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Infrared Spectrum of the $RuH_2(H_2)_4$ Complex in Solid Hydrogen

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Summary: Laser-ablated ruthenium atoms react with pure hydrogen during condensation at 4 K to form a major product with a broad 2690 cm^{-1} absorption and sharp 2003, 1984, 1857, 1850, 1541, 874, 773, 708, and 588 cm^{-1} absorptions, which are assigned to the $RuH_2(H_2)_4$ complex on the basis of isotopic shifts and agreement with isotopic frequencies calculated by density functional theory. This ruthenium dihydride complex completes the stable organometallic series $RuH_2(H_2)(PCy_3)_3$ and $RuH_2(H_2)_2(PCy_3)_2$ and shows that saturation of Ru by dihydrogen can be obtained in the absence of other supporting ligands.

The first hexahydride of ruthenium, $RuH_6(PCy_3)_2$, occupies a special place in the evolution of the understanding of hydride and dihydrogen binding to transition-metal centers, as a reinvestigation of its structure determined that two η^2-H_2 ligands are in fact bound to the RuH_2 center. Thus, the complex can be represented as $RuH_2(H_2)_2(PCy_3)_2$.[1,2] The analogous tetrahydride also contains an η^2-H_2 ligand, as characterized by the NMR relaxation time (T_1) being shorter than for the classical hydride, and the same applies to the $RuH_2(H_2)(PPh_3)_3$ congener.[2,3] These synthetically important ruthenium complexes[4−6] are necessarily prepared in the presence of stabilizing ligands, which limit the number of more weakly bound η^2-H_2 ligands that can attach to the metal center.[1−7]

We have employed pure hydrogen as reagent and solid matrix to form transition-metal polyhydrides for infrared spectroscopic investigation, and our recent preparation of the $WH_4(H_2)_4$ complex is a good example of the binary complexes that can be formed.[8,9] These complexes have η^2-H_2 ligand properties that compare favorably with the celebrated organometallic derivatives such as $W(CO)_3(PR_3)_2(H_2)$, for example.[10,11] We wish to investigate the catalytically important metal ruthenium in a pure hydrogen environment in order to determine the maximum dihydrogen coordination possible without competition from the more strongly bonding ligands. We here prepare and characterize the $RuH_2(H_2)_4$ complex with infrared spectra of both the classical RuH_2 and in particular the nonclassical $Ru(H_2)$ subunits. This is a surprising result in view of our inability to trap the isolated RuH_2 molecule, but the RuH_2 molecule is bent in its ground state, in just the structure that it adopts at the center of the organometallic ruthenium dihydride complexes[2,3] and the present subject complex. We also trap the related $RuH(H_2)_4$ complex. These investigations of high dihydrogen coordination gain importance from the prospects of using metal hydrides for hydrogen storage.[12]

Laser-ablated Ru atoms were condensed and reacted with hydrogen gas during condensation on a CsI window cooled to 4 K by a closed-cycle refrigerator.[8,9] Infrared spectra of a solid sample formed by freezing laser-ablated Ru atoms and H_2 are illustrated in Figure 1. The strongest two absorptions at 2003 and 1984 cm^{-1} are in the region expected for Ru−H vibrations, as such modes have been observed at 1950, 1946, 1927, and 1890 cm^{-1} for ruthenium dihydride complexes in Nujol.[2] The 2003 and 1984 cm^{-1} bands shift to 1445 and 1428 cm^{-1} in solid deuterium, which define H/D ratios of 1.386 and 1.389, which are appropriate for a second-row transition-metal hydride stretching vibration.[8] The HD counterparts fall at 1994 and 1438 cm^{-1}, midway within each pair, which identifies vibrations of two equivalent Ru−H bonds. These bands cannot be due to the simple RuH_2 molecule alone, because of the other eight absorptions associated by common behavior on ultraviolet irradiation that are given in Table S1 in the Supporting Information. The broad 2690 cm^{-1} band characteristic of H−H vibrational modes in η^2-H_2 ligands,[9,10] the three 1857, 1850, and 1541 cm^{-1} bands in the region for metal−η^2-H_2 ligand stretching modes, and the 588 cm^{-1} band for (H_2)−metal−(H_2) bending modes[9,10] require a complex with two or more η^2-H_2 ligands.

Accordingly, density functional theory (DFT) calculations were done using the Gaussian 03 package,[13] B3LYP density functional,[14] 6-311++G(3df,3pd) basis sets for H, and SDD pseudopotential and basis set[15] for Ru to provide product structures and vibrational frequencies. First, our calculation

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(1) Chaudret, B.; Poliblanc, R. *Organometallics* **1985**, *4*, 1722.

