## Reactivity Patterns of $H_2$ and CO with a Rhodium(II) Salen Derivative: Formation of Hydride, Formyl, and **Dimetal Ketone Complexes and Rhodium Reduction**

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Summary: A benzene soluble dimeric rhodium(II) salen derivative, [(ttbs)Rh]<sub>2</sub>, with a weak Rh-Rh bond (13 kcal  $mol^{-1}$ ) reacts with  $H_2$  and CO to produce hydride, metalloketone, and formyl complexes, but reaction of (ttbs)Rh-H with CO also induces migration of  $H^+$  from rhodium to the salen ligand to form a rhodium(I) dicarbonyl complex, (Httbs)Rh(CO)<sub>2</sub>.

Rhodium(II) porphyrin complexes manifest an unusually diverse reaction chemistry with H<sub>2</sub>, CO, and hydrocarbons which include formation of metalloformyl complexes,<sup>1</sup> CO reductive coupling,<sup>1a,2</sup> and methane activation.<sup>3</sup> Our objectives in this area have encompassed defining the scope of rhodium(II) complexes that can accomplish these thermodynamically difficult substrate reactions and extending this chemistry to flexible nonmacrocyclic ligand arrays which have the potential to manifest reaction pathways more versatile than those available to rigid tetradentate macrocyclic complexes. Several rhodium(II) salen derivatives that dimerize by Rh<sup>II</sup>—Rh<sup>II</sup> bonding have been previously reported<sup>4</sup> and would be good candidates for investigation; however the solubility characteristics for these complexes have precluded evaluation of substrate reactions in weakly interacting hydrocarbon solvents. This article reports on a benzene soluble rhodium(II) salen derivative, [N,N'ethylenebis(3,5-di-tert-butylsalicylaldiminato)]rhodium(II) dimer, [(ttbs)Rh]2 (1), thermodynamics for dissociation of 1 in benzene, and the reactivity patterns of 1 with a series of substrates including  $H_2$ , CO, CH<sub>2</sub>- $CH_2$ , and  $CH_4$ .

Toluene solutions of  $[(ttbs)Rh]_2$ , 1,<sup>5</sup> have relatively narrow <sup>1</sup>H NMR spectra associated with a diamagnetic dimer at temperatures below 233 K, which broaden and shift as the temperature is elevated (243-393 K), indicative of dissociation to form a paramagnetic monomer, (ttbs)Rh<sup>II</sup> (2) (eq 1). The limiting fast exchange

$$[(ttbs)Rh]_2 \rightleftharpoons 2(ttbs)Rh \tag{1}$$

averaged chemical shifts for the <sup>1</sup>H NMR resonances were used in determining thermodynamic values for the dissociation of 1 in benzene ( $\Delta H_1^{\circ} = 13.4 \pm 0.4$  kcal  $mol^{-1}$ ,  $\Delta S_1^{\circ} = 26.3 \pm 1.3$  cal K<sup>-1</sup> mol<sup>-1</sup>).<sup>6</sup> EPR param-



Figure 1. (a) EPR spectrum of (ttbs)Rh<sup>II</sup> in a powder sample of  $[(ttbs)Rh]_2$  (90 K):  $g_1 = 3.246$ ,  $g_2 = 1.833$ ,  $g_3 = 1.755$ . (b) EPR spectrum of (ttbs)RhPPh<sub>3</sub> (toluene, 90 K):  $g_1 = 2.209, A^{(31}P)_{g_1} = 835 \text{ MHz}; g_2 = 2.118, A^{(31}P)_{g_2} = 835 \text{ MHz}; g_3 = 1.991, A^{(31}P)_{g_3} = 975 \text{ MHz}, A^{(103}Rh)_{g_3} = 49 \text{ MHz}.$ 

eters from spectra of powder samples of 1 (90 K) ( $g_1 =$  $3.246, g_2 = 1.833, g_3 = 1.755$ ) (Figure 1) are ascribed to the trapped (ttbs)Rh<sup>II</sup> monomer and are used in placing the unpaired electron in a  $d\pi (d_{yz})^{7,8}$  orbital like that

