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$Rh^{II}-Rh^{II}$ Bond Homolysis in a $[(salen)Rh^{II}]_2$ Derivative: Thermodynamic, Kinetic, and Reactivity Studies

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Introduction

Low-spin d^7 complexes of rhodium(II) with multidentate nitrogen and oxygen donor ligands have a wide array of substrate reactions relevant to organometallic transformations.[1−7] Rhodium(II) complexes usually occur as M−M-bonded complexes, but most reactions of these complexes occur through monomeric metalloradicals.[8−10] In the course of evaluating the reactivity of a rhodium(II) salen derivative, ([*N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylaldiminato)]rhodium(II) dimer, $[(ttbs)Rh]_2$ (**1**)),[7] we observed that $[(ttbs)Rh]_2$ (**1**) reacts faster and has a broader range of substrate reactions in benzene than in tetrahydrofuran. As an example, **1** in benzene rapidly reacts with ethene to form $(ttbs)Rh-CH_2CH_2-Rh(ttbs)$ but **1** in THF fails to react with ethene to an observable extent.[11] Proton NMR shift and line shape measurements indicate that the homolytic dissociation of **1** is qualitatively much greater in toluene than in THF and are used quantitatively to determine thermodynamic and activation parameters for the dissociation of the diamagnetic dimer (**1**) into the paramagnetic ($s = {}^1/_2$) monomer of $(ttbs)Rh^{II}$ (**2**) in toluene.

Experimental Section

Materials. All deuterated solvents (benzene-d_6, toluene-d_8, and THF-d_8, Aldrich) were degassed by employing three freeze−pump−thaw cycles and then dried by refluxing over sodium and benzophenone. Other solvents and reagents (Aldrich or Strem) were used as purchased without further purification, unless otherwise noted. Samples of $[(ttbs)Rh]_2$ were weighed and put into vacuum-adapted NMR tubes, and benzene-d_6, toluene-d_8, or THF-d_8 solvent was vacuum-transferred into the volumetric NMR tubes. The NMR sample tubes were degassed by three freeze−pump−thaw cycles, submerged in liquid nitrogen to freeze their contents, and flame-sealed in vacuo.

^1H NMR Experimental Procedures. NMR experiments were performed on Bruker 500 MHz AMX-500 and 200 MHz AC-200 nuclear magnetic resonance spectrometers equipped with Bruker VT-1000 temperature control units. The temperature inside the NMR sample tube was calibrated (±0.1 K) using the difference in chemical shifts of ethylene glycol or methanol standards.[12] Samples were placed in the NMR spectrometer, and the temperature was equilibrated for 45 min before spectra were acquired. Spectra were calibrated against the toluene-d_8 methyl resonance ($\delta(CH_3) = 2.09$ ppm; $T = 296$ K) and corrected for the temperature dependence of the toluene chemical shifts. The chemical shifts and line widths for the proton resonances of $[(ttbs)Rh]_2$ were recorded for a series of temperatures in the range 190−383 K. The chemical shifts (δ_{obs}) and line shapes of the ttbs proton resonances were found to change reversibly as the temperature was sequentially raised and lowered.

The line widths ($\Delta\nu_{1/2}$) of the CH_2 resonances at different temperatures were obtained by using the gNMR[13] simulation program to calculate the line shapes as a function of line width for comparison with the observed line shapes ($J_{AB} = J_{A'B'} = -12$ Hz; $J_{AA'} = J_{BB'} = 6.8$ Hz; $\delta_A = 4.6$; $\delta_B = 2.70$). The increase in the line widths ($\Delta\nu_{1/2}$) is ascribed to the lifetime broadening that results from dissociation of the diamagnetic dimer into the paramagnetic monomer, $(ttbs)Rh^{II}$. The temperature dependences of the line broadenings of the two methylene CH_2 peaks at 4.6 and 2.7 ppm were used to obtain the activation parameters for the dissociation of $[(ttbs)Rh]_2$ into its monomer.

