties of these derivatives are not very sensitive to the change in the *trans* nitrile ligand. The p$K_a$ values of the dihydrogen complexes have been determined using the equilibrium: *trans*-[(dppe)$_2$Ru(H)(RCN)][BF$_4$] + HBF$_4$·OEt$_2$ ⇄ *trans*-[(dppe)$_2$Ru($\eta^2$-H$_2$)(RCN)][BF$_4$]$_2$ + Et$_2$O by $^1$H NMR spectroscopy.

## Introduction

The dihydrogen molecule can be activated toward heterolytic cleavage when coordinated to a cationic metal center. This was first realized by Crabtree and Lavin in the deprotonation reaction of the H$_2$ ligand in [(PPh$_3$)$_2$(bq)Ir($\eta^2$-H$_2$)H]$^+$ (bq = 7,8-benzoquinolato) in the presence of alkyllithium reagents in preference to the loss of hydride ligand.[1] The heterolysis of dihydrogen has been observed for a variety of complexes and has been shown to depend on the nature of the metal center as well as the ancillary ligand environment.[2] Lau and co-workers[2l] recently prepared and characterized various dihydrogen complexes of ruthenium with triazacyclononane, trimethyltriazacyclononane, and hydrotris(pyrazolyl)borate as ancillary ligands. They found their dicationic complexes to be more acidic than their monocationic hydrotris(pyrazolyl)borate and cyclopentadienyl counterparts. Morris et al.[2p] reported a highly acidic dicationic dihydrogen complex, *trans*-[(dppe)$_2$Ru($\eta^2$-H$_2$)(CNH)][OTf]$_2$ that was found to be stable with respect to loss of protons or H$_2$ in the presence of strong acids like HOTf. However, it should not be implied that the dicationic dihydrogen complexes would be stronger acids than the monocationic derivatives. Harman and Taube[3] found the dicationic osmium complex, [Os(H$_2$)(NH$_3$)$_5$]$^{2+}$ to be a weak acid that is stable toward moderately strong bases such as NaOMe.

The dicationic dihydrogen complexes of transition metals reported to date are very few in number. Therefore, we sought to synthesize and characterize a series of isostructural dicationic dihydrogen complexes of ruthenium bearing bis(1,2-diphenylphosphanyl)ethane (dppe) and nitrile ligands. In addition, we also wanted to study the variation in some of the properties of dihydrogen complexes, for example, the H−H distances and the acidities with a change in the steric and the electronic properties of the nitrile ligand that is *trans* to the dihydrogen moiety.

[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India
E-mail: jagirdar@ipc.iisc.ernet.in

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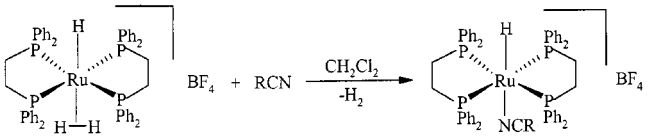
## Results and Discussion

### Synthesis and Characterization of the New Ruthenium Hydride Complexes

The complexes *trans*-[(dppe)$_2$Ru(H)(RCN)][BF$_4$] [R = CH$_3$ (**1**), CH$_3$CH$_2$ (**2**), CH$_3$CH$_2$CH$_2$ (**3**), CH$_2$=CH (**4**), *p*-CH$_3$−C$_6$H$_4$−CH$_2$ (**5**), C$_6$H$_5$ (**6**), (CH$_3$)$_2$N (**7**)] were prepared from *trans*-[(dppe)$_2$Ru($\eta^2$-H$_2$)(H)][BF$_4$] by the substitution of the dihydrogen ligand by the nitrile, analogous to the preparation of *trans*-[(dppe)$_2$Os(H)(CH$_3$CN)][BF$_4$] reported by Schlaf et al.[2i] [Equation (1)].




R = CH$_3$- (**1**), CH$_3$CH$_2$- (**2**), CH$_3$CH$_2$CH$_2$- (**3**), CH$_2$=CH- (**4**), *p*-CH$_3$-C$_6$H$_4$-CH$_2$- (**5**), C$_6$H$_5$- (**6**), (CH$_3$)$_2$N- (**7**)

(1)

The products were obtained in fairly good yields as summarized in Table 1. They are all colorless to off-white solids. Purification of the complexes was achieved by crystallization by slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution containing the hydride complex and a slight excess of the appropriate nitrile. In the absence of the excess nitrile in the crystallization solution, we observed that loss of the nitrile ligand bound to ruthenium takes place due to its lability. This results in the decomposition of the hydride complex into intractable products.