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<sup>(5) (</sup>a) The free ligand, (ttbs)H<sub>2</sub>, is synthesized by the Schiff-base condensation of ethylenediamine with 3,5-di-*tert*-butylsalicylaldehyde in ethanol. <sup>1</sup>H NMR of (ttbs)H<sub>2</sub> (C<sub>6</sub>D<sub>6</sub>):  $\delta$  14.02 (s, 2H, -OH), 7.78 (s, In extranol. -In TVMK of (tD8) $\mu_2$  (C<sub>6</sub>D<sub>6</sub>):  $\delta$  14.02 (8, 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<sub>2</sub>-), 1.63 (s, 18H, t-Bu), 1.30 (s, 18H, t-Bu). IR (Nujol mull),  $\nu_{C=N}$ : 1630 cm<sup>-1</sup>. LR FABMS: m/e 493 (calc 493.38). Anal. Calc for C<sub>32</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.00; H, 9.82; N, 5.69. Found: C, 78.36; Huai Calt by 5.76 (b) [(ttbs)Rh]2, 1, is prepared by gently refluxing the rhodium acetate dimer and the free ligand, (ttbs)H2, with sodium ethoxide as the base in ehanol for 6 h under nitrogen gas. Photolysis of (ttbs)RhCH<sub>3</sub> ( $\lambda$  < 350 nm) in benzene is an alternate method to obtain 1. <sup>1</sup>H NMR of 1 (toluene-d<sub>8</sub>, 230 K):  $\delta$  7.74 (br, 4H, phenyl), 6.95 (br, 4H, H-C=N), 6.83 (br, 4H, phenyl), 4.65 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>)

<sup>b. 50 (bf, 4H, H<sup>-</sup>C-H<sub>2</sub>(H<sub>2</sub>), 0.50 (bf, 4H, phenyl), 4.00 (H, 4H, CH<sub>2</sub>CH<sub>2</sub>), 2.64 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 1.99 (s, 36H, t-Bu), 1.49 (s, 36H, t-Bu). FAB
MS: m/e 1186 (calc 1186.5).
(6) The <sup>1</sup>H NMR peak positions at a fixed temperature in the range 295-370 K result from the limiting fast exchange mole fraction averaged positions of [(ttbs)Rh]<sub>2</sub> and the paramagnetic monomer, (ttbs)</sup> Rh. The temperature dependence of the shift positions results from both the temperature dependence of  $K_1$  and the contact shift of (ttbs)-Rh<sup>II</sup>. An expression derived for this case assuming Curie behavior uses the observed <sup>1</sup>H NMR shifts at a series of temperatures to give the best fit  $\Delta H_1^{\circ}$ ,  $\Delta S_1^{\circ}$ , and the slope of the contact shift by nonlinear least squares curve fitting. Three sets of <sup>1</sup>H NMR resonances were independently used in solving for  $\Delta H_1^{\circ}(12.94-13.77 \text{ kcal mol}^{-1})$ ;  $\Delta S_1^{\circ}(25.26-27.93 \text{ cal } \text{K}^{-1} \text{ mol}^{-1})$ .

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## Communications

previously reported for (salen)Co<sup>II</sup>,<sup>8</sup> but different from rhodium(II) porphyrins where the odd electron is in a  $d\sigma(d_{z^2})$  orbital.<sup>9</sup> Donor molecules like PPh<sub>3</sub> elevate the  $d_{z^2}$  of (ttbs)Rh^II above the  $d_{yz}$  and yield EPR parameters associated with the  $(d_{xy}d_{xz}d_{yz})^6(d_{z^2})^1$  ground configuration ((ttbs)Rh PPh<sub>3</sub> (toluene, 90 K):  $g_1 = 2.209, A({}^{31}P)_{g_1} =$ 835 MHz;  $g_2 = 2.118$ ,  $A({}^{31}P)_{g_2} = 835$  MHz;  $g_3 = 1.991$ ,  $A({}^{31}P)_{g_3} = 975$  MHz,  $A({}^{103}Rh)_{g_3} = 49$  MHz) (Figure 1).

Benzene solutions of 1 react with H<sub>2</sub>, CO, and ethene to form (ttbs)Rh-H (3), (ttbs)Rh-C(O)-Rh(ttbs) (4), and (ttbs)Rh-CH<sub>2</sub>CH<sub>2</sub>-Rh(ttbs) (5),<sup>10 a-c</sup> respectively (Figure 2) in a manner that parallels the reactivity of rhodium(II) porphyrins<sup>11-13</sup> (eqs 2-4), but 1 fails to

> $[(ttbs)Rh]_2 + H_2 = 2(ttbs)Rh-H$ (2)