Preparation of $(ttbs)H_2$. The free ligand *N*,*N*′-Ethylenebis(3,5-di-*tert*-butylsalicylaldimine), $ttbsH_2$, was synthesized by the Schiff-base condensation reaction of 1 molar equiv of ethylenediamine with 2 molar equiv of 3,5-di-*tert*-butylsalicylaldehyde (3,5-di-*tert*-butyl-2-hydroxybenzaldehyde) in ethanol. The aldehyde was synthesized from 2,4-di-*tert*-butylphenol (Aldrich) using the method described by Karhu.[14] ^1H NMR (C_6D_6): δ 14.02 (s, 2H, −OH), 7.78 (s, 2H, H−C═N), 7.55 (d, 2H, phenyl), 6.96 (d, 2H, phenyl, $^4J_{H-H} = 2.3$ Hz), 3.26 (s, 4H, $-CH_2CH_2-$), 1.63 (s, 18H, *t*-bu), 1.30 (s, 18H, *t*-Bu). IR (Nujol mull): $\nu_{C=N}$ 1630 cm^{-1}. FAB MS: *m*/*e* 493 (calc 493.38). Anal. Calc for $C_{32}H_{48}N_2O_2$: C, 78.00; H, 9.82; N, 5.69. Found: C, 78.36; H, 9.98; N, 5.76.

Preparation of $[(ttbs)Rh]_2$. The free ligand $H_2(ttbs)$ (0.556 g, 1.13 mmol), was dissolved in ethanol with heating under nitrogen, followed by the addition of an ethanol solution of sodium ethoxide (2.26 mmol). After 15 min, a slurry of the rhodium acetate dimer, $Rh_2(OCOCH_3)_4$ (0.25 g, 0.566 mmol), was added to the reaction flask, and the reaction mixture was maintained at 60 °C for 6 h. The product, $[(ttbs)Rh]_2$, appeared as a maroon precipitate and was collected and stored under nitrogen (isolated yield 65%). ^1H NMR (toluene-d_8, 230 K): δ 7.74 (br, 4H, phenyl), 6.95 (br, 4H, H−C═N), 6.83 (br, 4H, phenyl), 4.65 (m, 4H, $-CH_2CH_2-$), 2.64 (m, 4H, $-CH_2CH_2-$), 1.99 (s, 36H, *t*-Bu), 1.49 (s, 36H, *t*-Bu). ^1H NMR (THF-d_8, 300 K): δ 7.73 (d, 4H, H−C═N−Rh, $^3J_{^{103}Rh-H} = 1.5$ Hz), 7.24 (d, 4H, phenyl, $^4J_{H-H} = 2.4$ Hz), 6.89 (d, 4H, phenyl, $^4J_{H-H} = 2.4$ Hz), 3.42 (m, 4H, $-CH_2CH_2-$), 2.99 (m, 4H, $-CH_2CH_2-$), 1.31 (s, 36H, t-bu), 1.27 (s, 36H, *t*-Bu). FAB MS: *m*/*e* 1186 (calc 1186.5). Anal. Calc for $Rh_2C_{64}H_{92}N_4O_4$: C, 64.80; H, 7.82; N, 4.72. Found: C, 65.08; H, 7.92; N, 4.65.

Results and Discussion

^1H NMR Spectra Resulting from Dissolution of $[(ttbs)Rh]_2$ in C_6D_6, $C_6D_5CD_3$, and THF-d_8. The ^1H NMR spectra for $[(ttbs)Rh]_2$ (**1**) in C_6D_6 and $C_6D_5CD_3$ at room temperature are broadened in a manner that suggests the presence of paramagnetic monomers, but at low temperatures in $C_6D_5CD_3$

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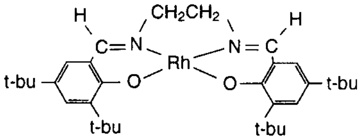

