of 3.6 ± 0.1 kcal/mol translates to a K_a ratio of 405. This is not the maximal value but indicates the range expected for true two point binding.[15]

Supplementary Material Available: Details on the OPLS parameters for **1**, **2**, **3**, and chloroform are provided (5 pages). Ordering information is given on any current masthead page.

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Syntheses and Reactivity of Ruthenium Hydride Complexes Containing Chelating Triphosphines. 1. Characterization of the Molecular Dihydrogen Complex $RuH_2(H_2)$(Cyttp) (Cyttp = $PhP(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$)

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Since the first report of compounds containing a molecular dihydrogen (η^2-H_2) ligand,[1] the number of η^2-H_2 complexes has increased rapidly; in fact, two reviews on this subject have appeared recently.[2] Consequently, many of the previously assigned high-valent metal polyhydrides have been reformulated as lower-valent metal dihydrogen complexes.[2] For example, $RuH_4(PPh_3)_3$[3] is now considered to be $RuH_2(H_2)(PPh_3)_3$.[4a,b] In order to make chemical and structural comparisons between metal hydrides containing monodentate phosphines and those containing chelating polydentate phosphines, we have synthesized several ruthenium hydride compounds that contain chelating triphosphine ligands, one of which is $RuH_2(H_2)$(Cytpp), Cyttp = $PhP[CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2]_2$, which is the first reported example of a molecular dihydrogen complex containing a chelating triphosphine.

Metathesis reactions of $RuCl_2$(Cyttp)[5] with excess NaH in THF under a dihydrogen atmosphere at 40–50 °C overnight (ca. 10 hours) yield RuH_4(Cyttp). On the basis of proton and $^{31}P\{^1H\}$ NMR evidence[6] and the chemical reactions described below, the compound is best formulated as the ruthenium dihydrogen complex *cis-mer*-$RuH_2(H_2)$(Cyttp).[6] At room temperature, its ^1H NMR spectrum in the hydride region (Figure 1) shows a broad resonance at ca. −8.2 ppm ($\omega_{1/2}$ = 40 Hz). Integration of the hydride resonance shows that the number of hydrogen atoms per ruthenium ranges from approximately 3.2 to 3.6. Since the compound is diamagnetic, we are formulating it as RuH_4(Cyttp). Low integration values for hydride resonances have been reported previously for similar compounds of monophosphines; for example, the number of hydrides observed for $RuH_4[P(p\text{-tolyl})_3]_3$ was 3.0–3.2, based on integration of the proton NMR spectrum.[3c] It is tempting to attribute the low integration value to partial dissociation of dihydrogen in solution, as was done for $RuH_4[P(p\text{-tolyl})_3]_3$.[3c] Dissociation of the η^2-H_2 ligand in solution would explain the rapid reactions with D_2 and other small molecules; however, solid RuH_4(Cyttp) appears stable to loss of H_2 for a few hours at 0.1 Torr.

The broad hydride resonance of $RuH_2(\eta^2\text{-}H_2)$(Cyttp) at ca. −8.2 ppm is separated into two broad signals when the temperature is lowered below 240 K; one signal is at ca. −6.5 ppm and the other is at ca. −9.5 ppm with an intensity ratio of ca. 1:1. In contrast to the two peaks observed for our RuH_4(Cyttp) complex, both $RuH_4(PPh_3)_3$[4a] and $RuH_4(PCy_3)_3$[8g] show only one resonance in the hydride region. To confirm the presence of the nonclassical hydride $Ru(H_2)$ unit, we have used the T_1 criterion reported by Crabtree[4] and others.[8] The T_1 value was measured by the inverse-recovery method. At room temperature in toluene-d_8, the T_1 value for the broad hydride resonance signal is 38 ms; it decreases to 18 ms at 260 K. At 230 K, the T_1 for the resonance at −6.5 ppm is 16 ms, while that for the −9.5 ppm resonance is 18 ms. As the temperature is decreased further, the T_1 values for both resonances increased, but at a different rate, as shown in Figure 1. All the T_1 values observed for our $RuH_2(\eta^2\text{-}H_2)$(Cyttp) are in the range for molecular dihydrogen complexes (usually < 100 ms). Considering that the molecule is highly fluxional and that the T_1 value for the −9.5 ppm resonance increased much faster than that at −6.5 ppm, we suggest that the actual T_1 values for the −9.5 ppm resonance probably are much larger than the measured ones.[9] The resonance at −9.5 ppm is, therefore, assigned to classical Ru–H bonds, while that at −6.5 ppm is assigned to the nonclassical $Ru(H_2)$. The behavior of these two resonances is very similar to that observed for $[IrH(H_2)(bq)(PPh_3)_2]^+$.[4b]

