

# Equilibrium Thermodynamics To Form a Rhodium Formyl Complex from Reactions of CO and H<sub>2</sub>: Metal $\sigma$ Donor Activation of CO

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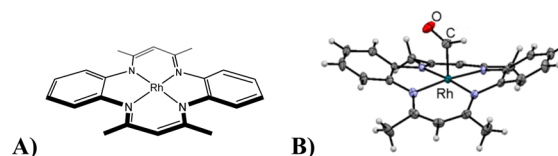
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**S** Supporting Information

**ABSTRACT:** A rhodium(II) dibenzotetramethylaza[14]-annulene dimer  $[(\text{tmtaa})\text{Rh}]_2$  (**1**) reacts with CO and H<sub>2</sub> in toluene and pyridine to form equilibrium distributions with hydride and formyl complexes  $((\text{tmtaa})\text{Rh}-\text{H}$  (**2**);  $(\text{tmtaa})\text{Rh}-\text{C}(\text{O})\text{H}$  (**3**)). The rhodium formyl complex  $((\text{tmtaa})\text{Rh}-\text{C}(\text{O})\text{H})$  was isolated under a CO/H<sub>2</sub> atmosphere, and the molecular structure was determined by X-ray diffraction. Equilibrium constants were evaluated for reactions of  $(\text{tmtaa})\text{Rh}-\text{H}$  with CO to produce formyl complexes in toluene ( $K_{2(298\text{ K})(\text{tol})} = 10.8$  ( $1.0 \times 10^3$ ) and pyridine ( $K_{2(298\text{ K})(\text{py})} = 2.2$  ( $0.2 \times 10^3$ )). Reactions of **1** and **2** in toluene and pyridine are discussed in the context of alternative radical and ionic pathways. The five-coordinate 18-electron Rh(I) complex  $[(\text{py})-(\text{tmtaa})\text{Rh}^{\text{I}}]^-$  is proposed to function as a nucleophile toward CO to give a two-electron activated bent Rh-CO unit. Results from DFT calculations on the  $(\text{tmtaa})\text{Rh}$  system correlate well with experimental observations. Reactions of **1** with CO and H<sub>2</sub> suggest metal catalyst design features to reduce the activation barriers for homogeneous CO hydrogenation.

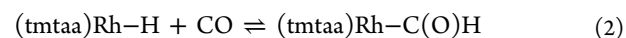
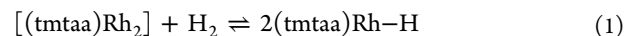
Development of catalyst materials for conversion of synthesis gas (CO/H<sub>2</sub>) to organic oxygenates under mild conditions is a major objective for transition metal catalysis.<sup>1-7</sup> The practical significance of developing new strategies for the catalytic hydrogenation of carbon monoxide stems from the inevitable necessity to use synthesis gas from biomass and coal to replace petroleum for liquid fuels and chemical manufacturing. Both homogeneous and heterogeneous transition metal catalyzed hydrogenation of carbon monoxide to produce organic oxygenates use metal formyl (M-C(O)H) intermediates as a seminal event in the addition of H<sub>2</sub> with CO.<sup>1,8-12</sup> Early kinetic and mechanistic studies of homogeneous catalytic hydrogenation of CO using carbonyl complexes of Co,<sup>9</sup> Rh,<sup>13</sup> and Ru<sup>14,15</sup> at very high pressures clearly implicated metal formyl species in rate-limiting steps for each of these catalyst systems. Unfavorable thermodynamics for metal hydride (M-H) addition with CO to produce formyl species was identified as a rationale for the requirement of using extreme CO pressures to obtain modest rates of organic oxygenate formation.<sup>16</sup> Numerous  $\eta^1$ -C-bonded metal formyl complexes are known from directed synthesis through reactions of coordinated CO with hydride donors  $[\text{M}-\text{CO}]^+ + \text{H}^- \rightleftharpoons \text{M}-\text{C}(\text{O})\text{H}$  which produce transient formyl complexes that dissociate to M-H and CO as the thermodynamic

products.<sup>17-23</sup> Metal formyl complexes that function as productive intermediates in the hydrogenation of carbon monoxide necessitate being formed as thermodynamic products from reactions of a metal species with H<sub>2</sub> and CO. Rh(II) porphyrins<sup>24-29</sup> were the first late transition metal complexes reported to react with H<sub>2</sub> and CO to produce observable quantities of metal formyl species  $2\text{M} + \text{H}_2 + 2\text{CO} \rightleftharpoons 2\text{M}-\text{C}(\text{O})\text{H}$  at mild conditions ( $P_{\text{CO}}, P_{\text{H}_2} < 1$  atm;  $T = 298$  K). This article reports on equilibrium thermodynamics for reactions of rhodium(II) dibenzotetramethylaza[14]annulene dimer  $[(\text{tmtaa})\text{Rh}]_2$ <sup>30</sup> (**1**) (Figure 1) with CO and H<sub>2</sub> in



