All 2D spectra were obtained in the absolute-value mode.

Summary

In summary, the high sensitivity and the high resolution of ^{31}P NMR signals usually obtained by the combination of cross-polarization, magic angle, and high-power proton-decoupling techniques provide a sound base for feasible 2D *J*-resolved experiments. Since the pulse sequence and spectral interpretation in the solid state are directly analogous to those in solution, homonuclear ^{31}P *J*-resolved 2D NMR spectroscopy has the potential to become a routine technique for chemists interested in solid materials such as metal phosphine complexes. Also, the experiment could be easily extended to give a heteronuclear $^{31}P-^{103}Rh$ *J*-resolved 2D spectrum if a triply tuned probe were available. Further work is in progress in our laboratory.

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Reactions of H_2 (D_2) with a Rhodium(II) Metalloradical: Kinetic Evidence for a Four-Centered Transition State

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Metal-catalyzed hydrogenation of substrates involves addition of hydrogen to the metal center as an obligatory step.[1] The importance of this class of reactions has stimulated efforts to understand the scope of mechanistic pathways operative in reactions of H_2 with metal complexes. Formation of dihydrides by addition to a single metal center ($M + H_2 \rightarrow M(H)_2$) and monohydrides by reaction with two metal sites ($2M + H_2 \rightarrow 2MH$) are both frequently observed.[2] Concerted addition of H_2 to form dihydrides through a three-centered triangular transition state has been thoroughly documented by kinetic studies,[3-5] observation of η^2-dihydrogen complexes,[6] and theoretical considerations.[7] Formation of monohydrides by addition of H_2 to two metal centers is less fully investigated, but both multistep heterolytic[8] and concerted homolytic[9-12] cleavage of dihydrogen have been recognized. This article describes the reaction of H_2 (D_2) with (tetramesitylporphyrinato)rhodium(II),[13] (TMP)Rh$^\bullet$ (**1**), to form (TMP)Rh-H through a four-centered transition state.

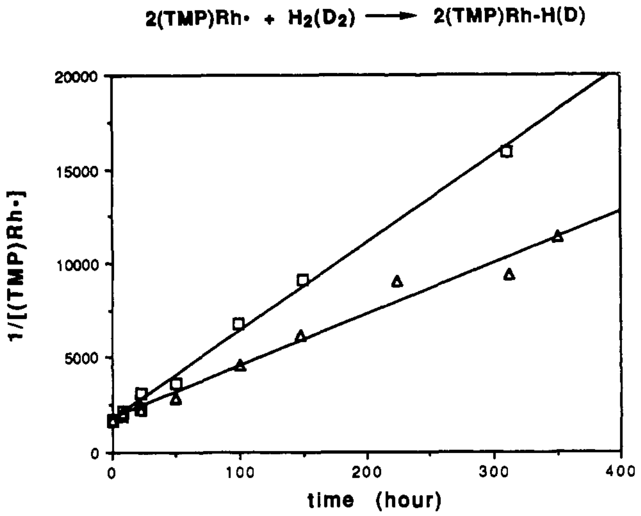

Figure 1. Representative second-order kinetic plots for the reaction of (TMP)Rh$^\bullet$ with H_2 (□) and D_2 (△) in C_6D_6 at 296 K ($[(TMP)RH^\bullet]_i = (5.9 \pm 0.1) \times 10^{-4}$ M; $P_{H_2} = P_{D_2} = 0.838 \pm 0.002$ atm; $[H_2] = 2.40 \times 10^{-3}$ M) ($k_{H_2}(296\ K) = 2.7\ L^2\ mol^{-2}\ s^{-1}$; $k_{D_2}(296\ K) = 1.6\ L^2\ mol^{-2}\ s^{-1}$; $k_{H_2}/k_{D_2}(296\ K) = 1.7$).