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Table 1. Preparation and analytical data for *trans*-[$(dppe)_2Ru(H)(RCN)][BF_4]$ complexes

| R | Starting materials [A][b] (mg) | [B][b] (mg) | Yield % (mg) | Analysis (%)[a] C | H | N | P[c] |
|---|---|---|---|---|---|---|---|
| $CH_3$ (**1**) | 0.06 (59) | 1.22 (50) | 75 (47) | 63.63 (63.15) | 5.43 (5.07) | 1.38 (1.36) | *n.d.* |
| $CH_3CH_2$ (**2**) | 0.20 (197) | 0.56 (30) | 71 (149) | 63.78 (63.46) | 5.50 (5.19) | 1.10 (1.34) | 11.81 (11.92) |
| $CH_3(CH_2)_2$ (**3**) | 0.20 (197) | 0.57 (39) | 70 (149) | 63.83 (63.76) | 5.30 (5.31) | 1.00 (1.33) | *n.d.* |
| $CH_2$=CH (**4**) | 0.20 (197) | 0.47 (24) | 73 (153) | 63.12 (63.58) | 5.09 (5.00) | 0.98 (1.34) | 11.46 (11.95) |
| *p*-$CH_3-C_6H_4-CH_2$ (**5**) | 0.20 (197) | 0.45 (59) | 64 (140) | 65.60 (65.59) | 5.23 (5.19) | 1.25 (1.25) | *n.d.* |
| $C_6H_5$ (**6**) | 0.20 (197) | 0.49 (50) | 54 (119) | 65.08 (65.07) | 5.36 (4.96) | 1.42 (1.29) | *n.d.* |
| $(CH_3)_2N$ (**7**) | 0.20 (197) | 0.49 (34) | 62 (132) | 62.66 (62.56) | 5.40 (5.21) | 2.66 (2.65) | *n.d.* |

[a] Calculated values are given in parentheses. – [b] [A] = [*trans*-$[(dppe)_2Ru(H_2)(H)][BF_4]$]; [B] = [nitrile] (mmol). – [c] *n.d.* not determined.

Table 2. $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopic data (δ) of *trans*-$[(dppe)_2Ru(H)(RCN)][BF_4]$ complexes in $CD_2Cl_2$

| R | δ(Ru–H) | $J(H,P_{cis})$ Hz | δ(R) | δ($CH_2-CH_2$) | δ(Ph) | δ[P(dppe)] |
|---|---|---|---|---|---|---|
| $CH_3$ (**1**) | –15.98 (qnt, 1 H) | 20 | 1.58 (s, 3 H, C*H*$_3$) | 2.61 (m, 4 H) 1.96 (m, 4 H) | 6.65–7.54 (m, 40 H) | 65.55 |
| $CH_3CH_2$ (**2**) | –16.00 (qnt, 1 H) | 20 | 1.93 (q, 2 H, C*H*$_2$) 0.69 (t, 3 H, C*H*$_3$) | 2.41 (m, 4 H) 1.96 (m, 4 H) | 6.69–7.27 (m, 40 H) | 64.54 |
| $CH_3(CH_2)_2$ (**3**) | –16.00 (qnt, 1 H) | 20 | 1.9 (m, 4 H, $CH_3CH_2CH_2$) 0.69 (t, 3 H, C*H*$_3$) | 2.40 (m, 4 H) 1.95 (m, 4 H) | 6.66–7.5 (m, 40 H) | 64.10 |
| $CH_2$=CH (**4**) | –15.25 (qnt, 1 H) | 20 | 5.8 (d, 2 H, C*H*$_2$=CH) 5.42 (t, 1 H, $CH_2$=C*H*) | 2.38 (m, 4 H) 1.96 (m, 4 H) | 6.68–7.41 (m, 40 H) | 64.11 |
| *p*-$CH_3-C_6H_4-CH_2$ (**5**) | –15.85 (qnt, 1 H) | 20 | 6.83 (m, 4 H, $C_6H_4$) 2.22 (m, 2 H, C*H*$_2$) 1.0 (m, 3 H, C*H*$_3$) | 2.33 (m, 4 H) 1.90 (m, 4 H) | 6.83–7.51 (m, 40 H) | 65.87 |
| $C_6H_5$ (**6**) | –15.28 (qnt, 1 H) | 20 | 6.71–7.54 (m, 5 H, $C_6H_5$) | 2.61 (m, 4 H) 1.95 (m, 4 H) | 6.71–7.54 (m, 40 H) | 63.79 |
| $(CH_3)_2N$ (**7**) | –16.60 (qnt, 1 H) | 20 | 0.99 (s, 6 H, C*H*$_3$) | 2.32 (m, 4 H) 1.98 (m, 4 H) | 6.99–7.53 (m, 40 H) | 65.74 |

