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Communications

Synthesis and Reactivity of Stretched-Dihydrogen−Ruthenium Complexes. Unexpected Formation of a Vinylidene Ligand

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Summary: Reaction of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ *with pyridine and quinoline ligands having hydroxy and amino substituents, L−XH leads to the formation of the new stretched-dihydrogen complexes* $RuH(H_2)(L{-}X)(PCy_3)_2$*. In the presence of an excess of triethylvinylsilane, the hydrido vinylidene complexes* $RuH(C{=}C(H)SiEt_3)(L{-}X)(PCy_3)_2$ *are obtained.*

Since the original discovery by Kubas of dihydrogen coordination to a transition metal, a very large number of dihydrogen complexes has been reported.[1] Complexes with short H−H distances were first characterized, but it soon appeared that the H−H bond could be elongated up to values close to 1.3 or 1.4 Å.[2] An important study by Taube and co-workers revealed the importance of the electronic effect of the *trans* ligand for this elongation.[2f] The reason for this stretching is understood in terms of d_π back-donation from an electron-rich metal center into the σ^* antibonding orbitals of dihydrogen. However, the nature of the H−H bonding for H−H distances above 1.3 Å is still a theoretical problem.[3] Related to the stretching of the H−H bond is the rotation barrier of dihydrogen. Barriers to rotation between 0.4 and *ca.* 3 kcal mol^{-1} have been measured by Eckert using inelastic neutron scattering (INS).[4] However, this method cannot be used for higher rotation barriers, which explains the absence of observation of the quasi elastic peaks when the H−H distance reaches *ca.* 1 Å. Evidence for the presence of a restricted rotation of the H_2 ligand has been obtained in a ruthenium complex,[5] whereas we have measured (by NMR) rotation barriers of HD as high as *ca.* 10 kcal mol^{-1} in $\{Cp_2Nb(HD)[P(OMe)_3]\}PF_6$ and $[Cp_2Ta(HD)(CO)]BF_4$.[6] In the lattercase, the presence of very large exchange couplings was demonstrated for the corresponding dihydrogen isotopomer.[6b] Stretched-dihydrogen complexes may therefore be good candidates for the observation of very large exchange couplings. Furthermore, whereas the

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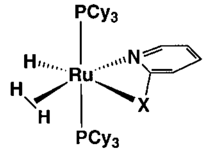
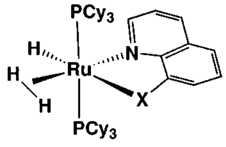
reactivity of unstretched-dihydrogen complexes is already well documented, especially the electrophilic character of coordinated dihydrogen, little attention has been paid to the reactivity of stretched-dihydrogen derivatives.

We have studied for several years the chemistry of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**).[7] Substitution of one of the hydrides by a halo or a thiolato group leads to the 16-electron derivatives $RuH(H_2)X(PCy_3)_2$, displaying an elongated H−H bond (1.03 Å for X = I).[8] We report in this communication the synthesis of new stretched-dihydrogen derivatives through reaction of **1** with electron-releasing ligands such as pyridine and quinoline with hydroxy and amino substituents as well as their spectroscopic characterization and unexpected reactivity with triethylvinylsilane.