Results

Benzene solutions of (TMP)Rh$^\bullet$ (**1**) ($\sim 5 \times 10^{-4}$ M) react with H_2 ($P_{H_2} = 0.2-1.0$ atm) to form the hydride complex (TMP)Rh-H (**2**) (eq 1), which is identified in solution by ^1H NMR spectroscopy

$$2(TMP)Rh^\bullet + H_2 \rightleftharpoons 2(TMP)Rh{-}H \qquad (1)$$

of the characteristic hydride resonance ($\delta_{Rh-H} = -39.99$ ppm; $J_{^{103}Rh-H} = 44$ Hz) and in the solid state by IR spectroscopy of the Rh-H stretching vibration ($\nu_{Rh-H} = 2095\ cm^{-1}$). Reaction 1 proceeds effectively to completion as observed by ^1H NMR spectroscopy for the range of conditions investigated ($[(TMP)Rh^\bullet] = (3-5) \times 10^{-4}$ M; $P_{H_2} = 0.2-1.0$ atm; $T = 296-373$ K) which is expected for a reaction of H_2 that forms a hydride complex with a Rh-H bond energy of $\sim 60\ kcal\ mol^{-1}$.[13] Reaction 1 is well suited for kinetic studies because it is free from any competitive processes such as solvent reactions, M-M bond formation, and hydrogenation of the ligand, which have complicated previous studies of H_2 reactions with metalloradicals.[10-12] The rate for reaction 1 is observed to have a second-order dependence on the molar concentration of (TMP)Rh$^\bullet$ at conditions where the process is pseudo zero order in hydrogen (Figure 1). Second-order rate plots are linear throughout the entire reaction time, as required for a process that proceeds effectively to completion (Figure 1). Variation of the H_2 concentration ($P_{H_2}(296\ K) = 0.2-0.9$ atm.) demonstrates a first-order rate dependence on the molar concentration of H_2 and an overall third-order rate law for reaction 1 ($rate_1 = k_1[(TMP)Rh^\bullet]^2[H_2]$). Temperature dependence of the third-order rate constant (k_1) was used in deriving estimates for the transition-state and Arrhenius activation parameters

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($\Delta H_1^\ddagger(H_2)$ = 4.9 kcal mol^{-1}, $\Delta S_1^\ddagger(H_2)$ = −40 cal K^{-1} mol^{-1}; $A(H_2)$ = 2.9 × 10^4, $\Delta E_1^\ddagger(H_2)$ = 5.5 kcal mol^{-1}). Parallel studies for the reaction of D_2 with (TMP)Rh$^\bullet$ provide the kinetic isotope effect on the rate (k_{H_2}/k_{D_2}(296 K) = 1.6; k_{H_2}/k_{D_2}(353 K) = 1.3) and activation parameters ($\Delta H_1^\ddagger(D_2)$ = 5.5 kcal mol^{-1}, $\Delta S_1^\ddagger(D_2)$ = −39 cal K^{-1} mol^{-1}, $A(D_2)$ = 5.0 × 10^4, $\Delta E_1^\ddagger(D_2)$ = 6.1 kcal mol^{-1}).

Discussion

The rate law for reaction 1 (rate$_1$ = k_1[(TMP)Rh$^\bullet$]^2[H_2]) establishes that the transition state contains two (TMP)Rh$^\bullet$ metalloradicals and H_2. A large negative activation entropy ($\Delta S_1^\ddagger$ = −40 cal K^{-1} mol^{-1}) and small activation enthalpy ($\Delta H_1^\ddagger$ = 4.9 kcal mol^{-1}) are also consistent with organizing three molecules into a transition state (TS) where evolution of two Rh–H bonds substantially compensates for the H–H bond breaking. Transition states of this general type

$$\mathrm{Rh{\cdot\cdot}H{\cdot\cdot}H{\cdot\cdot}Rh}$$

have been previously implicated in reactions of dihydrogen with iodine atoms[14] and cobalt(II) metalloradicals.[10–12] We have also recently invoked this type of TS for the reaction of methane with (TMP)Rh$^\bullet$ (Rh··CH$_3$··H··Rh) on the basis of the rate law (rate$_f$ = k_f[(TMP)Rh$^\bullet$]^2[CH_4]), activation parameters ($\Delta S^\ddagger$ = −39 cal K^{-1} mol^{-1}; $\Delta H^\ddagger$ = 7.1 kcal mol^{-1}), and the kinetic isotope effect (k_{CH_4}/k_{CD_4}(296 K) = 8.2).[13]