The $^1H$ NMR spectra of the complexes show quintets for the hydride ligand confirming the coupling of the hydride with the four *cis*-phosphorus (dppe) ligands. The value of *J*(H,P) is remarkably similar in all these derivatives (20 Hz) indicating that the variation of the *trans*-nitrile ligand has no effect on the coupling constant. The $^{31}P\{^1H\}$ NMR spectra consist of only one singlet for the dppe phosphorus nuclei. This suggests that all the four phosphorus atoms are equivalent in solution. The $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopic data for these complexes are summarized in Table 2.

In order to obtain some insight with regard to the cavity formed by the sterically encumbered $[(dppe)_2Ru(H)]^+$ fragment, we examined the X-ray crystal structure of *trans*-$[(dppe)_2Ru(H)(p\text{-}CH_3-C_6H_4-CH_2CN)][BF_4]$ (**5**). Unfortunately, the structure solution could not be achieved satisfactorily because the *p*-$CH_3-C_6H_4-CH_2CN$ group was severely disordered (the structure details can be found in the Supporting Information). Nevertheless, it is instructive to note that the nitrile should be almost *rod-shaped* in order to be accommodated *trans* to the hydride. Attempts to prepare hydride complexes with more bulky *trans* nitrile ligands failed and the starting hydride-dihydrogen complex *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(H)][BF_4]$ was recovered.

### Preparation and Properties of the Dihydrogen Complexes

The protonation of the starting hydride complexes *trans*-$[(dppe)_2Ru(H)(RCN)][BF_4]$ with excess 54% $HBF_4{\cdot}OEt_2$ yielded the corresponding dihydrogen complexes, *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(RCN)][BF_4]_2$ [R = $CH_3$ (**1a**), $CH_3CH_2$ (**2a**), $CH_3CH_2CH_2$ (**3a**), $CH_2$=CH (**4a**), *p*-$CH_3-C_6H_4-CH_2$ (**5a**), $C_6H_5$ (**6a**), $(CH_3)_2N$ (**7a**)]. These reactions were carried out in $CD_2Cl_2$ under 1 atm. of either dihydrogen or argon. The dihydrogen complexes were characterized by NMR spectroscopy. All of these derivatives were found to be stable in solution at room temperature for periods as long as two days before undergoing decomposition into the starting hydride complex and a proton equivalent (exists as $HOEt_2^+BF_4^-$).

Table 3. $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopic data (δ) of *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(RCN)][BF_4]_2$ complexes in $CD_2Cl_2$

| R | δ[Ru(η²-H₂)] | δ(R) | δ(CH₂−CH₂) | δ(Ph) | δ[P(dppe)] |
|---|---|---|---|---|---|
| $CH_3$ (**1a**) | −11.2(br s, 2 H) | 1.45 (s, 3 H, $CH_3$) | 2.80 (m, 4 H)<br>2.28 (m, 4 H) | 7.08−7.33 (m, 40 H) | 55.19 |
| $CH_3CH_2$ (**2a**) | −11.1(br s, 2 H) | 2.54 (q, 2 H, $CH_2$)<br>0.5 (t, 3 H, $CH_3$) | 2.84 (m, 4 H)<br>2.28 (m, 4 H) | 6.90−7.21 (m, 40 H) | 53.99 |
| $CH_3(CH_2)_2$ (**3a**) | −11.2(br s, 2 H) | 1.49 (m, 4 H, $CH_3CH_2CH_2$)<br>0.46 (t, 3 H, $CH_3$) | 2.84 (m, 4 H)<br>2.29 (m, 4 H) | 7.1−7.4 (m, 40 H) | 53.99 |
| $CH_2$=CH (**4a**) | −10.95(br s, 2 H) | 6.4 (t, 1 H, $CH_2$=$CH$)<br>6.2 (d, 2 H, $CH_2$=CH) | 2.86 (m, 4 H)<br>2.29 (m, 4 H) | 7.0−7.2 (m, 40 H) | 54.24 |
| *p*-$CH_3-C_6H_4-CH_2$ (**5a**) | −11.38(br s, 2 H) | 6.66−7.63 (m, 4 H, $C_6H_4$)<br>2.11 (m, 2 H, $CH_2$)<br>1.08 (m, 3 H, $CH_3$) | 2.87 (m, 4 H)<br>2.32 (m, 4 H) | 6.66−7.63 (m, 40 H) | 54.43 |
| $C_6H_5$ (**6a**) | −10.94(br s, 2 H) | 6.9−7.4 (m, 5 H, $C_6H_5$) | 2.80 (m, 4 H)<br>2.30 (m, 4 H) | 6.9−7.4 (m, 40 H) | 55.34 |
| $(CH_3)_2N$ (**7a**) | −11.69(br s, 2 H) | 1.3 (s, 6 H, $CH_3$) | 2.82 (m, 4 H)<br>2.27 (m, 4 H) | 7.14−7.53 (m, 40 H) | 54.95 |