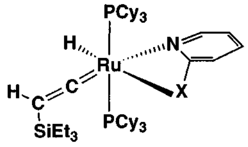


2, X = O
3, X = NH

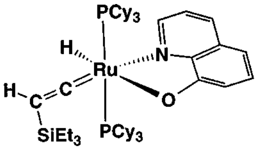


4, X = O
5, X = NH

The reactions of a suspension of **1** in pentane with 1 equiv of L−XH (L = C_5H_4N (py), C_9H_6N (quin); X = O, NH) yield a solid that is analyzed as $RuH(H_2)(L{-}X)(PCy_3)_2$ (L−X = py-O, **2**; L−X = py-NH, **3**; L−X = quin-O, **4**; L−X = quin-NH, **5**).[9] Compounds **2**−**5** show a Ru−H band between 2073 and 2000 cm^{-1} in their IR spectra recorded in Nujol mulls. A high-field triplet is observed near −11 ppm (J_{PH} = *ca.* 14 Hz) in ^{1}H NMR together with the characteristic resonances of PCy_3 and peaks for the heterocycles between 6 and 8 ppm. The presence of three ruthenium-bound hydrogens is deduced both from the integration and from partially decoupled ^{31}P NMR spectra (in which only the alkyl protons of the phosphines are irradiated), which display a quartet pattern near 45−50 ppm. The minimum of the relaxation time (T_1) of these signals was observed near 240 K and measured to be respectively 37 ms (**2**), 36 ms (**3**), 29 ms (**4**), and 24 ms (**5**). The first two values are higher than those found for **4** and **5**, in agreement with some lengthening of the H−H distance within a hypothetical dihydrogen ligand. This probably reflects the fact that complexes **2** and **3** accommodate strained four-membered rings in which the ligand bite angle is small, whereas in **4** and **5** a five-membered ring is present which allows an ideal octahedral geometry for the complex. Therefore, a deviation from the ideal octahedral geometry might contribute to the stretching of the H−H bond. This effect may at least partially account for the different structures of $Cp^*RuH_3(PCy_3)$ and $Tp^*RuH(H_2)(PCy_3)$,[10] whereas a similar effect has been shown to modify the characteristics of systems containing large-bite-angle phosphine ligands together with both hydride and dihydrogen ligands.[11] Compounds **2**−**5** are not very reactive (vide infra) but nevertheless react rapidly with 1 atm of D_2 at room temperature to give partially deuterated complexes. Only in the case of **3** did we succeed in measuring a J_{HD} value, which was found to be near 3 Hz. This value can be in agreement with a classical trihydride structure or the presence of a very stretched dihydrogen ligand, for which a J_{HD} value of 9 Hz within the coordinated HD molecule would be calculated. In that case, using an empirical equation developed by Morris, the corresponding H−H distance would be 1.27 Å.[12]



6, X = O
7, X = NH



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In order to calculate the H−H distance within coordinated H_2, we needed relaxation data on a similar monohydride complex. We therefore attempted the dehydrogenation of **2**−**5** with excess $CH_2{=}CH(SiEt_3)$ in toluene at room temperature. The new monohydride complexes **6**−**8** could be isolated.[9] The reaction of **5** with triethylvinylsilane proceeded, but the product of the reaction could not be isolated. Complexes **6**−**8** display ^{1}H NMR signals attributed to the phosphine and L−X ligands and a high-field triplet near −9 ppm (J_{PH} = *ca.* 20 Hz). The presence of a single hydride was again ascertained by selective decoupling of the protons of the phosphine ligands. In addition, a triplet was observed