 $[(ttbs)Rh]_2 + CO \rightleftharpoons (ttbs)Rh - C(O) - Rh(ttbs)$  (3)

$$\begin{array}{l} [(ttbs)Rh]_2 + CH_2 = CH_2 \rightleftharpoons \\ (ttbs)Rh - CH_2CH_2 - Rh(ttbs) \ (4) \end{array}$$

react to an observable extent with methane ( $P_{CH_4} = 0.9$ atm, T = 298 K) or neat toluene which are prominent

**1989**, *111*, 5010. (10) (a) <sup>1</sup>H NMR of **3** (C<sub>6</sub>D<sub>6</sub>, P<sub>H2</sub> = 0.8 atm, *T* = 298 K):  $\delta$  7.82 (s, 2H, phenyl), 7.15 (s, 2H, H–C=N), 7.08 (s, 2H, phenyl), 2.79 (br, 4H,  $-CH_2CH_2-$ ), 1.99 (s, 18H, t-Bu), 1.45 (s, 18H, t-Bu), -25.2 (br, 1H, Rh–H). (b) <sup>1</sup>H NMR of 4 (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.69 (d, 4H, phenyl, <sup>4</sup>J<sub>H–H</sub> = 2.4 Hz), 7.02 (d, 4H, phenyl, <sup>4</sup>J<sub>H–H</sub> = 2.4 Hz), 6.98 (d, 4H, H–C=N, <sup>3</sup>J<sub>Rh–H</sub> = 2.2 Hz), 3.75 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 2.55 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 1.85 (s, 36H, t-Bu), 1.39 (s, 36H, t-Bu). <sup>13</sup>C NMR (<sup>13</sup>CO derivative, C<sub>6</sub>D<sub>6</sub>):  $\delta$  144.5 (t, <sup>1</sup>J<sub>108Rh-13C</sub> = 46 Hz). (c) <sup>1</sup>H NMR of 5 (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.63 (d, 4H, phenyl<sup>4</sup>J<sub>4</sub>, m = 2.4 Hz), 7.28 (d, 4H, H–C=N <sup>3</sup>J<sub>Rn</sub> = 1.8 Hz), 6.97 bhenyl,  $J_{H-H} = 2.4$  Hz), 7.28 (d, 4H, H-C=N,  $J_{Rh-H} = 1.8$  Hz), 6.97 (d, 4H, phenyl,  $J_{H-H} = 2.4$  Hz), 2.50 (br, 8H,  $-CH_2CH_2$ ), 1.68 (s, 36H, t-Bu), 1.46 (s, 36H, t-Bu), 2.62 (br, 4H, Rh-CH<sub>2</sub>-CH<sub>2</sub>-Rh). <sup>13</sup>C NMR (<sup>13</sup>CH<sub>2</sub><sup>13</sup>CH<sub>2</sub> derivative of 5, parameters that simulate the <sup>1</sup>H decoupled <sup>13</sup>C NMR spectrum):  $\delta 34.58$  (AA'XX';  $J_{AA'} = {}^{1}J_{C-C} = 34.40$  Hz,  $J_{XX'} = {}^{3}J_{Rh-Rh} = 0$  Hz,  $J_{AX} = {}^{1}J_{Rh-C} = 32.30$  Hz,  $J_{AX'} = {}^{2}J_{Rh-C} = -7.06$  Hz).  ${}^{3}J_{\text{Rh}-\text{Rh}} = 0$  Hz;  $J_{AX} = {}^{1}J_{\text{Rh}-\text{C}} = 32.30$  Hz;  $J_{AX} = {}^{2}J_{\text{Rh}-\text{C}} = -7.06$  Hz). FAB MS: 594, (ttbs)Rh fragment (calc for (ttbs)Rh-CH<sub>2</sub>CH<sub>2</sub>-Rh(ttbs) 1211.5). (d) <sup>1</sup>H NMR of 6 (C<sub>6</sub>D<sub>6</sub>):  $\delta$  13.67 (s, 1H, -OH), 7.69 (s, 1H, H-C=N), 7.66 (d, 1H, phenyl,  ${}^{4}J_{\text{H}-\text{H}} = 2.5$  Hz), 7.56 (d of d, 1H, H-C=N-Rh,  ${}^{3}J_{\text{Rh}-\text{H}} = 1.7$  Hz,  ${}^{4}J_{^{13}\text{C}-\text{H}} = 3.6$  Hz), 7.52 (d, 1H, phenyl,  ${}^{4}J_{\text{H}-\text{H}} = 2.5$  Hz), 6.98 (d, 1H, phenyl,  ${}^{4}J_{\text{H}-\text{H}} = 2.5$  Hz), 6.80 (d, 1H, phenyl,  ${}^{4}J_{\text{H}-\text{H}} = 2.5$  Hz), 3.58 (t, 2H,  $-CH_{2}$ -CH<sub>2</sub>-,  ${}^{3}J_{\text{H}-\text{H}} = 5.7$  Hz), 3.45 (t, 2H,  $-CH_{2}$ -CH<sub>2</sub>-,  ${}^{3}J_{\text{H}-\text{H}} = 5.7$  Hz), 1.60 (s, 9H, t-Bu), 1.30 (s, 9H, t-Bu), 1.24 (s, 9H, t-Bu). <sup>13</sup>C NMR (<sup>1</sup>H decoupled CaDe):  $\delta$  184 66 (d of d -CO trans to H-C=N. <sup>13</sup>COMR (<sup>1</sup>H