

# Interception and Characterization of Alkyl and Acyl Complexes in Rhodium-Catalyzed Hydroformylation of Styrene

Eleanor R. Nelsen and Clark R. Landis\*

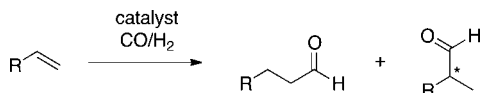
Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

**S** Supporting Information

**ABSTRACT:** Reaction of  $[\text{Rh}(\text{H})(\text{CO})_2(\text{BDP})]$  (BDP = bis(diazaphospholane)) with styrene at low temperatures enables detailed NMR characterization of four- and five-coordinate rhodium alkyl complexes  $[\text{Rh}(\text{styrenyl})(\text{CO})_n(\text{BDP})]$  presumed to be intermediates in rhodium-catalyzed hydroformylation. The five-coordinate acyl complexes  $[\text{Rh}(\text{C}(\text{O})\text{styrenyl})(\text{CO})_2(\text{BDP})]$  are also observed and characterized. The equilibrium distribution of these species suggests an inversion of thermodynamic preference for branched vs linear species from the alkyl to the acyl stage.

Rhodium-catalyzed hydroformylation of alkenes (Scheme 1) has long been important to the production of commodity chemicals and increasingly shows promise for fine, and even enantiopure, chemical production.<sup>1</sup>

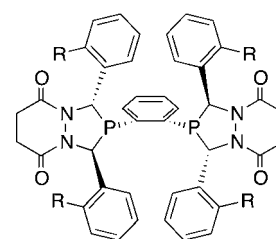
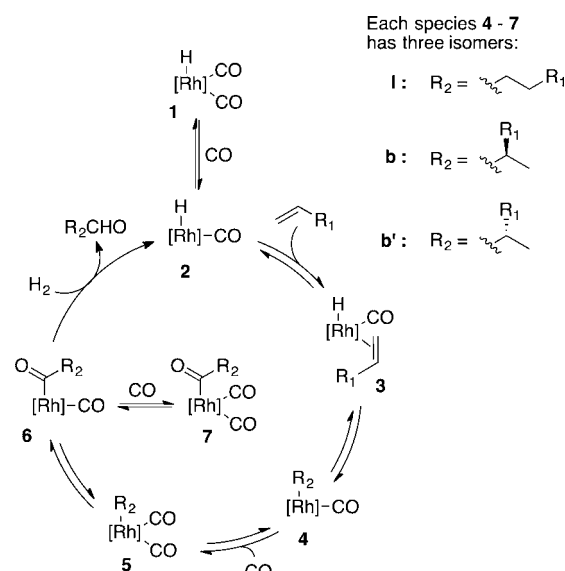
## Scheme 1. Hydroformylation of Alkenes



A general mechanism was first presented by Breslow and Heck for cobalt-catalyzed hydroformylation some 50 years ago (see Scheme 2).<sup>2</sup> However, fundamental questions concerning the origins of regioselectivity and enantioselectivity in rhodium-catalyzed hydroformylation remain unanswered because key reaction intermediates have not been characterized structurally, kinetically, or thermodynamically. Herein we report the first interception of linear and branched rhodium alkyl intermediates along a hydroformylation pathway, characterization of their structures by multinuclear NMR spectroscopy, and estimation of their relative thermodynamic stabilities. Furthermore we demonstrate that the thermodynamic preference for linear vs branched isomers inverts upon conversion of the rhodium alkyls to the rhodium acyls.