**Figure 1.** (A) Illustration of the  $(\text{tmtaa})\text{Rh}$  unit. (B) ORTEP representation of  $(\text{tmtaa})\text{Rh}-\text{C}(\text{O})\text{H}$  structure with thermal ellipsoids shown on non-hydrogen atoms at 50% probability level and hydrogen atoms shown as open circles.

toluene and pyridine media. The  $(\text{tmtaa})\text{Rh}$  system has provided the first opportunity for evaluation of simultaneous equilibria that produce both hydride  $((\text{tmtaa})\text{Rh}-\text{H}$  (**2**)) and formyl  $((\text{tmtaa})\text{Rh}-\text{C}(\text{O})\text{H}$  (**3**)) species from reactions of a metal complex with H<sub>2</sub> and CO (eqs 1,2). This system is particularly valuable in recognizing the metal donor activation of CO, providing experimental benchmarks for the thermodynamic criteria to obtain metallo-formyl species and identifying structural features that promote and inhibit reactions relevant to CO hydrogenation.



Toluene solutions of the Rh(II) dimer (**1**) react with CO and H<sub>2</sub> to form a hydride species  $((\text{tmtaa})\text{Rh}-\text{H}$  (**2**)) ( $\delta$  Rh-H = -24.1 ppm,  $J^{103}\text{Rh}-\text{H} = 58.3$  Hz) in equilibrium with a formyl complex  $((\text{tmtaa})\text{Rh}-\text{C}(\text{O})\text{H}$  (**3**)) ( $\delta$  Rh-C(O)-H = 11.5 ppm,  $J^{103}\text{Rh}-\text{C}(\text{O})-\text{H} = 0.6$  Hz;  $J^{13}\text{C}-(\text{O})\text{H} = 157$  Hz,  $\Delta\nu(\text{C}=\text{O}) = 1697$  cm<sup>-1</sup>,  $\Delta\nu(\text{C}-\text{H}) = 2675$  cm<sup>-1</sup>) (eqs 1, 2). The equilibrium constant for reaction 2 in toluene was evaluated using molar concentrations from <sup>1</sup>H NMR

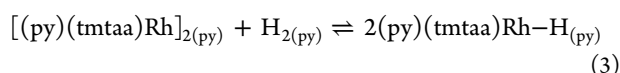
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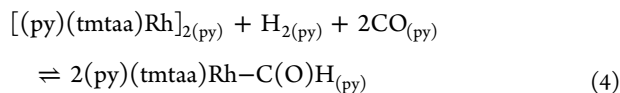
integrations of **2** and **3** and the solubility of CO in toluene<sup>31</sup> ( $K_2(298\text{ K}) = 10.8 (1.0) \times 10^3$ ,  $\Delta G_2^\circ(298\text{ K}) = -5.5 (0.1) \text{ kcal mol}^{-1}$ ).

The rhodium formyl complex ((tmtaa)Rh–C(O)H) (**3**) was crystallized from toluene under an atmosphere of CO/H<sub>2</sub>, and the structure was determined by single crystal X-ray diffraction (Figure 1). The C–O internuclear distance (1.181 Å) and Rh–C–O angle (128.28°) are comparable to those observed for the analogous octaethylporphyrin rhodium formyl complex (OEP)–Rh–C(O)H (C–O = 1.175 Å; Rh–C–O = 129.6°), and the Rh–C internuclear distance of 1.930 Å is substantially shorter than the Rh–CH<sub>2</sub>– distance of 2.050 Å observed in (tmtaa)Rh–CH<sub>2</sub>CH<sub>3</sub> (Supporting Information (SI)). The distinct nonplanarity of tmtaa contrasts with the near planar structures for aromatic porphyrin macrocycles. The flexibility of the antiaromatic 16  $\pi$ -electron macrocycle permits the tmtaa structure to change in response to the steric demands at the metal center.