Reactions of H_2 with radicals such as H$^\bullet$, Cl$^\bullet$, and H$_3$C$^\bullet$ are generally classified as atom abstractions and are typically observed to manifest large kinetic isotope effects, k_{H_2}/K_{D_2}(298 K) ~ 10.[15,16] Both theory and experiment implicate a pathway involving linear three-centered transition states (H··H··X) for reactions in this class.[15–17] Atom abstractions are characteristic of radical reactions where the dissociation energy for the bond formed is comparable to or larger than the H–H bond energy (104 kcal mol^{-1}). The Rh–H bond energies for porphyrin complexes are on the order of 60 kcal mol^{-1},[13,18] and thus hydrogen atom abstraction from dihydrogen by (TMP)Rh$^\bullet$ has a prohibitively large activation enthalpy ($\Delta H^\ddagger$ > 44 kcal mol^{-1}). The preferred route for H_2 reactions of (TMP)Rh$^\bullet$, cobalt(II) metalloradicals,[9–12] and an iodine atom[14] is through a four-centered TS (X··H··H··X) where two X··H interactions in the transition state provide a lower activation enthalpy pathway. A three-centered TS is more entropy favorable than the four-centered TS by ~20–25 cal K^{-1} mol^{-1}, but high temperatures are required for this pathway to be competitive.

The observed kinetic isotope effect associated with reaction 1 (k_{H_2}/k_{D_2}(296 K) = 1.6) is small compared to that for atom abstractions by H$^\bullet$, Cl$^\bullet$, and $^\bullet$CH$_3$ (k_{H_2}/k_{D_2}(298 K) ~ 10).[15,16] Kinetic isotope effects on reactions of H_2 (D_2) with metal complexes, for the few examples reported, have invariably been small (k_{H_2}/k_{D_2}(298 K) ~ 1–2).[3,4,19,20] There are apparently no reported deuterium isotope effect studies for reactions of metalloradicals or iodine atoms with H_2 (D_2) for comparison with reaction 1. The most thoroughly investigated system is the oxidative addition of H_2 (D_2) to *trans*-[(Ph$_3$P)$_2$Ir(Cl)(CO)], where k_{H_2}/k_{D_2} values of 1.18–1.06 (T = 273–300 K) have been reported.[4] The triangular (bent) transition state associated with oxidative addition to a single metal center is expected to have a smaller isotope effect than the linear TS exclusively on the basis of having a larger residual zero-point energy in the TS.[21] An analysis of the factors that contribute to k_{H_2}/k_{D_2} has illustrated that the net isotope effect is more complicated and depends on several large compensating contributions.[4] A product of four terms is responsible for the net kinetic isotope effect (k_{H_2}/k_{D_2} = (MMI)(EXC)(ZPE)($Q_t(H_2)/Q_t(D_2)$)).[21] The mass and moment of inertia term (MMI) is always greater than unity, and in the case of H_2 versus D_2 can be large (MMI ~ 2–5).[4] The tunneling factor ($Q_t(H_2)/Q_t(D_2)$) has a minimum value of 1, and thus, observation of small kinetic isotope effects for reactions of H_2 (D_2) with metal complexes must result from the product of the excitation (EXC) and zero point energy (ZPE) terms being substantially less than unity. The excitation term results from the thermal population of vibronic states, and the dominant contribution comes from low-frequency bending modes in the TS which are not present in the reactants.[21] The ZPE term ($e^{-(E_0^\ddagger(H_2)/RT\,-\,E_0^\ddagger(D_2))/RT}$) results from the difference in the sum of the zero-point energies for vibrational modes of the transition states and reactants. In reactions of large molecules the ZPE term is often the dominant contribution that causes k_H/k_D to vary significantly from unity.[21] The difference in zero-point energies between the reactants H_2 and D_2 (1.84 kcal mol^{-1} (ν_{H_2} = 4400 cm^{-1}; ν_{D_2} = 3112 cm^{-1}))[22] establishes the maximum value for this term, but the practical limit occurs in atom abstraction reactions with symmetric linear three-centered transition states where the observed values are ~$e^{1200/RT}$ (7.6 (298 K)).[15,16] The ZPE contribution is smaller for bent and unsymmetrical (late or early) transition states and can become less than 1 when the sum of the vibrational frequencies for the TS is larger than those for the reactants.