(2) (a) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598. (b) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. J. *Organometallics* **2000**, *19*, 1652.

(3) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(4) Belderain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001.

(5) Kubas, G. J. *Proc. Natl. Acad. Sci.* **2007**, *104*, 6901, and references therein.

(6) Lau, C. P.; Ng, S. M.; Jia, G.; Lin, Z. *Coord. Chem. Rev.* **2007**, *251*, 2223.

(7) Busch, S.; Leitner, W. *Chem. Commun.* **1999**, 2305.

(8) Andrews, L. *Chem. Soc. Rev.* **2004**, *33*, 123, and references therein.

(9) Wang, X.; Andrews, L.; Infante, I.; Gagliardi, L. *J. Am. Chem. Soc.* **2008**, *130,* 1972 ($WH_4(H_2)_4$).

(10) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(11) Kubas, G. J.; Ryan, R. P.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339.

(12) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283.

(13) Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.

(14) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, Y.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

10.1021/om800507u CCC: $40.75

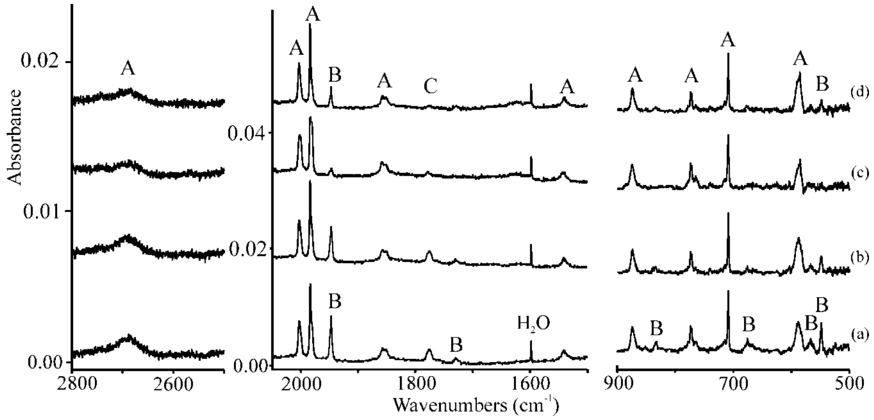

Figure 1. Infrared spectra for the ruthenium atom and H_2 reaction products in pure H_2 at 4 K: (a) Ru + H_2 deposition for 30 min; (b) after >380 nm irradiation; (c) after >220 nm irradiation; (d) after annealing to 6.5 K. The absorbance scale is given for trace a, and traces b−d are displaced for clarity using the same scale.

for RuH_2 predicts a $^3B_1$ ground state with a 98° valence angle, a 1.581 Å bond length, a symmetric Ru−H stretching mode at 2082 cm^{-1} with 56 km/mol infrared intensity, and an antisymmetric Ru−H mode at 2023 cm^{-1} with 210 km/mol intensity. Next, calculations were performed by adding η^2-H_2 ligands stepwise to the ground-state RuH_2 molecule, and successively lower energy complexes were formed until $RuH_2(H_2)_4$ in the singlet ground electronic state was obtained with 61 kcal/mol lower energy than $RuH_2 + 4\ H_2$: a fifth H_2 molecule would not bind to the metal center. The frequencies and infrared intensities calculated for this binary complex are compared in Table S1 (Supporting Information) with the 10 observed frequencies labeled A in Figure 1 (1857 cm^{-1} and 1850 cm^{-1} share one label). The calculated frequencies are 2−4% higher, which is the deviation found for harmonic frequencies relative to observed values,[8,16,17] except for the symmetric Ru−(H_2) stretching and the lowest rocking mode, which are more difficult to compute accurately. The agreement is very good, and the fact that we have observed the 10 strongest infrared absorptions as defined by calculation makes this identification of $RuH_2(H_2)_4$ compelling.

Infrared spectra of our $RuH_2(H_2)_4$ complex in solid hydrogen and the larger ligated $RuH_2(H_2)_2(P^iPr_3)_2$ complex in Nujol[2b] may be compared: the latter exhibits strong 1946, 822 cm^{-1} and weak 2586, 1673 cm^{-1} bands. In view of the more strongly interacting Nujol medium relative to solid hydrogen, our most comparable strong 1984, 874 cm^{-1} and weak 2690, 1850 cm^{-1} bands for the common Ru−H and Ru−(H_2) subunits are in general agreement.