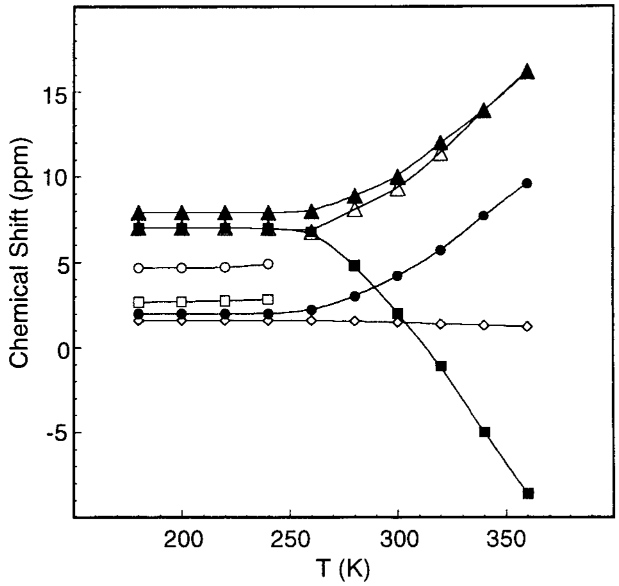

Figure 1. Temperature dependences of the observed ^1H NMR chemical shifts for a solution of $[(ttbs)Rh]_2$ with an initial concentration of 4.60 × 10^{-3} M in toluene-d_8 (180−360 K): (△) phenyl 4-H; (▲) phenyl 6-H; (□) CH_2; (○) CH_2; (●) 3-*tert*-butyl; (■) imine; (◇) 5-*tert*-butyl.

or at ambient temperature in THF, narrow ^1H NMR spectra are observed for **1**. Variable-temperature NMR studies of (ttbs)Rh in toluene-d_8 solution were performed over the temperature range 183−360K, and the temperature dependences for the chemical shifts of all the proton resonances are presented in Figure 1. At temperatures below 220 K, (ttbs)Rh exists exclusively as a diamagnetic dimer, as evidenced by the narrow ^1H NMR peaks that have negligible chemical shift changes as the temperature is lowered further.

The ^1H NMR resonances of **1** begin to broaden at ∼220 K and continue to broaden without large chemical shift changes in the range 220−260 K. The line shape changes that occur without large differences in the chemical shifts are ascribed to lifetime broadening associated with the rate of homolysis of the diamagnetic dimer (**1**) to form the paramagnetic monomer, $(ttbs)Rh^{II}$ (**2**) (eq 1). As the temperature is elevated from 260

$$[(ttbs)Rh]_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} 2(ttbs)Rh \tag{1}$$

K, larger chemical shift changes begin to occur, which is ascribed to the formation of substantial quantities of the paramagnetic monomer (**2**) that rapidly interchange with the diamagnetic dimer (**1**). The mole-fraction-averaged shift positions in the temperature range 290−370 K reflect the equilibrium distribution of **1** and **2** in limiting fast exchange.

When **1** is dissolved in THF-d_8, sharp ^1H NMR spectra of the diamagnetic dimer (**1**) are observed throughout the temperature range (296−383 K). The absence of significant changes in the chemical shift and line width with temperature indicates that the dissociation of **1** into **2** is much less complete and slower in THF than in benzene or toluene.

Table 1. Thermodynamic Parameters for the Dissociation of $[(ttbs)Rh]_2$ into the Monomer in Toluene, Derived from the Temperature Dependence of the Proton Chemical Shifts Using Eq 2

proton obsd	$\Delta H_1°$ (kcal mol^{-1})	$\Delta S_1°$ (cal mol^{-1} K^{-1})	C_M (ppm K)
3-*tert*-butyl	13.2 ± 0.5	26.3 ± 1.2	2783 ± 120
phenyl 4-H	12.9 ± 0.6	25.3 ± 1.1	3626 ± 95
phenyl 6-H	13.8 ± 0.6	27.9 ± 1.8	2977 ± 110
imine	13.6 ± 0.5	28.7 ± 1.4	−7883 ± 195

Thermodynamic Parameters for the Homolytic Dissociation of $[(ttbs)Rh]_2$ Determined from ^1H NMR Chemical Shifts. Thermodynamic parameters for the dissociation of $[(ttbs)Rh]_2$ (**1**) into the paramagnetic monomer (ttbs)Rh (**2**) (eq 1) were obtained from the analysis of the temperature dependences of the ^1H NMR chemical shifts in the limiting fast exchange region (280−380 K). Equation 2 gives the relationship

$$\delta_{\mathrm{obs}} = \left[\delta_D + \frac{\delta_D}{8[D]_i} e^{-\Delta H°/RT+\Delta S°/R} - \frac{\delta_D}{8[D]_i}\left(16[D]_i e^{-\delta H°/RT+\Delta S°/R} + e^{-2(\Delta H°/RT+\Delta S°/R)}\right)^{1/2}\right] + \left[-\frac{e^{-\Delta H°/RT+\Delta S°/R}}{8[D]_i} + \frac{1}{8[D]_i}\left(16[D]_i e^{-\Delta H°/RT+\Delta S°/R} + e^{-2(\Delta H°/RT+\Delta S°/R)}\right)^{1/2}\right](C_M T^{-1} + \delta_m) \tag{2}$$