Our working hypothesis is that the (TMP)Rh$^\bullet$ and H_2 units will orient in the TS so as to optimize the Rh··H interaction while minimizing the interligand repulsions. A linear four-centered TS (Rh··H··H··Rh) where the porphyrin planes are parallel and the mesityl substituents are in a staggered conformation should be the preferred TS structure. The kinetic isotope effect for reaction 1 is small, and the question is whether or not this observation provides evidence against the linear four-centered TS model. A primary issue is whether there are features of linear three- and four-centered transition states that can reconcile the large differences in the observed kinetic isotope effects. The reactants that produce three- and four-centered transition states (X$^\bullet$ + H_2 (D_2)) and (2X$^\bullet$ + H_2 (D_2)) each have the symmetric stretch as the only vibrational mode. A linear three-centered TS (X··H··H) has two stretching modes and two bending modes, while a four-centered TS (X··H··H··X) results in three stretches and four bending modes. A significant point is that all of these TS vibrational modes are isotope sensitive. A linear four-centered TS has one more stretching and two more bending modes than a three-centered TS which contribute to reducing both the ZPE and EXC terms. The presence of two more isotope-sensitive low-frequency bending modes in the TS can potentially reduce the EXC term by a factor of 2, and the additional stretching and bending modes increase the zero-point energy of the TS which reduces the ZPE term. Four-centered transition states are thus expected to produce smaller kinetic isotope effects than a three-centered TS irrespective of whether the TS structure is linear or bent. This conclusion relates specifically to reactions of H_2 and D_2 where all of the new vibrational modes in the TS are isotope sensitive. The small isotope effect observed for the reaction of (TMP)Rh$^\bullet$ with H_2 (D_2) thus cannot be used to distinguish between linear and nonlinear four-centered transition states.

We have recently used the observation of a relatively large isotope effect in the reaction of methane with (TMP)Rh$^\bullet$ (k_{CH_4}/k_{CD_4}(296 K) = 8.2) as evidence for a linear (C··H··Rh) unit in a four-centered TS (Rh··C··H··Rh).[13] This conclusion was based in part on reports that oxidative addition of alkane C–H bonds with a metal center through a triangular three-centered TS yield

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small isotope effects (k_H/k_D(296 K) ~ 1–2,[23] and hydrogen atom abstractions from methane which proceed through a linear "three"-centered TS (C··H··X) have large isotope effects (k_H/k_D(298 K) ~ 9).[16b,24] A linear four-centered TS for the methane reaction (Rh··C··H··Rh) can potentially produce kinetic isotope effects comparable to a linear three-centered TS (C··H··X) because there are the same number and type of isotope sensitive (H (D)) vibrations in both transition states. This situation for C–H bond reactions contrasts with that for H_2 where the presence of two hydrogens produces twice as many isotope sensitive modes in a linear four-centered TS as there are in a linear three-centered TS.