The organometallic complexes are characterized by fluxional behavior near room temperature, which involves exchange of classical hydride and dihydrogen ligand positions.[2−5] For our subject complex prepared and trapped in cryogenic solids, we found isotopic exchange under energized conditions during laser ablation and UV excitation. Although we do not observe isolated RuH_2, owing to its immediate and favorable reaction to bind additional H_2 molecules, the reaction must proceed first through RuH_2 on to the higher $RuH_2(H_2)_4$ complex. Reaction 1 is computed to be exothermic by 19 kcal/mol at the B3LYP level, and to have an activation energy of 8 kcal/mol.[18] Since the addition of 4 H_2 molecules is exothermic by another 61 kcal/mol, reaction 2, the product is initially energized, and during this reaction, isotopic hydride/dihydrogen positional exchange occurs. This is manifested in reactions with HD and with $H_2 + D_2$ mixtures where the major product dihydride absorption arises from the precursor insertion reaction, as in (1), but a minor yield of the other isotopic product is also observed. Infrared spectra in the Ru−H stretching region (Figure 2) reveal the strongest band for the Ru−H stretching mode of $RuHD(HD)_4$ and two weaker bands for $RuH_2(D_2)(HD)_3$ using the pure HD reagent. In like fashion, spectra for the $H_2 + D_2$ mixture show the strongest band for the RuH_2 mode in a complex and a weaker band for RuHD coordinated to isotopic dihydrogen molecules. Similar H/D isotopic exchange has been observed in analogous tungsten and rhodium complexes.[9,19]

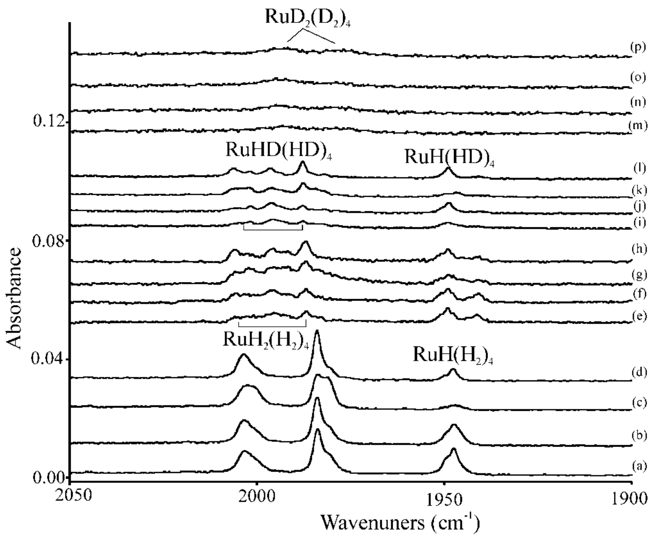

Figure 2. Infrared spectra for the ruthenium atom and isotopic dihydrogen reaction products in the solids state at 4 K: (a) Ru + H_2 deposition for 30 min; (b) after annealing to 6 K; (c) after >220 nm irradiation; (d) after annealing to 6.5 K; (e) Ru + H_2 + D_2 deposition for 30 min; (f) after annealing to 7 K; (g) after 240−380 nm irradiation; (h) after annealing to 8 K; (i) Ru + HD deposition for 30 min; (j) after annealing to 7 K; (k) after 240−380 nm irradiation; (l) after annealing to 8 K; (m) Ru + D_2 deposition for 30 min; (n) after annealing to 8 K; (o) after 240−380 nm irradiation; (p) after annealing to 10 K.

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(16) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(17) Andersson, M. P.; Uvdal, P. L. *J. Phys. Chem. A* **2005**, *109*, 3937.

(18) Balasubramanian, K.; Wang, J. Z. *J. Chem. Phys.* **1989**, *91*, 7761.

(19) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2002**, *106,* 3706 (Rh + H_2).

$$\mathrm{Ru}\ (^5\mathrm{F}) + \mathrm{H_2} \rightarrow \mathrm{RuH_2}\ (^3\mathrm{B_1}) \tag{1}$$

$$\mathrm{RuH_2}\ (^3\mathrm{B_1}) + 4\mathrm{H_2} \rightarrow \mathrm{RuH_2(H_2)_4}\ (^1\mathrm{A}) \tag{2}$$

The minor product bands labeled B in Figure 1 at 1948, 1730, 833, 675, 567, and 549 $\mathrm{cm^{-1}}$ are in the spectral regions of the major product A bands. Ultraviolet irradiation decreases the B bands, and they are recovered on sample annealing. A deuterium counterpart is observed, at 1404 $\mathrm{cm^{-1}}$, only for the strongest band (H/D ratio 1.387). The solid HD experiment gave two sharp bands at 1949 and 1405 $\mathrm{cm^{-1}}$, shifted slightly owing to the different medium, which characterizes the vibration of a single Ru−H bond, and the associated bands again identify a larger complex.