decoupled)  $\begin{array}{l} C_6 D_6): \ \delta \ 184.66 \ (d \ of \ d, \ -CO \ trans \ to \ H-C=N, \ ^1J^{109}_{Rh^{-13}C} = 68 \ Hz, \\ \mathcal{J}^{19}_{C^{-13}C} = 10 \ Hz), \ 187.75 \ (d \ of \ d, \ -CO \ cis \ to \ H-C=N, \ ^1J^{109}_{Rh^{-13}C} = 68 \\ Hz, \ ^2J^{13}_{C^{-13}C} = 10 \ Hz), \ ^{13}C \ NMR \ (^{1}H \ coupled, \ C_6 D_6): \ as \ above, \ but \end{array}$ additionally a four bond coupling from the innie proton  $^{4}J_{1H-18C} = 3.6$ Hz is observed on the trans carbonyl ( $\delta = 184.66$  resonance). FAB MS: m/e 651 (calc m/e 650.26). (e) <sup>1</sup>H NMR of 7 (C<sub>6</sub>D<sub>6</sub>):  $\delta$  11.46 (d of d, 1H,  $-^{13}$ CHO,  $^{1}J_{13}_{C-H} = 197.8$  Hz.  $^{2}J_{108}_{Bh-H} = 3.5$  Hz), 7.80 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.3$  Hz), 7.56 (d, 2H, H-C=N,  $^{3}J_{108}_{Bh-H} = 2.2$  Hz) 6.98 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.3$  Hz), 3.09 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 2.47 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 1.91 (s, 18H, t-Bu), 1.41 (s, 18H, t-Bu),  $^{13}$ C NMR:  $\delta$  214.6 (d,  $^{1}J_{108}_{Rh-^{13}C} = 33.7$ Hz, Rh $^{-13}$ CHO). (f)  $^{14}$  NMR of 8 (C<sub>6</sub>D<sub>8</sub>):  $\delta$  7.78 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.5$  Hz), 7.36 (d, 2H, H-C=N,  $^{3}J_{108}_{Rh-H}$ = 1.8 Hz), 7.01 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.5$  Hz), 3.51 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 2.86 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>-), 1.96 (s, 18H, t-Bu), 1.38 (s, 18H, t-Bu), 3.95 (d of q,  $^{13}$ C(O)OCH<sub>2</sub>CH<sub>3</sub>,  $^{3}J_{H-H} = 7.3$  Hz,  $^{3}J_{13}_{C-R} = 2.9$  Hz), 0.71 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>,  $^{3}J_{H-H} = 7.3$  Hz). (f) 68 ( $^{2}J_{108}_{Rh-13C} =$ 48 Hz). FAB MS (m/e): 666 (calc 666.29). (g) <sup>1</sup>H NMR of 9 (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 7.76 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.0$  Hz), 7.45 (2H, H-C=N), 7.05 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.0$  Hz), 2.96 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>-), 2.73 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 1.91 (s, 18H, t-Bu), 1.42 (s, 18H, t-Bu), 0.5 -1.5 (m, n-C4\_{5}). HR FAB MS (m/e): 884.3762 (calc 884.3749). (h) (ttbs)Rh-CH<sub>3</sub>: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.80 (d, 2H, phenyl,  $^{4}J_{H-H} = 2.4$  Hz), 7.28 (d, 2H,  $^{4}J_{H-C} = 7.0$  M $^{3}J_{H-H} = 7.0$  Hz) 7.05 (d) additionally a four bond coupling from the imine proton  ${}^{4}J_{^{1}H^{-13}C} = 3.6$ NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.80 (d, 2H, phenyl,  ${}^{4}J_{H-H} = 2.4$  Hz), 7.28 (d, 2H, H-C=N,  ${}^{3}J_{\text{Rh}-\text{H}} = 2.0$  Hz), 7.05 (d, 2H, phenyl,  ${}^{4}J_{\text{H}-\text{H}} = 2.4$  Hz), 2.45 (br, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-), 1.96 (s, 18H, t-Bu), 1.44 (s, 18H, t-Bu), 1.68 (d, 3H, Rh-CH<sub>3</sub>,  ${}^{2}J_{Rh-H} = 2.8$  Hz). FAB MS: m/e 609 (calculated m/e608.3)