In summary, the reaction of (TMP)Rh$^{\bullet}$ with hydrogen proceeds through a four-centered TS that provides a low activation enthalpy pathway for the concerted formation of two (TMP)Rh–H. The kinetic isotope effect is relatively small, but this result cannot at this time be used in differentiating between linear and bent transition states because of the inability to determine both the vibrational structure of the TS and the contribution of tunneling to k_{H_2}/k_{D_2}. Linear four-centered transition states can be expected to produce substantially smaller kinetic isotope effects than the better known three-centered TS because of the reduction of both the EXC and ZPE terms that results from doubling of the isotope-sensitive vibrations in the TS. Bonding and steric considerations suggest that a linear four-centered TS is preferable, but confirming experimental evidence is lacking. Reactions of (TMP)Rh$^{\bullet}$ and other radicals with substrates like H_2 and CH_4, where atom abstractions are thermodynamically unfavorable, can be accomplished by an alternate low activation enthalpy pathway involving the concerted reaction of two radicals through a four-centered TS.

Experimental Section

Materials. (Tetramesitylporphyrinato)rhodium(II) was prepared by published procedures.[13] H_2 and D_2 were purchased from Matheson Gas Products. Deuterated NMR solvents were degassed by freeze–pump–thaw cycles and then refluxed over sodium/benzophenone until the indicator turned purple.

General Methods. All manipulations were performed in an inert-atmosphere box under nitrogen/argon or by vacuum-line techniques. NMR data were recorded on an IBM-Bruker WP200SY spectrometer at ambient temperature unless otherwise noted.

Kinetic Studies. All reactions of hydrogen and deuterium were performed in 507 PP Wilmad sealed NMR tubes immersed in a constant-temperature bath (±0.10 °C). The progress of each reaction was evaluated by monitoring the changes in relative concentrations of (TMP)Rh$^{\bullet}$ and (TMP)Rh–H as observed by ^1H NMR spectroscopy. Absolute concentrations of rhodium porphyrin species were measured with respect to a known concentration of H_2 as an internal standard. The molar concentration of H_2 in benzene as a function of temperature and hydrogen pressure is given by the following expression: $[H_2] = [2.3421 \times 10^{-3} + 2.2592 \times 10^{-5}(T_2\ (°C))][T_2(K) \times P_1\ (Torr)/T_1\ (K)][1/760\ Torr]$, where T_1 and P_1 are the temperature and pressure at which the concentration is calculated. The solubility of D_2 in benzene is assumed to be the same as H_2.

Kinetic experiments were monitored at a series of hydrogen pressures (P_{H_2} = 150–650 Torr) and used to determine that the reaction is first order in H_2. Plots of $[(TMP)Rh^{\bullet}]^{-1}$ versus time yielded straight lines until completion of the reaction, which clearly indicates that reaction 1 is second order in $[(TMP)Rh]^{\bullet}$ and thus third order overall (rate = $k[(TMP)Rh^{\bullet}]^2[H_2]$). Rate constants ($k_{H_2}$(296 K) = 2.5 ± 0.4 $L^2\ mol^{-2}\ s^{-1}$; k_{D_2}(296 K) = 1.6 ± 0.2 $L^2\ mol^{-2}\ s^{-1}$; k_{H_2}(353 K) = 11.2 ± 1.3 $L^2\ mol^{-2}\ s^{-1}$; k_{D_2}(353 K) = 8.4 ± 1.6 $L^2\ mol^{-2}\ s^{-1}$) are averages from four independent kinetic measurements for each reaction. The error ranges correspond to one standard deviation from the mean. Rate constants measured for independent samples are observed to agree within approximately ±15%, but the absolute error in any single measurement could be as large as 30%.