Pyridine solutions of [(tmtaa)Rh]<sub>2</sub> react with H<sub>2</sub> to give equilibrium distributions with a hydride complex (tmtaa)Rh–H<sub>(py)</sub> (eq 3) ( $\delta \text{ Rh–H} = -13.6 \text{ ppm}$ ,  $J^{103}\text{Rh–H} = 35.7 \text{ Hz}$ ). The  $\delta \text{ Rh–H}^1\text{H}$  NMR resonance shifts downfield, and  $J^{103}\text{Rh–H}$  decreases as the donor strength of the solvent medium increases from toluene ( $\delta \text{ Rh–H} = -24.1 \text{ ppm}$ ,  $J^{103}\text{Rh–H} = 58.5 \text{ Hz}$ ) to THF ( $\delta \text{ Rh–H} = -20.2 \text{ ppm}$ ,  $J^{103}\text{Rh–H} = 47.6 \text{ Hz}$ ) and then pyridine as the strongest donor ( $\delta \text{ Rh–H} = -13.6 \text{ ppm}$ ,  $J^{103}\text{Rh–H} = 35.7 \text{ Hz}$ ). The equilibrium constant for reaction 3 was evaluated by integration of the <sup>1</sup>H NMR for each of the constituents ( $K_3(298\text{ K}) = 5.0(0.9)$ ,  $\Delta G_3^\circ(298\text{ K}) = -1.0(0.1) \text{ kcal mol}^{-1}$ ).

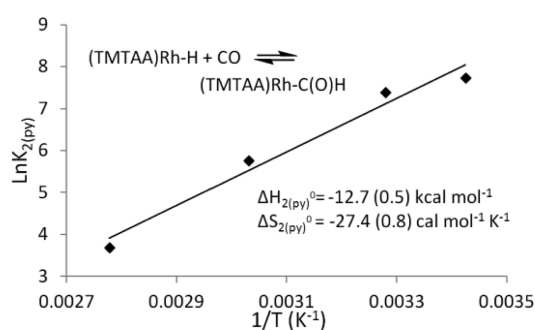


Solutions of **1** in pyridine react with CO/H<sub>2</sub> to produce equilibria with the hydride ((py)(tmtaa)Rh–H<sub>(py)</sub>) and a formyl complex ((py)(tmtaa)Rh–C(O)H<sub>(py)</sub>);  $\delta \text{ Rh–C(O)–H} = 13.84 \text{ ppm}$ ,  $J^{103}\text{Rh–C(O)–H} = 0.8 \text{ Hz}$ ;  $J^{13}\text{C–(O)H} = 159.6 \text{ Hz}$  (eqs 2–4 (py)).



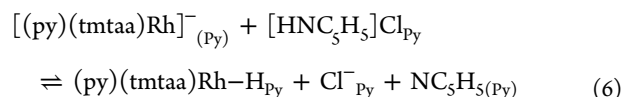
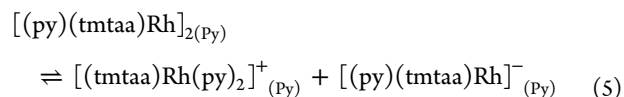
The equilibrium constant for reaction 2 in pyridine was evaluated from integration of the <sup>1</sup>H NMR and the solubility of CO in pyridine<sup>32</sup> ( $K_2(298\text{ K})(\text{py}) = 2.2(0.2) \times 10^3$ ,  $\Delta G_2^\circ(298\text{ K})(\text{py}) = -4.5 (0.1) \text{ kcal mol}^{-1}$ ). The temperature dependence of  $K_2(298\text{ K})(\text{py})$  was used to evaluate  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  ( $\Delta H_2^\circ(\text{py}) = -12.7 (0.5) \text{ kcal mol}^{-1}$ ,  $\Delta S_2^\circ(\text{py}) = -27.4 (0.8) \text{ cal K}^{-1} \text{ mol}^{-1}$ ) (Figure 2). Pyridine is a strong donor and coordinates with the hydride and formyl complexes, but the near cancellation of the reactant and product solvation terms makes the process only 1.0 kcal mol<sup>-1</sup> more favorable in toluene ( $\Delta G_2^\circ(298\text{ K})(\text{tol}) = -5.5 (0.1) \text{ kcal mol}^{-1}$ ) when compared to pyridine ( $\Delta G_2^\circ(298\text{ K})(\text{py}) = -4.5 (0.1) \text{ kcal mol}^{-1}$ ). The overall reaction of the Rh<sup>II</sup>–Rh<sup>II</sup> bonded dimer with H<sub>2</sub> and CO to produce the formyl complex (eq 4(py)) is highly favorable in pyridine ( $\Delta G_4^\circ(298\text{ K})(\text{py}) = -10.0 (0.2) \text{ kcal mol}^{-1}$ ).