The $^1H$ NMR spectrum of the dihydrogen complexes shows a broad singlet in the hydride region whose line widths ($\Delta\nu_{1/2}$) are in the range 36 to 43 Hz. This signal is shifted downfield with respect to the starting hydride complex. The $^{31}P\{^1H\}$ NMR spectrum also shows a singlet for the dppe phosphorus atoms that is also shifted downfield in relation to the precursor hydride complex. The $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopic data are summarized in Table 3.

The classification of **1a**−**7a** as dihydrogen complexes is based on variable temperature $^1H$ spin-lattice relaxation time ($T_1$, ms) measurements and the observation of H, D coupling constants of the η²-HD isotopomers **1b**−**7b**. The measured and the calculated $T_1$ minima data[4] as a function of temperature are given in Table 4. All of these derivatives exhibit short $T_1$ minima (18−21 ms) demonstrating that there is an intact H−H bond in these complexes. These values have been obtained directly from the experiments and also by fitting the equations that describe the dominant dipolar relaxation mechanism to the variable temperature $T_1$ data as described earlier by Morris and co-workers.[5] From the $T_1$ minima, the H−H distances can be calculated after appropriate corrections[6] have been made for the relaxation contributions from other nuclei in the vicinity. The analysis of $T_1$ data leads to three possible values for the H−H distance depending upon the relative rate at which the $H_2$ ligand undergoes rotation (slow, fast, and intermediate).[5,7] Table 4 also lists the H−H distances (for slow and fast rotation regimes of $H_2$) as determined from the $T_1$ minima for the complexes **1a**−**7a**. The H−H distances thus obtained fall in the range 1.12 to 0.87 Å for the slow and the fast spinning regimes, respectively.

Table 4. Observed and calculated spin-lattice relaxation times ($T_1$ minima; 400 MHz) and the H−H distances of the dihydrogen ligand in the complexes *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(RCN)][BF_4]_2$ **1a**−**7a** in $CD_2Cl_2$

| R | $T_1$(obs), ms (T, K) | $T_1$(calc), ms | $r_{HH}$ (Å)[a] |
|---|---|---|---|
| $CH_3$ (**1a**) | 18.98 (283) | 19.39 | 0.87/1.10 |
| $CH_3CH_2$ (**2a**) | 20.41 (273) | 21.39 | 0.88/1.12 |
| $CH_3(CH_2)_2$ (**3a**) | 20.34 (283) | 20.76 | 0.88/1.11 |
| $CH_2$=CH (**4a**) | 19.98 (273) | 20.08 | 0.88/1.11 |
| *p*-$CH_3-C_6H_4-CH_2$ (**5a**) | 19.83 (283) | 19.92 | 0.88/1.11 |
| $C_6H_5$ (**6a**) | 18.25 (283) | 18.22 | 0.87/1.09 |
| $(CH_3)_2N$ (**7a**) | 20.15 (273) | 20.72 | 0.89/1.12 |

[a] For fast rotation/static regimes of the $H_2$ ligand.