between the fast-exchange-averaged chemical shift (δ_{obs}) at temperature T in terms of the chemical shifts for the diamagnetic dimer (δ_D), the Curie paramagnetic monomer (δ_M) ($\delta_M = C_M T^{-1} + \delta_m$, where δ_m is the chemical shift for M when $T^{-1} = 0$), the initial concentration of the dimer ($[D]_i$), and the thermodynamic parameters ($\Delta H°$, $\Delta S°$) for dissociation of D into 2 M.[15,16] Nonlinear-least-squares fitting of the measured δ_{obs} values for a series of temperatures T to eq 2 was used to determine values for $\Delta H°$, $\Delta S°$, and the slope of the paramagnetic shift (C_M).[15,16] Four ^1H NMR resonances (3-*tert*-butyl, phenyl 4-H, phenyl 6-H, and imine) were used in determining four independent sets of thermodynamic values for the dissociation of $[(ttbs)Rh]_2$ (Table 1, Figure 2). Excellent agreement between measurements from the four different types of protons ($\Delta H_1° = 13.3 \pm 0.5$ kcal mol^{-1}; $\Delta S_1° = 26.5 \pm 1.4$ cal K^{-1} mol^{-1}) provides confidence in this methodology to obtain thermodynamic data for the M−M bond dissociation process.

Activation Parameters for the Dissociation of $[(ttbs)Rh]_2$ Determined from ^1H NMR Line Broadening. The ^1H NMR spectrum of $[(ttbs)Rh]_2$ (**1**) in toluene-d_8 exhibits line broadening without large shifts as the temperature is increased in the range 220−260 K. The line shapes for the CH_2 resonances were simulated for a series of temperatures using the gNMR program.[13] The origin of the change in the line width parameter needed to simulate a line shape is assigned to lifetime broadening associated with dissociation of the diamagnetic dimer **1** into the paramagnetic monomer **2**.

The expression that describes this exchange case is given by eq 3, which reduces to $T_{2(ex)}{}^{-1} = \tau_d{}^{-1}$ for nuclei in paramagnetic species where the mean lifetime (τ_p) is long and the electron−

$$\pi\Delta\nu_{1/2(ex)} = T_{2(ex)}{}^{-1} = \tau_d{}^{-1}[(A\tau_p/2)^2][1 + (A\tau_p/2)^2]^{-1} \tag{3}$$

nuclear coupling constant (A) is sufficiently large that $(A\tau_p/2)^2$

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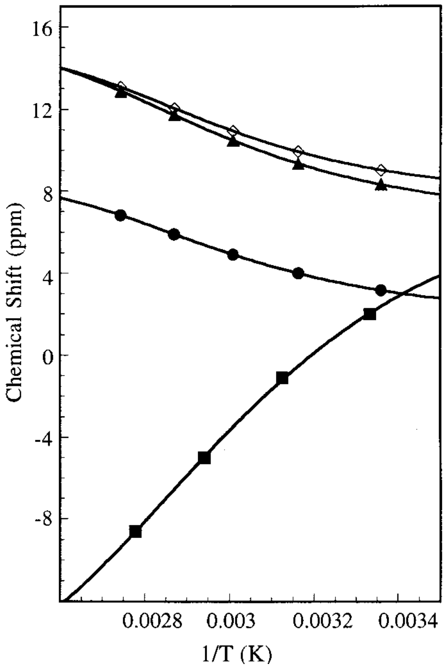

Figure 2. Observed ^{1}H NMR chemical shifts for a 4.60 × 10^{-3} M solution of $[(ttbs)Rh]_2$ in toluene-d_8 for a series of temperatures: (●) 3-tert-butyl; (■) imine; (▲) phenyl 4-H; (◇) phenyl 6-H. Solid lines was calculated from evaluation of eq 1 using the best fit values of $\Delta H_1°$ and $\Delta S_1°$ for the dissociation of **1** and the slope (C_M) of the paramagnetic shift for the observed protons in **2**.