Dissociation of the rhodium(II) dimer ([ (tmtaa)Rh]<sub>2</sub>) in toluene is shown to occur by homolytic cleavage to form metal-centered radicals ((tmtaa)Rh<sup>II•</sup>) by <sup>1</sup>H NMR T<sub>2</sub> measurements.<sup>33</sup> The temperature dependence of the line broadening for [(tmtaa)Rh]<sub>2</sub> in toluene associated with formation of (tmtaa)Rh<sup>II•</sup> was used to determine the activation enthalpy for



**Figure 2.** A van't Hoff plot of  $\ln K_2$  vs  $1/T$  for reaction of (tmtaa)Rh–H with CO to give (tmtaa)Rh–C(O)H in pyridine.

homolysis of **1** to (tmtaa)Rh<sup>•</sup> (24 kcal mol<sup>-1</sup>) and the Rh<sup>(II)</sup>–Rh<sup>(II)</sup> bond dissociation enthalpy (BDE) for **1** (22(1) kcal mol<sup>-1</sup>)<sup>33</sup> which is comparable to a 17 kcal mol<sup>-1</sup> Rh<sup>(II)</sup>–Rh<sup>(II)</sup> BDE for the octaethylporphyrin rhodium(II) dimer ([ (OEP)–Rh<sup>(II)</sup>]<sub>2</sub>).<sup>34</sup> Dissolution of [(tmtaa)Rh]<sub>2</sub> in pyridine results in a solution where only the pyridine-coordinated Rh<sup>(II)</sup>–Rh<sup>(II)</sup> bonded dimer is observed in the <sup>1</sup>H NMR. The absence of <sup>1</sup>H NMR line broadening when a solution of [(tmtaa)Rh]<sub>2</sub> in pyridine (SI) is heated to 373 K is consistent with Rh<sup>II</sup>–Rh<sup>II</sup> bond cleavage occurring by heterolysis. Addition of pyridinium chloride to solutions of [(tmtaa)Rh]<sub>2</sub> in pyridine results in the immediate formation of (tmtaa)Rh–H(py) and [(tmtaa)Rh–(py)<sub>2</sub>]<sup>+</sup>Cl<sup>–</sup> which is reactivity associated with heterolysis of the Rh–Rh bond in [(tmtaa)Rh]<sub>2</sub> (eqs 5, 6).

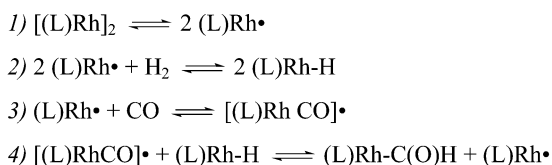


Assembly of a formyl unit on a metal center requires that CO has access to the metal site. Homolysis of the Rh<sup>(II)</sup>–Rh<sup>(II)</sup> in **1** gives the metal-centered radical (tmtaa)Rh<sup>II•</sup> for metal site reactions in toluene, and donor induced heterolysis of **1** produces the five-coordinate 18-electron Rh(I) anion ([ (py)–(tmtaa)Rh]<sup>–</sup>) for metal centered reactions in pyridine. Reactions of the (tmtaa)Rh system in toluene and pyridine are proposed to follow alternate Rh(II) metallo-radical and Rh(I) metallo-anion CO activation pathways respectively (Scheme 1 A, B). All of the reactions relevant to CO hydrogenation occur much faster in pyridine when compared to analogous reactions in toluene. Pyridine donor promoted Rh<sup>II</sup>–Rh<sup>II</sup> and Rh–H heterolysis and the general capability to support ionic reaction pathways in pyridine compared to higher energy radical pathways in toluene result in faster reactions in pyridine.