The partial incorporation of deuterium into the $H_2$ ligand could, in general, be accomplished by exposing the dihydrogen complex to $D_2$ gas or the use of deuterated acid (in the current work, $DBF_4{\cdot}OEt_2$ has been used) to deuterate the starting hydride complex. It was proposed that a combination of the lability and the acidity of the $H_2$ ligand is responsible for the formation of the HD isotopomers.[8] The HD isotopomers, *trans*-$[(dppe)_2Ru(\eta^2\text{-}HD)(RCN)][BF_4]_2$ [R = $CH_3$, $CH_3CH_2$, $CH_3CH_2CH_2$, $CH_2$=CH, *p*-$CH_3-C_6H_4-CH_2$, $C_6H_5$, $(CH_3)_2N$] were obtained from the starting hydride complexes by the addition of excess $DBF_4$ [prepared from $HBF_4$ and $D_2O$ in the ratio 3:1 (v/v)] in $CD_2Cl_2$. The $^1H$ NMR spectra at room temperature exhibit a sharp triplet of quintets after nullifying the signal due to η²-$H_2$ from the known spin-lattice relaxation times ($T_1$, ms). The intensity ratio of the triplet resonance is approximately 1:1:1 with $J$(H,D) values in the range 26−28 Hz. Further splitting of each of the triplet signals into quintets, although not fully resolved, is due to coupling with the four dppe phosphorus atoms with a corresponding $J(H,P_{cis})$ of ca. 5 Hz. There does not seem to be a consistent trend for the $J$(H,D) values, which are relatively insensitive to the nature of the nitrile *trans* to the $H_2$. This is typical of complexes that have η²-HD bound *trans* to a strong-field π-acid ligand.[9] Figure 1 shows the hydride region of the $^1H$ NMR spectrum of *trans*-$[(dppe)_2Ru(\eta^2\text{-}HD)(p\text{-}CH_3-C_6H_4-CH_2-CN)][BF_4]_2$. The HD resonances of all the complexes suffer from upfield shifts from the $H_2$ signals (Δδ from 34 to 43 ppb) which is typical for the dihydrogen complexes reported thus far.[10] The shift that is observed in the case of $H_2$/HD gas is on the order of +36 ppb.[11]

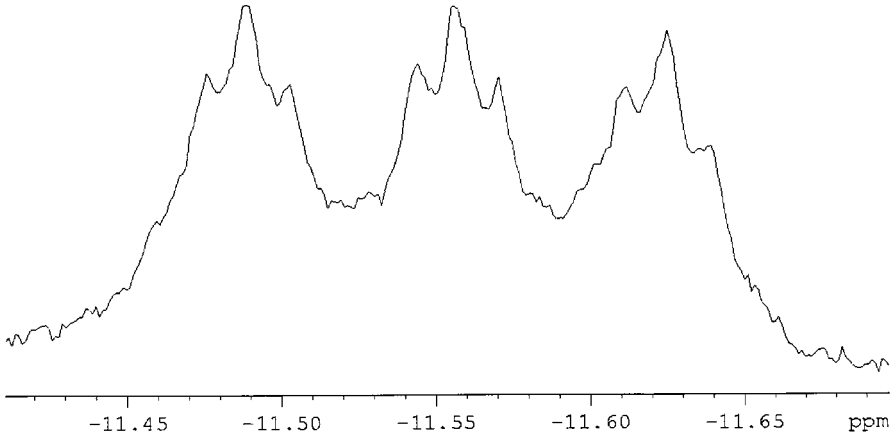



Figure 1. $^1$H NMR spectrum (hydride region) of *trans*-[(dppe)$_2$Ru($\eta^2$-HD)(*p*-CH$_3$−C$_6$H$_4$−CH$_2$CN)][BF$_4$]$_2$ (400 MHz, 298 K) in $CD_2Cl_2$; resonance due to $\eta^2$-H$_2$ ligand has been nullified

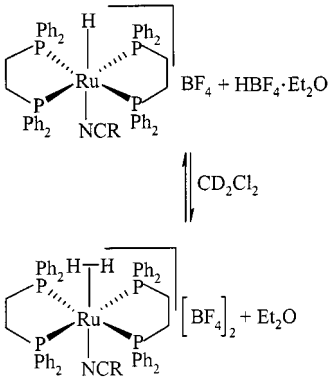
The H-H distances ($r_{HH}$) could be calculated from the inverse relationship between $r_{HH}$ and $J$(H,D) of the HD isotopomer.[12] Thus, distances on the order of 0.96−0.97 Å have been obtained for our complexes. Gusev et al.[13] analyzed the $T_1$ minima and $J$(H,D) values of certain reported dihydrogen complexes that have $J(H,D) \geq 25$ Hz. According to this analysis, in complexes of the type *trans*-[(P-P)$_2$M(H)($\eta^2$-H$_2$)]$^+$ (M = Fe, Ru; P-P = chelating phosphane), it is necessary to invoke the fast rotation approximation in order to obtain a reasonable H−H distance for the H$_2$ ligand. However, Morris and Wittebort[7] have shown that the rotation around M−H$_2$ in a majority of complexes is either in the fast motion regime or is a librational motion. Table 5 lists the H−H distances for the complexes **1a**−**7a** calculated from the $J$(H,D) values. The H−H distances obtained from the H−D coupling constants lie between the distances (slow and fast) obtained from $T_1$ values, suggesting that the relaxation of the dihydrogen ligand in this series of complexes is significantly dominated by libration and torsional motions as described earlier by Morris and Wittebort.[7] Many examples have been reported in the literature where such a situation has been observed.[7] The relatively long H−H distances found for these derivatives is consistent with the tight binding of H$_2$ to the ruthenium center.