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[9] Selected NMR data for compounds **2**−**8** are as follows. **2**: ^{1}H NMR (C_6D_6; δ): 8.16 (d), 7.22 (t), 6.38 (t), 6.34 (d) (4H, py); −12.64 (t, 3H, $^2J_{PH}$ = 14.3 Hz, $RuH(H_2)$). $^{31}P\{^1H_{PCy_3}\}$ NMR (C_6D_6; δ): 49.1 (q, J_{PH} = 14 Hz). T_1(min) (250.13 MHz, 233 K, C_7D_8): 37 ms. **3**: ^{1}H NMR (C_6D_6; δ): 8.11 (d), 7.04 (t), 6.09 (t), 5.72 (d) (4H, py); 3.85 (s, 1H, NH); −11.90 (t, 3H, $^2J_{PH}$ = 14.6 Hz, $RuH(H_2)$). $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 49.5 (s). T_1(min) (250.13 MHz, 233 K, C_7D_8): 36 ms. **4**: ^{1}H NMR (C_6D_6; δ): 9.24 (d), 7.69 (d), 7.55 (pt), 7.37 (d), 6.82 (d), 6.74 (d) (6H, qu); −11.61 (t, 3H, $^2J_{PH}$ = 14.5 Hz, $RuH(H_2)$). $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 45.4 (s). T_1(min) (250.13 MHz, 243 K, C_7D_8): 29 ms. **5**: ^{1}H NMR (C_6D_6; δ): 9.22 (m), 7.53 (m), 7.35 (m), 6.75 (dd), 6.68 (d), 6.41 (d) (6H, qu); 4.31 (s, 1H, NH); −10.99 (t, 3H, $^2J_{PH}$ = 13.0 Hz, $RuH(H_2)$). $^{31}P\{^1H_{PCy_3}\}$ NMR (C_6D_6; δ): 44.0 (q, J_{PH} = 13 Hz). T_1(min) (250.13 MHz, 233 K, C_7D_8): 24 ms. **6**: ^{1}H NMR (C_6D_6; δ): 8.33 (m), 7.11 (t), 6.35 (pt), 6.18 (d) (4H, py); 2.41 (t, J_{PH}=3.5 Hz, 1H, C=CH); 1.29 (t, J_{HH} = 7.9 Hz, 9H, $SiCH_2CH_3$); 0.98 (q, J_{HH} = 7.9 Hz, 6H, $SiCH_2CH_3$); −9.02 (t, 1H, $^2J_{PH}$ = 19.6 Hz, RuH). T_1(min) (250.13 MHz, 233 K, C_7D_8): 160 ms.$^{31}P\{^1H\}$ NMR (C_6D_6; δ): 41.9 (s). ^{13}C NMR (62.860 MHz, C_6D_6; δ): 6.58 ($SiCH_2CH_3$), 8.70 ($SiCH_2CH_3$), 82.35 (C_β), 321.53 (C_α). ^{29}Si NMR (49.662 MHz, C_6D_6; δ): −158. **7**: ^{1}H NMR (C_6D_6; δ): 8.15 (m), 6.79 (m), 5.96 (m), 5.48 (m) (4H, py); 3.29 (s, 1H, NH); 2.38 (t, J_{PH} = 3.6 Hz, 1H, C=CH); 1.30 (t, J_{HH} = 7.7 Hz, 9H, $SiCH_2CH_3$); 0.99 (q, J_{HH} = 7.7 Hz, 2H, $SiCH_2CH_3$); −9.80 (t, 1H, $^2J_{PH}$ = 20.3 Hz, RuH). T_1(min) (250 MHz, 233 K, C_7D_8): 166 ms. $^{31}P\{^1H_{PCy_3}\}$ NMR (C_6D_6; δ): 42.0 (d, J_{PH} = 20 Hz). ^{13}C NMR (62.860 MHz, C_6D_6; δ): 6.65 ($SiCH_2CH_3$), 8.88 ($SiCH_2CH_3$), 82.15 (C_β), 315.65 (C_α). ^{29}Si NMR (49.662 MHz, C_6D_6; δ): −167. **8**: ^{1}H NMR (C_6D_6; δ): 9.14 (m), 7.63 (d), 7.48 (t), 7.20 (d), 6.86 (dd), 6.70 (d) (6H, qu); 2.42 (t, J_{PH} = 3.4 Hz, 1H, C=CH); 1.31 (t, J_{HH} = 7.0 Hz, 9H, $SiCH_2CH_3$); 0.99 (q, J_{HH} = 7.1 Hz, 6H, $SiCH_2CH_3$); −8.52 (t, 1H, $^2J_{PH}$ = 20.5 Hz, RuH). T_1(min) (250.13 MHz, 233 K, C_7D_8): 166 ms. $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 38.4 (s). ^{13}C NMR (62.860 MHz, C_6D_6; δ): 7.12 ($SiCH_2CH_3$), 8.87 ($SiCH_2CH_3$), 82.40 (C_β), 318.70 (C_α). ^{29}Si NMR (49.662 MHz, C_6D_6; δ): −164.