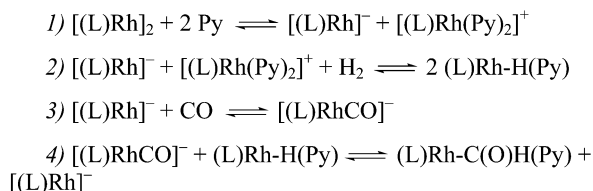
Activation of CO is usually associated with binding at Lewis acid metal centers which promotes reaction of nucleophiles at the carbonyl carbon.<sup>17–23</sup> The activation of CO by metal-centered radicals shown in Scheme 1 is the result of electron donation from Rh(II) to CO (CO  $\pi^*$ ) to give bent one-electron activated Rh–CO units. Metallo-radical electron donation to CO thus activates the carbonyl carbon for reactions with radicals. EPR<sup>35,36</sup> and NMR<sup>37</sup> contact shift studies for CO complexes of sterically encumbered Rh(II) porphyrins illustrate a precedent for a bent [Rh<sup>(II)</sup>–CO]<sup>•</sup> unit

**Scheme 1. Proposed Alternate Radical and Ionic Pathways for Reactions of the [(tmtaa)Rh]<sub>2</sub>/H<sub>2</sub>/CO System in (A) Toluene and (B) Pyridine (L = tmtaa)**

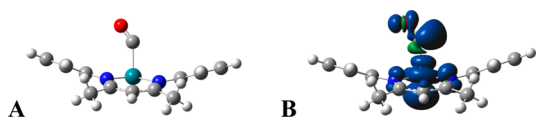
**A) Radical chain reaction (Toluene)**



**B) Metallo-anion chain reaction (Pyridine)**

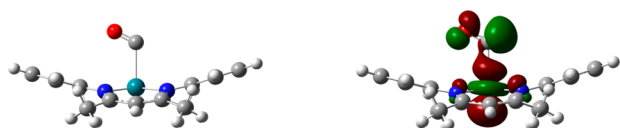


that results from a small net Rh<sup>(II)</sup>-CO interaction ( $\Delta G^{\circ}_{(298\text{K})\text{Rh-CO}_{\text{diss}}} = -3 \text{ kcal mol}^{-1}$ ).<sup>37</sup> Energy minimized DFT computations<sup>38</sup> for [(tmtaa)RhCO]• illustrate the “half-bent” Rh-CO structural unit and spin density distribution that directs one-electron reactions to the carbonyl carbon (Figure 3).



**Figure 3.** Energy minimized DFT computations (B3LYP, 3-21G) for [(tmtaa)Rh<sup>II</sup>CO]• structure and (B) spin density (Rh<sup>II</sup>-C-O = 144.5°).

The five-coordinate 18-electron complex ((py)(tmtaa)-Rh)<sup>-</sup> has a filled d<sub>z<sup>2</sup></sub>, and thus a pair of electrons occupies the potential sixth site around the metal. Substrates that can function as electron pair acceptors have the potential to give oxidative addition to the metal center and experience two-electron reductive activation. The results of DFT computations for [(tmtaa)RhCO]<sup>-</sup> illustrate a bent Rh<sup>I</sup>C=O unit with a substantial negative charge that directs reactions of electrophiles to the carbonyl carbon (Figure 4). Protonation of the



**Figure 4.** Energy minimized DFT computations (B3LYP, 3-21G) for [(tmtaa)Rh<sup>I</sup>CO]<sup>-</sup> structure and electron density in the highest occupied MO (Rh<sup>I</sup>-C-O = 128.8°).

carbonyl carbon in the bent Rh<sup>I</sup>C=O unit produces the formyl complex ((tmtaa)Rh-C(O)H). An important feature for this type of CO activation is that electronically saturated 18 electron complexes such as [(py)(tmtaa)Rh]<sup>-</sup> react as nucleophiles and are not deactivated by coordinating media such as pyridine, water, and methanol.<sup>25,39-42</sup>

The observed Rh<sup>(II)</sup>-Rh<sup>(II)</sup> BDE and equilibrium thermodynamics for the H<sub>2</sub> and CO substrate reactions for the (tmtaa)