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Figure 2. (a) Proton decoupled <sup>13</sup>C NMR of the formyl group in the (ttbs)Rh-13CHO complex (C<sub>6</sub>D<sub>6</sub>): ( $\delta$ (13C) 214.6,  ${}^{1}J_{103}_{Rh}$  = 33.7 Hz). Insert: <sup>1</sup>H NMR of the formyl hydrogen ( $\delta$ (<sup>1</sup>H) 11.46, <sup>1</sup> $J_{^{13}C^{-1}H} = 197.8$  Hz, <sup>2</sup> $J_{^{103}Rh-H} = 3.5$ Hz). (b) <sup>13</sup>C NMR of the carbonyl group in (ttbs)Rh-<sup>13</sup>C-(O)-Rh(ttbs) (C<sub>6</sub>D<sub>6</sub>) ( $\delta$  144.5,  ${}^{1}J_{103}_{Rh}-{}^{13}C$  = 46 Hz). (c) <sup>1</sup>H decoupled <sup>13</sup>C NMR of the ethylene bridge in the (ttbs)Rh- $^{13}CH_2^{13}CH_2-Rh(ttbs)$  complex  $(C_6D_6)$  (parameters that simulate the observed  $^{1}H$  decoupled  $^{13}C$  NMR):  $\delta$  34.58  $(AA'XX'; {}^{1}J_{1^{3}C-1^{3}C} = 34.40 \text{ Hz}, {}^{3}J_{Rh-Rh} = 0 \text{ Hz}, {}^{1}J_{1^{3}Rh-1^{3}C} =$ 32.30 Hz,  ${}^{2}J_{103}{}_{Rh}-{}^{13}{}_{C} = -7.06$  Hz).

reactions of rhodium porphyrins.<sup>3</sup> An unusual feature in the reactivity pattern of **3** is that CO ( $P_{CO} = 0.8$  atm) reacts rapidly and quantitatively with 3 to reduce the rhodium center  $(Rh(III) \rightarrow Rh(I))$  by migration of a proton from rhodium to a phenolate oxygen to form  $(Httbs)Rh(CO)_2$  (6) (eq 5).<sup>10d</sup> Reaction 5 contrasts with

> $(ttbs)Rh-H + 2CO \rightarrow (Httbs)Rh(CO)_{2}$ (5)



rhodium porphyrin hydrides ((por)Rh-H) which have a net reaction with CO that exclusively produces metalloformyl complexes, ((por)Rh-CHO).<sup>1</sup>

When  $[(ttbs)Rh]_2$  is reacted with CO in the presence of a near stoichiometric quantity of H<sub>2</sub>O, the metalloketone 4 rapidly forms and subsequently reacts away to produce both 6 and a formyl complex, (ttbs)Rh-CHO  $(7)^{10e}$  (Figure 2). When <sup>13</sup>CO is used in this reaction, concomitant formation of  ${}^{13}CO_2$ , 6, and 7 with disap-

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pearance of 4 is observed in the <sup>13</sup>C NMR. The stoichiometry for this reaction corresponds to formation of the hydride 3 by a water gas shift type reaction<sup>14</sup> (eq 6) and

$$(ttbs)Rh-C(O)-Rh(ttbs) + H_2O \rightarrow 2(ttbs)Rh-H + CO_2 (6)$$

$$(ttbs)Rh-H+CO \xrightarrow{(ttbs)Rh} (ttbs)Rh-CHO$$
(7)

$$(ttbs)Rh-CHO + CO \rightarrow (Httbs)Rh(CO)_2$$
 (8)

subsequent reaction of **3** with free or complexed CO to form **6** (eq 5) and the formyl complex **7** (eq 7), which then slowly reacts away to form **6** (eq 8) as the thermodynamic product.