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near 2.4 ppm (J_{PH} = *ca.* 3.5 Hz) and ethyl groups resulting from $SiEt_3$ moieties appeared near 1.0 (CH_2) and 1.3 ppm (CH_3). GE-HMQC $^1H-^{13}C\{^{13}C\}\{^{31}P\}$ experiments carried out on **6**−**8** allowed the observation of two peaks correlated to the new ^1H NMR triplets, namely near 320 and 82 ppm, which were attributed to the α- and β-carbons of a vinylidene group. We therefore assigned to **6**−**8** the structure $RuH(C{=}C(H)SiEt_3)(L{-}X)(PCy_3)_2$ (L−X = py-O, **6**; L−X = py-NH, **7**; L−X = quin-O, **8**) (see the structures given; the relative trans position of the vinylidene group and the pyridine nitrogen has not been established, and both trans and cis isomers are possible, as recently demonstrated in a similar complex[13]). A similar osmium vinylidene complex has recently been reported.[14] The mechanism of this transformation could not be precisely determined, since no intermediate between the hydrido dihydrogen derivatives and the hydrido vinylidene ones could be detected by NMR monitoring of the reaction. Nevertheless, it is clear that the reaction proceeds via some hydrogen transfer, as deduced from the observation by GLC of $SiEt_4$ in the reaction mixture, but no catalytic transfer hydrogenation producing (triethylsilyl)acetylene could be evidenced, nor dehydrogenation of a cyclohexyl ring of the phosphine ligand, as observed in relevant systems.[15] We therefore propose that dehydrogenation of **2**−**5** would produce a highly electron rich 16-electron fragment and allow the approach of the vinylsilane which after vinylic C−H activation and α-elimination reactions would lead to the formation of a vinylidene group. Vinylic C−H activation reactions by unsaturated electron-rich transition-metal centers have precedents.[16] In order to test the possible involvement of (triethylsilyl)acetylene in this reaction, **3** was reacted at room temperature with 1 or 10 equiv of (triethylsilyl)acetylene in a Schlenk tube for 2 days or in an NMR tube for 4 h. In all cases the formation of **7** is apparent, but it is always a very minor component of a complicated reaction mixture.

The relaxation time T_1 of the hydride signal was measured for **6**−**8** and found to be close to 160−170 ms (250 MHz, C_7D_8). After checking the absence of significant interaction between this hydride and a proton of the vinylidene ligand, we used this value as an estimation of the contribution to relaxation of all factors but H−H dipole−dipole relaxation within the dihydrogen ligand in **2**−**4**. This led to H−H distances of 1.30 Å (**2**), 1.29 Å (**3**), and 1.24 Å (**4**) assuming slow rotation of H_2 and 1.03, 1.025, and 0.98 Å assuming fast rotation. The comparison between the values found for **3** using J_{HD} or relaxation data (respectively 1.27 and 1.29 Å) leads us to propose a slow-rotation regime for the dihydrogen ligand in this compound. An alternative classical structure in which the three hydrides are located in the equatorial plane would lead to unreasonable values for the H−H separation.

In conclusion, we describe in this communication the synthesis of new ruthenium dihydrogen derivatives in which the dihydrogen ligand is stretched, due to the presence of good σ-donor ligands in the *trans* position. The value of the H−D coupling constant suggests both an important lengthening of the H−H bond and, coupled with T_1 data, slow rotation on the NMR time scale of the dihydrogen ligand. Complexes **2**−**5** are stable and reluctant toward H_2 dissociation but exchange readily with D_2, a typical reactivity for dihydrogen complexes, and react with triethylvinylsilane to give unexpected vinylidene complexes through vinylic C−H activation and α-elimination. Vinylidene ligands have been previously obtained through addition of alkynes to electrophilic metal center,[17] but this type of reaction is not selective in the present case. This new reactivity might therefore be specific to nucleophilic metal centers able to stretch a dihydrogen ligand. Other examples of the specific reactivity of stretched-dihydrogen complexes are presently under investigation.

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Supporting Information Available: Text giving experimental details of the synthesis and characterization of the new complexes **2**−**8** (3 pages). Ordering information is given on any current masthead page.

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