The weak band labeled C at 1775 $\mathrm{cm^{-1}}$ decreased on photolysis and shifted to 1291 $\mathrm{cm^{-1}}$ in solid deuterium (H/D ratio 1.375). With HD a hydrogen counterpart was observed at 1772 $\mathrm{cm^{-1}}$, but no deuterium counterpart was observed. This band is lower than the 1820 $\mathrm{cm^{-1}}$ band assigned to RuH in solid argon,[20] which suggests identification as the simple $\mathrm{RuH(H_2)}$ complex. Analogous $\mathrm{MH(H_2)(dppe)_2^+}$ cation complexes are well-known in the organometallic literature, and the Ru analogue has a Ru−H stretching frequency at 1961 $\mathrm{cm^{-1}}$.[21]

Laser-ablated Ru atoms are energetic enough to react and form the RuH diatomic molecule. Our calculation predicts a $^4\Sigma$ ground state and 1980 $\mathrm{cm^{-1}}$ harmonic frequency, which are in accord with higher level computations.[22] The quartet state $\mathrm{(H_2)RuH}$ complex is bound by 10 kcal/mol, with a strong Ru−H stretching frequency computed at 1886 $\mathrm{cm^{-1}}$, but higher complexes are not bound. However, on the doublet potential energy surface, higher complexes are stable. The $\mathrm{RuH(H_2)_2}$ complex is 34 kcal/mol lower, the $\mathrm{RuH(H_2)_3}$ complex 39 kcal/mol lower, and the highest $\mathrm{RuH(H_2)_4}$ complex 52 kcal/mol lower in energy than $^4\Sigma$ state RuH and two, three, or four $\mathrm{H_2}$ molecules. A RuH complex with five dihydrogen molecules eliminated $\mathrm{H_2}$ and converged again to $\mathrm{RuH(H_2)_4}$.

The observed B frequencies are compared in Table S2 (Supporting Information) with the calculated frequencies for the $\mathrm{RuH(H_2)_4}$ complex. The strong Ru−H stretching mode is predicted to fall 30 $\mathrm{cm^{-1}}$ below the strongest such mode for $\mathrm{RuH_2(H_2)_4}$, and the observed difference is 36 $\mathrm{cm^{-1}}$. The strongest H−H stretching mode is predicted 77 $\mathrm{cm^{-1}}$ higher for the former, and a broad blue shoulder is observed, but an assignment cannot be made. Five other frequencies are observed for species B, and the B3LYP calculated harmonic frequencies are 3−6% higher than the six observed values, except again for the Ru-($\mathrm{H_2}$) stretching mode, which is the expected correlation, and our identification of $\mathrm{RuH(H_2)_4}$ is substantiated by this comparison.

Two alternative identifications of species B can be ruled out. The $\mathrm{RuH_2(H_2)_3}$ complex and another hydrogen molecule are 13 kcal/mol higher energy than $\mathrm{RuH_2(H_2)_4}$, and the former strongest Ru−H stretching absorption is calculated to be 20 $\mathrm{cm^{-1}}$ below that for the latter and our band difference is 36 $\mathrm{cm^{-1}}$. In addition the second Ru−H stretching mode is not observed, and two prominent Ru−($\mathrm{H_2}$) stretching modes are calculated 100 $\mathrm{cm^{-1}}$ higher and thus further from the calculated and observed values for $\mathrm{RuH(H_2)_4}$. Finally, *trans*-$\mathrm{RuH_2(H_2)_4}$ is computed to be 7 kcal/mol higher in energy than the presently observed *cis*-$\mathrm{RuH_2(H_2)_4}$ isomer, in general agreement with calculations for trans organometallic complexes,[2b] but of more importance, the antisymmetric H−Ru−H vibration for the trans species is computed at 1723 $\mathrm{cm^{-1}}$, about 320 $\mathrm{cm^{-1}}$ lower than for the cis isomer and 290 $\mathrm{cm^{-1}}$ lower than for $\mathrm{RuH(H_2)_4}$. The *trans*-$\mathrm{RuH_2(H_2)_4}$ possibility is thus eliminated.