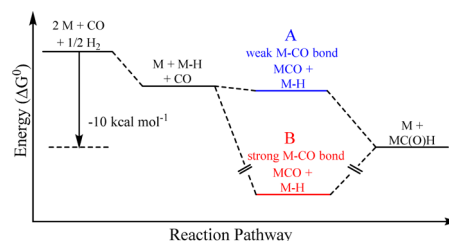
Rh system establish the difference between the Rh-H and Rh-C(O)H BDEs as ~3–4 kcal mol<sup>-1</sup> and place values for the (tmtaa)Rh-H (Rh-H ≈ 60–63 kcal mol<sup>-1</sup>) and the (tmtaa)Rh-C(O)H (Rh-C ≈ 57–60 kcal mol<sup>-1</sup>) in the ranges observed for rhodium porphyrin complexes.<sup>25,43</sup> Thermodynamically favorable reactions ( $\Delta G^{\circ}(298 \text{ K}) < 0 \text{ kcal mol}^{-1}$ ) of metal hydrides with CO to produce metal formyl complexes require that the M-H BDE not exceed the M-C(O)H BDE by more than ~9 kcal mol<sup>-1</sup> (Scheme 2).

**Scheme 2. Estimated  $\Delta H^{\circ}$  and M-X BDE Values Needed To Have  $\Delta G^{\circ}_{(298 \text{ K})} < 0 \text{ kcal mol}^{-1}$  for the Designated Reaction.**<sup>43</sup>

Reaction	$\Delta G^{\circ}(298\text{K}) < 0$
1) 2 M + H <sub>2</sub> ⇌ 2 M-H	M-H > 56
2) M <sub>2</sub> + H <sub>2</sub> ⇌ 2M-H	M-H - 1/2M-M > 52
3) M-H + CO ⇌ M-C(O)H	M-H - M-C(O)H < 9
4) M <sub>2</sub> + H <sub>2</sub> + 2 CO ⇌ 2 M-C(O)H	2 M-C(O)H - M-M > 86
5) 2 M + 2 CO + H <sub>2</sub> ⇌ 2 M-C(O)H	2 M-C(O)H > 94

Producing a metal formyl species from reactions of a metal center with H<sub>2</sub> and CO requires that the M-H BDE be larger than ~56 kcal mol<sup>-1</sup>, and the M-C(O)H BDE then must be larger than ~47 kcal mol<sup>-1</sup> to accomplish the overall process (M + 1/2 H<sub>2</sub> + CO ⇌ M-C(O)H) with  $\Delta G^{\circ}_{(298 \text{ K})} < 0 \text{ kcal mol}^{-1}$  (Scheme 2). The (tmtaa)Rh-C(O)H BDE is greater than ~57 kcal mol<sup>-1</sup> and larger than would be optimum for catalytic applications. The minimum thermodynamic criteria to obtain M-C(O)H species with  $\Delta G^{\circ}_{(298 \text{ K})} < 0$  should be easily achieved by many second and third transition series metal species which attain M-C BDE values in excess of 50 kcal mol<sup>-1</sup>.<sup>44,45</sup> Unfavorable thermodynamics to produce a metal formyl from a reaction of M-H with CO may not be the exclusive factor that has limited the range of metal formyl species observed at equilibrium. Any one of the intermediates that may occur in the process (M + 1/2 H<sub>2</sub> + CO ⇌ M-C(O)H) that is highly stabilized would become a sink for the metal species (M) and suppress the equilibrium concentration of metal formyl species.

The formation of strongly bonded metal CO complexes could be an important factor in explaining why metal carbonyls that have effective M-CO back  $\pi$ -bonding including H-Rh(CO)<sub>4</sub> have not produced observable concentrations of formyl species (Figure 5). Relatively small net binding energies of Rh(I) and Rh(II) macrocycles with CO are a significant factor in permitting the reaction of (tmtaa)Rh-H with CO to attain large equilibrium concentrations of the metal formyl species. Activation of CO by metal nucleophiles<sup>41,46</sup> such as



**Figure 5.** Approximate energy relationships for representative intermediates in the reaction of M + CO/H<sub>2</sub> to produce M-C(O)H. (A) Weakly bonded bent M-CO intermediate. (B) Strongly bonded linear M-CO with effective M to CO d $\pi$  to p $\pi$   $\pi$ -bonding.

$[(\text{py})(\text{tmtaa})\text{Rh}]^-$  is an underinvestigated area that is ripe for discovery. Application of catalyst design features that enhance the equilibrium concentrations of formyl intermediates can be expected to give substantial rate enhancements for homogeneous CO hydrogenation processes under mild conditions.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Solution spectra, equilibrium measurements, full crystallographic tables, and crystallographic information files (cif) are included in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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