Table 5. H−H Distances of *trans*-[(dppe)$_2$Ru($\eta^2$-H$_2$)(RCN)][BF$_4$]$_2$ complexes **1a**−**7a** obtained from $J$(H,D)

| R | $J$(H,D) Hz | $r_{HH}$ (Å) |
|---|---|---|
| CH$_3$ (**1a**) | 27 | 0.96 |
| CH$_3$CH$_2$ (**2a**) | 27 | 0.96 |
| CH$_3$(CH$_2$)$_2$ (**3a**) | 28 | 0.95 |
| CH$_2$=CH (**4a**) | 26 | 0.98 |
| *p*-CH$_3$−C$_6$H$_4$−CH$_2$ (**5a**) | 28 | 0.95 |
| C$_6$H$_5$ (**6a**) | 27 | 0.96 |
| (CH$_3$)$_2$N (**7a**) | 27 | 0.96 |

**Acidities of the Dihydrogen Complexes**

The acidities of the dihydrogen complexes have been measured on the pseudo aqueous p$K_a$ scale.[2c][2i][2k][2l][12b,14] The equilibrium constants for the protonation of the hydride complex using an acid whose aqueous p$K_a$ is known are determined in a nonaqueous medium. Then, the pseudo aqueous p$K_a$ of the dihydrogen complex is calculated with respect to the aqueous p$K_a$ of the protonating agent. The p$K_a$ values of the dihydrogen complexes **1a**−**7a** have been estimated by studying the equilibrium shown in Equation (2) using $^1$H NMR spectroscopy at −30 °C.




(2)

R = CH$_3$-, CH$_3$CH$_2$-, CH$_3$CH$_2$CH$_2$-, CH$_2$=CH-, *p*-CH$_3$-C$_6$H$_4$-CH$_2$-, C$_6$H$_5$-, (CH$_3$)$_2$N-

The relative molar concentrations of the hydrides, HBF$_4$·OEt$_2$, the dihydrogen complexes, and Et$_2$O were estimated from the $^1$H NMR spectral integrations of the respective signals. As suggested earlier by Kristjánsdóttir and Norton,[15] the p$K_a$ values of the dihydrogen complexes have been estimated from the equilibrium constants $K_{eq}$ of Equation (2) and the p$K_a$ of the protonating agent, here HBF$_4$·OEt$_2$ (−2.4)[16] using Equation (3).

$$pK_a[RuH_2]^{2+} = pK_a[HBF_4 \cdot Et_2O] + \log K_{eq} \quad (3)$$

[RuH$_2$]$^{2+}$ = *trans*-[(dppe)$_2$Ru($\eta^2$-H$_2$)(RCN)][BF$_4$]$_2$

The p$K_a$ values of the dicationic dihydrogen complexes **1a**−**7a** are summarized in Table 6. The magnitude of these p$K_a$ values are very approximate and accurate values could only be obtained when the actual non-ion-paired p$K_a$ of $HOEt_2^+BF_4^-$ in $CH_2Cl_2$ is determined and corrections are made for ion pairing for all of the species in solution.[17] All of these derivatives exhibit low p$K_a$ values indicating that they are quite acidic species. At this juncture, it is quite appropriate to compare the acidity of *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(CNH)][OTf]$_2$ reported by Morris et al.[2p] with those of ours. *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(CNH)][OTf]$_2$ is the first member of this class of compounds. This complex was found to be highly acidic since it was only completely formed in an excess of HOTf in $CH_2Cl_2$. Furthermore, it was proposed that the p$K_a$ of this complex was very near to that of HOTf in $CH_2Cl_2$ (the aqueous p$K_a$ of HOTf has been estimated to be −4.9).[2k] The complexes reported in this work are less acidic in comparison to that of Morris' (compare with the p$K_a$ of the protonating agent used, $HBF_4$·$OEt_2$ = −2.4). In general, the acidity of isostructural dihydrogen complexes decreases as ligands become more electron donating. The trend in the p$K_a$ values of our complexes does seem to corroborate this: the greater the electrophilicity of the metal center, the greater is the activation of the dihydrogen towards heterolysis. In addition to this series of dicationic dihydrogen complexes that are quite acidic and at the same time stable at room temperature with respect to loss of $H_2$, several other derivatives have also been reported earlier by other groups.[2k,10d,18]