Table 1. Calculated Bond Lengths (Å) for the $\mathrm{RuH(H_2)_4}$ and $\mathrm{RuH_2(H_2)_4}$ Complexes[a]

$\mathrm{RuH(H_2)_4}$			$\mathrm{RuH_2(H_2)_4}$[b]			bond
1.611			1.602			Ru−H
1.723	1.753	0.863	1.692	1.722	0.876	Ru−($\mathrm{H_2}$), H−H
1.717	1.725	0.874	1.692	1.723	0.876	Ru−($\mathrm{H_2}$), H−H
1.790	1.818	0.836	1.791	1.826	0.833	Ru−($\mathrm{H_2}$), H−H
1.811	1.823	0.831	1.791	1.826	0.833	Ru−($\mathrm{H_2}$), H−H

[a] Calculated using the B3LYP/6-311++G(3df,3pd)/SDD method. [b] The H−Ru−H bond angle is 81.2°.

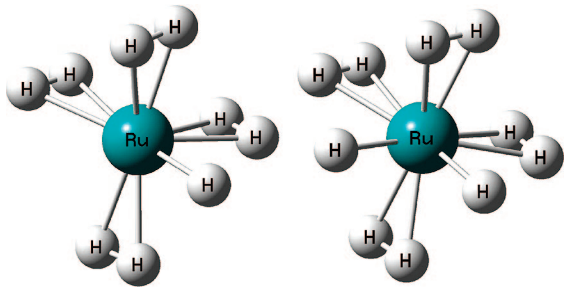

Figure 3. Structures calculated for the ruthenium hydride and dihydride tetrakis(dihydrogen) complexes at the B3LYP level of theory.

The results of our calculations show that four $\mathrm{H_2}$ molecules are bound more strongly to $\mathrm{RuH_2}$ than to RuH. First, the total binding energy is 9 kcal/mol higher, the average Ru−($\mathrm{H_2}$) distance is 0.012 Å shorter, and the average H−H distance is 0.004 Å longer (Table 1). And second, the observed strongest Ru−($\mathrm{H_2}$) stretching frequency is 120 $\mathrm{cm^{-1}}$ greater for the higher oxidation state complex. The unpaired electron in the doublet $\mathrm{RuH(H_2)_4}$ complex is largely on the Ru center on the basis of the computed spin density of 0.82. Structures for the product complexes illustrated in Figure 3 show very similar ligand bonding arrangements. Unfortunately, our $\mathrm{RuH_2(H_2)_4}$ complex, which is computed to be 80 kcal/mol more stable than Ru + 5 $\mathrm{H_2}$, does not survive removal of the hydrogen matrix.

The $\mathrm{RuH_2(H_2)_4}$ complex has properties in common with our recently characterized $\mathrm{WH_4(H_2)_4}$ complex.[9] There is a definite electronic interaction between the metal centers and the dihydrogen ligands as the multiplicity of each metal dihydride is reduced by 2 in the supercomplexes, and accordingly two metal valence d electrons are paired in the bonding to four dihydrogen ligands. In the Ru supercomplex, the average $\mathrm{H_2}$ ligand binding energy at the B3LYP level (zero point energy corrected) is 15 kcal/mol, and the same value was also reported for the W supercomplex.[9] Complex formation leads to electron rearrangement based on computed Mulliken charges for the metal dihydrides and the supercomplexes. For the $\mathrm{RuH_2}$ system, the dihydride molecule charges are +0.34, −0.17, and −0.17 and in the supercomplex these change to −0.39, −0.05, and −0.05 with +0.09, +0.10, +0.11, and +0.19 on the dihydrogen ligands. Similar changes were found for $\mathrm{WH_4}$ and its supercomplex, which show that the dihydrogen ligands donate charge to the metal center on forming the complex. Finally, our calculated H−H bond lengths for the Ru supercomplex are slightly shorter that those reported for the W supercomplex, and

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[20] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 9892 (Ru + CO, $\mathrm{H_2}$).

[21] See for example: Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375.

[22] Balasubramanian, K. *J. Chem. Phys.* **1990**, *93*, 8061.

our H—H stretching frequency, 2690 cm^{-1}, is higher than the 2500 cm^{-1} value observed for the W supercomplex. Thus, it appears that WH_4 forms a stronger binary complex with dihydrogen than does RuH_2.

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Supporting Information Available: Text, giving experimental and theoretical methods, and Tables S1 and S2, giving observed and calculated product frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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