Benzene solutions of the <sup>13</sup>CO derivative of 4 in the absence of excess <sup>13</sup>CO react with  $CH_3CH_2OH$  (eq 9) and  $HSnBu_3$  (eq 10) to form the hydride 3 and an ester complex (ttbs)Rh-<sup>13</sup>C(O)OCH<sub>2</sub>CH<sub>3</sub> (8)<sup>10f</sup> (eq 9) and the

$$(ttbs)Rh^{-13}C(O) - Rh(ttbs) + CH_3CH_2OH \rightarrow (ttbs)Rh - H + (ttbs)Rh^{-13}C(O)OCH_2CH_3 (9)$$

$$(ttbs)Rh^{-13}C(O) - Rh(ttbs) + HSnBu_3 \rightarrow (ttbs)Rh^{-13}CHO + (ttbs)Rh^{-SnBu_3} (10)$$

formyl complex (ttbs)Rh $^{-13}$ CHO and (ttbs)Rh $^{-SnBu_3}$ (9)<sup>10g</sup> (eq 10), respectively. Reaction 9 provides support for the formation of the hydride complex 3 by reaction 6, and reaction 10 illustrates a potential role of rhodium carbonyl species in producing the formyl complex 7 by reaction 7. The preformed hydride complex 3 reacts with CO to form (Httbs)Rh(CO)<sub>2</sub> as the only observed product, but when 3 is formed in the presence of excess (ttbs)Rh $^{-C}(O)^{-Rh}(ttbs)$ , the formyl complex 7 is produced in competition with 6. Using a related rhodium salophen derivative, Eisenberg has observed that the rhodium hydride complex reacts with CO to produce a formyl complex.<sup>15</sup> Rhodium porphyrin formyl complexes are known to form by reaction of a hydride, (por)Rh $^{-H}$ , with a rhodium carbonyl complex,<sup>12</sup> and the conditions where (ttbs)Rh—CHO is produced suggests that a related pathway may be operative in the rhodium salen system.

The (ttbs)Rh<sup>II</sup> monomer has a  $(d_{xz}d_{xy}d_{z^2})^6(d_{yz})^1$  ground configuration which contrasts with rhodium(II) porphyrins where  $(d_{xy}d_{xz}d_{yz})^6(d_{z^2})^1$  ground configurations are observed.<sup>9</sup> The reorganization energy associated with using the rhodium  $d_{z^2}$  in forming normal covalent bonds should provide an unfavorable contribution to the Rh-Rh, Rh-H, and Rh-C bond dissociation enthalpies for (ttbs)Rh complexes relative to the rhodium porphyrin systems. The observed reactions of H<sub>2</sub> and CO with  $[(ttbs)Rh]_2$  indicate that the  $(d_{yz}^1 \rightarrow d_{z^2}^1)$  reorganization energy  $(\Delta H_{yz-z^2})$  cannot be large (<8 kcal mol<sup>-1</sup>), but even a small contribution ( $\sim 3-6$  kcal) from this factor could be responsible for the small dissociation enthalpy observed for 1 (13 kcal  $mol^{-1}$ ) and the inability to detect reactions of 1 with methane and toluene which are the most thermodynamically difficult transformations studied.

Reactivity studies of [(ttbs)Rh]<sub>2</sub> illustrate that a rhodium complex with a nonmacrocyclic ligand that uses two nitrogen and two phenolate oxygen donors has the thermodynamic capability to accomplish many of the substrate reactions associated with rhodium porphyrins. Observation of the metalloformyl complex (7) is particularly significant in substantially extending the range of donor site arrays for rhodium which are candidates for promoting a key initial step in CO hydrogenation.<sup>16</sup> However, (ttbs)Rh–CHO in the presence of excess CO is thermodynamically unstable relative to the rhodium-(I) dicarbonyl complex, (Httbs)Rh(CO)<sub>2</sub>, and the flexible nonmacrocyclic ligand structure provides a pathway for a CO induced hydrogen migration from rhodium to a phenolate oxygen. The thermodynamic capability of several classes of rhodium(II) complexes to produce metalloformyl species from reactions with H<sub>2</sub> and CO could have significant applications in the hydrogenation of CO if stable ligand arrays can be identified which permit mechanistic pathways for the subsequent hydrogenation of the formyl species.

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