Table 6. Estimation of the acidities of *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(RCN)][$BF_4$]$_2$ complexes in $CD_2Cl_2$

| R | $K_{eq}$ [a] | p$K_a$[b] |
|---|---|---|
| $CH_3$ (**1a**) | 0.217 | -1.7 |
| $CH_3CH_2$ (**2a**) | 0.011 | -0.4 |
| $CH_3(CH_2)_2$ (**3a**) | 0.006 | -0.2 |
| $CH_2$=CH (**4a**) | 0.066 | -1.3 |
| *p*-$CH_3$−$C_6H_4$−$CH_2$ (**5a**) | 0.070 | -1.3 |
| $C_6H_5$ (**6a**) | 0.713 | -2.2 |
| $(CH_3)_2N$ (**7a**) | 0.461 | -1.9 |

[a] From equilibrium shown in Equation (2); determined at 243 K. − [b] Calculated from Equation (3).

## Conclusions

The complexes *trans*-[(dppe)$_2$Ru($H_2$)(RCN)][$BF_4$]$_2$ [R = $CH_3$ (**1a**), $CH_3CH_2$ (**2a**), $CH_3CH_2CH_2$ (**3a**), $CH_2$=CH (**4a**), *p*-$CH_3$−$C_6H_4$−$CH_2$ (**5a**), $C_6H_5$ (**6a**), $(CH_3)_2N$ (**7a**)] are formulated as dihydrogen complexes based on their short $T_1$ values and the observation of H, D coupling in the corresponding HD isotopomers. All of these derivatives are stable at room temperature. The long H−H distances and the relatively nonlabile nature of the $H_2$ ligand shows strong M−$H_2$ interactions in these complexes. The p$K_a$ values of these complexes indicate that they are quite acidic.

## Experimental Section

**General:** All reactions except those involving the dihydrogen complexes were carried out under dry and purified nitrogen atmosphere at room temperature using standard Schlenk[19] and inert atmosphere techniques, unless otherwise specified. The manipulations involving solutions of dihydrogen complexes were carried out under an atmosphere of dihydrogen or argon gas. 1,2-Bis(diphenylphosphanyl)ethane (dppe)[20] and the complex *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(H)][$BF_4$][21] were prepared according to published procedures.

The $^1$H and $^{31}$P NMR spectra were obtained on a AMX Bruker 400 MHz instrument. The shift of the residual protons of the deuterated solvent was used as an internal reference. All $^{31}$P NMR spectra were proton decoupled. $^{31}$P NMR chemical shifts have been measured relative to 85% $H_3PO_4$ in $CD_2Cl_2$. Variable temperature proton $T_1$ measurements were carried out at 400 MHz using the inversion recovery method (180°-τ-90° pulse sequence at each temperature).[22] Microanalyses were performed at the Institut für Anorganische Chemie, der Universität Göttingen, Germany and National Chemical Laboratory, Pune, India.

**Preparation of *trans*-[(dppe)$_2$Ru(H)($CH_3CN$)][$BF_4$] (1):** A method similar to the preparation of the osmium analogue of (**1**) reported[2i] earlier was employed for this preparation. *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(H)][$BF_4$] (60 mg, 0.06 mmol) was dissolved in 3 mL of $CH_2Cl_2$ under 1 atm. of dihydrogen. Acetonitrile (50 mg, 1.22 mmol) was then added with a syringe and the mixture was allowed to stir at room temperature for 12 h. Addition of 20 mL of $Et_2O$ caused complete precipitation of the pale yellow product. $Et_2O$ was removed with a cannula and the precipitate was dried by passing a slow stream of $H_2$. Yield: 47 mg (75%). The product was crystallized from a $CH_2Cl_2$ solution containing the hydride complex and a few drops of the nitrile by the diffusion of $Et_2O$ at room temperature. The $^1$H and $^{31}$P{$^1$H} NMR spectroscopic data are summarized in Table 2.

The complexes, *trans*-[(dppe)$_2$Ru(H)(RCN)][$BF_4$] [R = $CH_3CH_2$ (**2**), $CH_3CH_2CH_2$ (**3**), $CH_2$=CH (**4**), *p*-$CH_3$−$C_6H_4$−$CH_2$ (**5**), $C_6H_5$ (**6**), $(CH_3)_2N$ (**7**)] were similarly prepared from *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(H)][$BF_4$] and the corresponding nitrile as summarized in Table 1. All of these products were purified by crystallization from a solution containing the respective hydride complex and a few drops of the corresponding nitrile in $CH_2Cl_2$ by the diffusion of $Et_2O$. The $^1$H and $^{31}$P NMR spectroscopic data are summarized in Table 2.