The ratio of rate constants (k_{H_2}/k_{D_2}) was determined from kinetic runs utilizing H_2 and D_2 samples prepared at the same gas pressure and initial molar concentration of (TMP)Rh$^{\bullet}$ so as to minimize the accumulation of errors in k_{H_2}/k_{D_2} (k_{H_2}/k_{D_2}(296 K) = 1.6 ± 0.2; k_{H_2}/k_{D_2}(353 K) = 1.3 ± 0.2). Activation parameters for reaction 1 were derived from four k_1 measurements at both 296 and 353 K. The error ranges correspond to one standard deviation ($\Delta H_1^{\ddagger}(H_2)$ = 4.9 ± 1.0 kcal mol^{-1}; $\Delta S_1^{\ddagger}(H_2)$ = −40 ± 5 cal $K^{-1}\ mol^{-1}$; $A(H_2) = 2.9 \times 10^4$; $\Delta E_1^{\ddagger}(H_2)$ = 5.5 ± 1.0 kcal mol^{-1}; $\Delta H_1^{\ddagger}(D_2)$ = 5.5 ± 1.0 kcal mol^{-1}, $\Delta S_1^{\ddagger}(D_2)$ = −39 ± 5 cal $K^{-1}\ mol^{-1}$, $A(D_2) = 5.0 \times 10^4$, $\Delta E_1^{\ddagger}(D_2)$ = 6.1 ± 1.0 kcal mol^{-1}). Thermodynamic parameters from equilibrium studies could not be derived from the observations because reaction 1 effectively proceeded to completion for the range of conditions examined.

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Infrared Spectroscopic Study on the Hydration of Mercury(II), Cadmium(II), and Zinc(II) in Aqueous Solution and in the Hexahydrated Perchlorate Salts

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Introduction

In a recent theoretical study (SCF calculation) on the hexahydrated d^{10} ions zinc(II), cadmium(II), and mercury(II),[1] it was inferred that a comparatively broad distribution of the Hg–O bond lengths, as observed in a solution X-ray diffraction study,[2] could be explained in terms of a weak second-order Jahn–Teller (SOJT) effect.[3,4] This means that vibronic couplings between the nuclear and electronic motions occur in the hexaaquamercury(II) complex, primarily mixing the electronic A_g ground state of the mercury(II) ion with the lowest excited E_g state with an open d orbital, involving a vibrational mode of E_g symmetry. The calculations showed the d to s excitation energy to be lower for the hexaaqua complex of mercury(II) than for the zinc(II) and cadmium(II) complexes, implying a higher degree of vibronic coupling.[1]

In the present study, the hydration of the mercury(II) ion was investigated both in aqueous solution, using an infrared spectroscopic double-difference method,[5-7] and in the solid hexahydrate. In line with the theoretical calculation,[1] a comparative study of the hydrated Zn^{2+}, Cd^{2+}, and Hg^{2+} ions is presented.

Experimental Section

Materials. The solid hexahydrates of cadmium(II) and mercury(II) perchlorates were prepared as previously described.[8] The hydrated zinc perchlorate was obtained from GFS Chemicals. For the acidified solutions, perchloric acid was added to 0.05 mol dm^{-3}. The cation concentrations were determined by acid–base titrations of the eluate from a Dowex 50W resin and by standard EDTA titrations.[9] Partial deuteration (8.0 mol % HDO) was obtained by adding D_2O (99.98%) to the solution by weight. Three parallel preparations were made which differed by less than 0.5% in OD peak absorbance. Partial deuteration of the $Cd(ClO_4)_2 \cdot 6L_2O$ and $Hg(ClO_4)_2 \cdot 6L_2O$ compounds was obtained by recrystallization from an aqueous solution with an H/D ratio of 0.975.

Measurements. The infrared spectra were recorded at 8-cm^{-1} resolution with a Digilab FTS-45 spectrometer on line with a Digilab 2360-SPC computer. The solutions were contained between CaF_2 windows and a Teflon spacer (path length 49.8 ± 0.3 μm determined interferometrically) in a cell thermostated to 20.0 °C by circulating water in its metal frame.

Method. In the infrared spectroscopic method, the OD stretching vibration spectrum of the isotopically isolated, ion-perturbed HDO

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