The line widths of the hydride resonances changed with temperature; for example, at 303 K the $\omega_{1/2}$ is ca. 40 Hz and ca. 260 Hz at 250 K. Below 240 K, the line widths of the two resonances changed in a different manner. The line width for the resonance at δ −9.5 decreased as the temperature was lowered,[10] whereas, the line width for the resonance at δ −6.5 first decreased, and then it increased.[10] The line width behavior is consistent with several other $M(H_2)$ complexes.[8b,c]

Several factors have been suggested to be responsible for the broad lines (small T_2) observed for $M(\eta^2\text{-}H_2)$ signals, such as exchange of free and coordinated H_2, molecular motion (e.g., rotation) of the H_2 ligand, and dipolar interaction between the two hydrogen atoms of η^2-H_2.[8c] The values of T_2 decrease monotonically with increasing τ_c and approach a limiting value that is characteristic of a completely rigid solid. As the temperature is lowered, the molecular motions, including rotation of the η^2-H_2 ligand, are slowed and τ_c increases; thus T_2 is smaller at lower temperatures. The slowing rotation of the η^2-H_2 ligands

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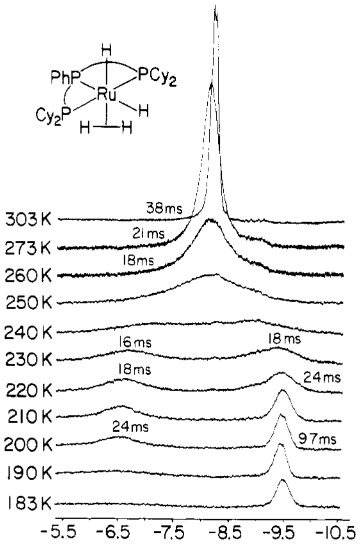

Figure 1. Variable temperature proton NMR spectra in the metal-hydride region. The calculated T_1 values are written on the −6.5 and −9.5 ppm peaks, which are assigned to the nonclassical Ru(η^2-H_2) and classical Ru-H units, respectively.

in $[MH(H_2)(dppe)_2]BF_4$ (M = Fe, Ru) was suggested for the broadening lines of the $M(H_2)$ resonances at lower temperatures.[8b] A changeover of the rotational behavior of the molecule from the extreme narrowing to the slow-motion regimes has also been suggested as a possible origin for the line broadening in the spectra of $M(H_2)$ complexes at low temperature.[4b] It is also possible that the line broadening in our system is caused by the exchange process involving rotation of the η^2-H_2 ligand beginning to freeze out, as suggested by one referee.

Like $RuH_4(PPh_3)_3$[3a,c] and $RuH_4(PCy_3)_3$,[8g] a broad band at ca. 1950 cm^{-1} was observed in the infrared spectrum of $RuH_2(\eta^2$-$H_2)$(Cyttp), which we attribute to the classical Ru-H bonds. We did not observe infrared bands that could be assigned to the nonclassical $Ru(H_2)$ unit.

We tried to determine the $^1J_{HD}$ coupling constant by use of the partially deuterated compound RuH_xD_{4-x}(Cyttp) ($x \cong 2$), which was prepared in situ by bubbling deuterium gas into a toluene solution of RuH_4(Cyttp).[11] However, no $^1J_{HD}$ coupling was resolved in the temperature range 323–200 K. Other investigators have also failed to observe $^1J_{HD}$ in highly fluxional complexes that contain molecular dihydrogen (e.g., in $[FeH(H_2)(dppe)_2]^+$ [8b] and $[IrH_2(H_2)_2(PCy_3)_2]^+$ [4c,d]).