**Preparation of *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)($CH_3CN$)][$BF_4$]$_2$ (1a):** In a typical experiment, a sample (15 mg) of *trans*-[(dppe)$_2$Ru(H)($CH_3CN$)][$BF_4$] (**1**) was placed in a 5 mm NMR tube provided with a septum. The tube was carefully evacuated and then filled with dihydrogen in three cycles. The hydride complex was then dissolved in $CD_2Cl_2$ (0.7 mL) and 10 μL of 54% $HBF_4$·$OEt_2$ was added. The reaction was found to be almost instantaneous and the protonation was complete within a few seconds. The solution was then analyzed by NMR spectroscopy. The $^1$H and $^{31}$P{$^1$H} NMR spectroscopic data are summarized in Table 3.

The corresponding dihydrogen complexes, *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)(RCN)][$BF_4$]$_2$ [R = $CH_3CH_2$ (**2a**), $CH_3CH_2CH_2$ (**3a**), $CH_2$=CH (**4a**), *p*-$CH_3$−$C_6H_4$−$CH_2$ (**5a**), $C_6H_5$ (**6a**), $(CH_3)_2N$ (**7a**) were similarly prepared and characterized. The $^1$H and $^{31}$P{$^1$H} NMR spectroscopic data of these derivatives are given in Table 3.

**Decomposition Reaction of *trans*-[(dppe)$_2$Ru($\eta^2$-$H_2$)($CH_3CN$)][$BF_4$]$_2$ (1a):** An NMR tube provided with a septum, loaded with *trans*-

$[(dppe)_2Ru(\eta^2\text{-}H_2)(CH_3CN)][BF_4]_2$ **(1a)** (10 mg) in $CD_2Cl_2$ (0.7 mL) under a hydrogen atmosphere was allowed to stand at room temperature for several days. $^1H$ NMR spectra were recorded periodically to monitor the stability of the dihydrogen complex. It was found that after ca. 36−72 h, the hydride complex *trans*-$[(dppe)_2Ru(H)(CH_3CN)][BF_4]$ (**1**) started to appear. This suggests that the dihydrogen complex is unstable for an extended period of time and that it undergoes decomposition to the hydride complex and a proton.

**Preparation of the H−D Isotopomers of *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(RCN)][BF_4]_2$ [R = $CH_3$, $CH_3CH_2$, $CH_3CH_2CH_2$, $CH_2$=CH, *p*-$CH_3-C_6H_4-CH_2$, $C_6H_5$, $(CH_3)_2N$]:** These derivatives were prepared in the following manner: Each of the hydride complexes (15 mg) was dissolved in 0.7 mL $CD_2Cl_2$ in a 5 mm NMR tube under an atmosphere of Ar followed by the addition of $DBF_4$ (prepared from $HBF_4{\cdot}OEt_2$ and $D_2O$ in a 3:1 ratio). The $\eta^2$-HD signals were observed in the $^1H$ NMR spectrum by nullifying the signal due to $\eta^2$-$H_2$ by the inversion recovery method using the relationship $T_1 = \tau_{null}/\ln 2$ and the known $T_1$ values of the dihydrogen complexes at room temperature.[8,23,24] The $J$(H,D) values together with the H−H distances for these complexes are summarized in Table 5.

**Acidity Measurements:** In a typical experiment, a 5 mm NMR tube was charged with 20 mg of the hydride complex. It was dissolved in 0.6 mL of $CD_2Cl_2$ and the solution was cooled to 243 K. The $^1H$ and $^{31}P\{^1H\}$ NMR spectra were then recorded with the probe at 243 K. One equivalent of 54% $HBF_4{\cdot}Et_2O$ was added to the tube, shaken for some time and transferred back to the probe at 243 K. The relative concentrations of all the species [as in Equation (2)] were calculated from the integrations of the respective peaks in the $^1H$ NMR spectra. The p$K_a$ values were calculated from the equilibrium depicted in Equation (2) and are summarized in Table 6.

**Supporting Information Available:** Observed and calculated spin-lattice relaxation time ($T_1$, ms; 400 MHz) data as a function of temperature of the dihydrogen ligand in the complexes *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(RCN)][BF_4]_2$ [R = $CH_3$ (**1a**), $CH_3CH_2$ (**2a**), $CH_3CH_2CH_2$ (**3a**), $CH_2$=CH (**4a**), *p*-$CH_3-C_6H_4-CH_2$ (**5a**), $C_6H_5$ (**6a**), and $(CH_3)_2N$ (**7a**)] and tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and an ORTEP diagram for **5**. Crystallographic data (excluding structure factors) for the structure(s) reported in the Supporting Information of this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159782. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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