$\gg$ 1.[17−20] The mean lifetime for the diamagnetic species (τ_d) yields the rate constant ($\tau_d^{-1} = k_1$) for unimolecular bond homolysis events that produce paramagnetic species with efficient nuclear relaxation ($(A\tau_p/2)^2 \gg 1$). Activation parameters for the dissociation of **1** ($\Delta H_1^\ddagger = 16 \pm 1$ kcal mol^{-1}; $\Delta S_1^\ddagger = 22 \pm 5$ cal K^{-1} mol^{-1}) were obtained from transition state theory (Figure 3). The activation enthalpy ($\Delta H_1^\ddagger$) is 2−3 kcal larger than $\Delta H_1°$, which is in the range frequently observed for bond homolysis processes.[19−21]

The thermodynamic and activation parameters are used to derive the equilibrium constant (K_1) and rate constant (k_1) for homolytic dissociation of $[(ttbs)Rh]_2$ in toluene at 298 K (K_1(298 K) = 1.1 × 10^{-4}; k_1(298 K) = 6.7 × 10^5 s^{-1}). A second-order rate constant for bimolecular recombination of (ttbs)Rh• is derived from K_1 and k_1 (k_{-1} (298 K)= 6 × 10^9 L mol^{-1} s^{-1}).

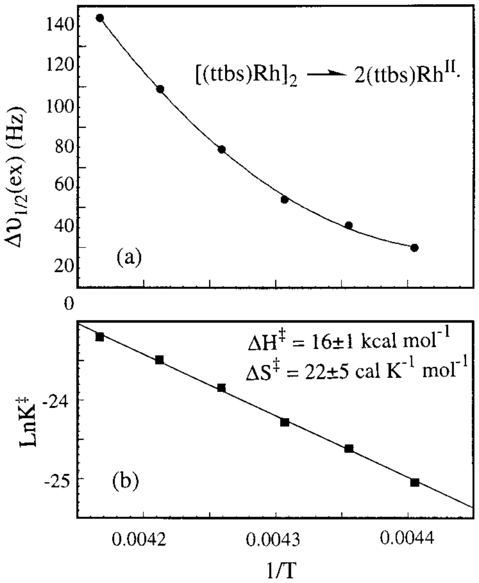

Figure 3. (a) Temperature dependence of $\Delta\nu_{1/2(ex)}$ for the CH_2 resonance of $[(ttbs)Rh]_2$ in toluene-d_8. (b) Determination of the apparent activation parameters for bond homolysis of $[(ttbs)Rh]_2$ from ^{1}H NMR line broadening in toluene-d_8.

The value for k_{-1} (298 K) approaches the diffusion-controlled limit and is in the range observed for bimolecular radical recombination.[20−22]

The absence of ^{1}H NMR shifts or line broadening for $[(ttbs)Rh]_2$ in THF (295−383 K) results in a lower limit of ~20 kcal mol^{-1} for the enthalpy of the homolysis in THF, which contrasts with the measured dissociation enthalpy of 13.3 ± 0.5 kcal mol^{-1} for **1** in toluene. This counterintuitive observation can be rationalized as resulting from the combined effects of a $d_{xz}{}^2 d_{xy}{}^2 d_{z^2}{}^2 d_{yz}{}^1$ ground electronic configuration for $(ttbs)Rh^{II}$ in a noncoordinating medium like toluene[1] and the weak donor properties of THF. Dimerization of $(ttbs)Rh^{II}$• in toluene occurs either through formation a $d_{yz}-d_{yz}$ π bond or through an electronic reorganization to the $d_{xz}{}^2 d_{xy}{}^2 d_{yz}{}^2 d_{z^2}{}^1$ excited electronic configuration and formation of a standard $d_{z^2}-d_{z^2}$ $Rh^{II}-Rh^{II}$ σ bond. Interaction of the THF donor molecule with the $(ttbs)Rh^{II}$ metal center is enhanced by moving an electron out of the filled d_{z^2} orbital and producing an electronic configuration with the odd electron in the d_{z^2} orbital, which also promotes formation of the stronger $d_{z^2}-d_{z^2}$ σ bond. The increased enthalpy of dissociation for $[(ttps)Rh]_2$ in THF compared to toluence also indicates that THF binds more strongly with the $Rh^{II}-Rh^{II}$-bonded dimer than with the paramagnetic monomer.

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