The hydride complex reacts with other ligands as if it were "RuH_2(Cyttp)". It inserts CO_2 to form a bidentate formate ligand in the resulting $RuH(HCO_2)$(Cyttp), and it adds CO, $P(OMe)_3$, and $P(OPh)_3$ instantly and irreversibly to form six-coordinate *cis-mer*-RuH_2L(Cyttp) complexes. It also reacts with N_2 reversibly to form *cis-mer*-$RuH_2(N_2)$(Cyttp). The N≡N stretching frequency of the N_2 compound was observed at 2100 cm^{-1}, which is consistent with Morris' proposal that when the $\nu_{N\equiv N}$ of the dinitrogen ligand is greater than 2060 cm^{-1} in a d^6 metal complex, then the nonclassical form, $M(H_2)$, is favored over the corresponding classical dihydride, MH_2.[8a] An X-ray structure determination of $RuH_2(N_2)$(Cyttp) shows that the N_2 ligand is trans to one of the hydrides and attached "end-on" to form a nearly linear Ru-N-N linkage.[12] These reactions and structures will be reported soon.

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(11) If one bubbles D_2 gas into a solution of RuH_4(Cyttp) in benzene-d_6 or toluene-d_8, the intensity of the hydride resonance decreases and eventually almost disappears, presumably due to formation of RuD_4(Cyttp), as indicated by the ^{31}P NMR spectrum of the solution. The ^{31}P NMR parameters are almost identical with those of RuH_4(Cyttp), and the lines become wider compared to RuH_4(Cyttp).

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Thermal Evolution of an Oxide-Bound Organometallic Complex in Ultrahigh Vacuum: Stepwise Conversion of Tris(allyl)rhodium to Rhodium Metal on $TiO_2(001)$

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Chemical vapor deposition of an organometallic complex onto the surface of an oxide followed by mild thermal degradation is of demonstrated importance to "heterogeneous" catalysis[1] and modern materials synthesis.[2] We have described the chemistry of bulk oxide supported organorhodium compounds[3] and the hydrogenolysis of bis(allyl)rhodium on $TiO_2(001)$ prepared and modified in ultrahigh vacuum (UHV).[4] We now report the stepwise thermal evolution of TiO_2-bound bis(allyl)rhodium studied in UHV by photoelectron spectroscopy and on powdered supports by infrared methods. Thermolysis of the oxide-bound organometallic to the metal occurs *in stages* involving hydride complex intermediates, and our data strongly support the notion of covalency between the oxide and the organometallic and several of its derivatives.

The preparation of single crystal $TiO_2(001)$ for subsequent vapor phase deposition of tris(allyl)rhodium has been described,[4,5] as have experiments for studying deposition of the organometallic in UHV. He(I) radiation (21.2 eV) and Mg Kα radiation were used for ultraviolet and X-ray photoelectron spectroscopy respectively, with data collected in a pulse counting mode. X-ray photoelectron spectra were referenced to the Ti $2p_{3/2}$ peak at 458.5 eV. Samples prepared on bulk TiO_2 were made by depositing $Rh(allyl)_3$ on Degussa P-25 at a loading of 0.16 wt % rhodium. Infrared spectra were obtained by using a Perkin-Elmer Model 1710 Fourier transform infrared spectrometer.

Three peaks below the Fermi level are observed in the O(2p) UPS spectra for clean $TiO_2(001)$ (Figure 1A). The assignment of these peaks has been discussed.[4,6] After exposure of the TiO_2 surface to $Rh(allyl)_3$ (2000 L), the oxygen 2p binding energy maximum shifts from 7.1 to 8.1 eV (Figure 1B).[4] This indicates formation of a bond between the rhodium and the surface oxygens. The oxygen 2p binding energy maximum at 5.2 eV was barely affected by this deposition reaction showing that the rhodium complex interacts with only certain surface states of the oxide. The binding energy of Rh($3d_{5/2}$) electrons (309.0 eV)[7] was measured by XPS (Figure 2B) concommitantly with UPS determinations. Thermolysis of the supported bis(allyl) compound by resistive heating up to 150 °C was performed in 2-h stages, and both UPS and XPS determinations were made following each increase in annealing temperature. Two distinct plateaus were observed in both spectra, one in the region 60–100 °C and the other from 120 °C to 150 °C. These two regions correspond to

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