Synthesis of new phosphine ligands has enabled remarkable progress in controlling the chemo-, regio-, and enantioselectivity of rhodium-catalyzed hydroformylation.<sup>3</sup> Recent design motifs include scaffolding effects,<sup>4,5</sup> secondary coordination sphere hydrogen bonding,<sup>6</sup> and supramolecular constructions.<sup>7</sup> The 3,4-bis(diazaphospholane) (BDP) class of ligands introduced in 2004 (see Figure 1) combine high activity—greater than one turnover per second—and useful selectivities

## Scheme 2. General Mechanism for Hydroformylation



**Figure 1.** Structure of (*S,S*)-3,4-bis(diazaphospholane) (BDP). This work uses *rac*-BDP with R = H.

for the enantioselective hydroformylation of various alkene substrates.<sup>8</sup>

Previous work from this group on the Rh(BDP)-catalyzed hydroformylation of styrene demonstrated that both the branched-to-linear ratio and percent *ee* of the product increases with increasing partial pressure of CO ( $P_{\text{CO}}$ ). These observations, along with the results of isotopic labeling experiments and *in situ* IR monitoring, are consistent with a kinetic model in which CO dissociation from the resting state **1** is required to initiate the cycle. For the kinetically favored (*R*)-branched alkyl species **4**,  $\beta$ -hydride elimination is competitive with trapping by CO to give product. Thus, CO promotes

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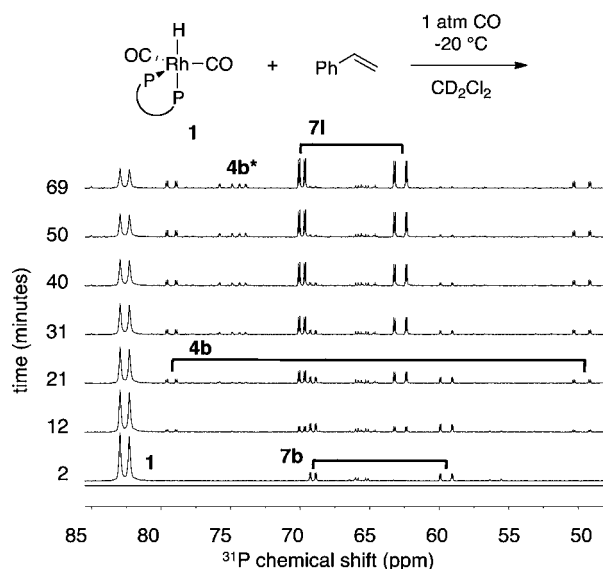
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formation of (*R*)-branched product but inhibits entry of catalyst from the resting state, leading to an overall independence of the rate with respect to [CO]. Production of linear and (*S*)-branched aldehydes show inhibition, only, by CO.<sup>9</sup>

However, the data supporting this kinetic model are indirect; direct observation of critical intermediates could provide additional insight into the fundamental thermodynamics and kinetics that control selectivity. To date the most detailed characterization of species along the hydroformylation pathway comes from Brown and Kent's NMR studies of the reaction of styrene with [Rh(H)(CO)(PPh<sub>3</sub>)<sub>3</sub>] in the absence of H<sub>2</sub>.<sup>10</sup> These studies revealed formation of branched and linear acyls of the formula Rh(acyl)(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>, with the branched acyl formed first and followed by equilibration to the more stable linear acyl. Since that time, however, the few examples of related intermediates have been limited to slow and/or unselective catalysts or synthesis of analogous iridium complexes.<sup>11</sup> Because Rh(BDP) catalysts exhibit such high hydroformylation activities, we speculated that reaction of styrene with RhH(BDP)(CO)<sub>2</sub> at low temperatures and in the absence of H<sub>2</sub> would proceed to alkyl or acyl intermediates at rates convenient for characterization by NMR.

The hydrido dicarbonyl complex **1** (made with *rac*-BDP, R = H) cleanly forms upon exposure of [Rh(acac)(BDP)] to 140 psi 1:1 CO/H<sub>2</sub> overnight at 60 °C in dichloromethane. The <sup>1</sup>H and <sup>31</sup>P NMR spectra of **1** are consistent with a fluxional trigonal bipyramidal species with axial–equatorial coordination of the biphosphine, as has been seen for other small-bite-angle ligands.<sup>12</sup>

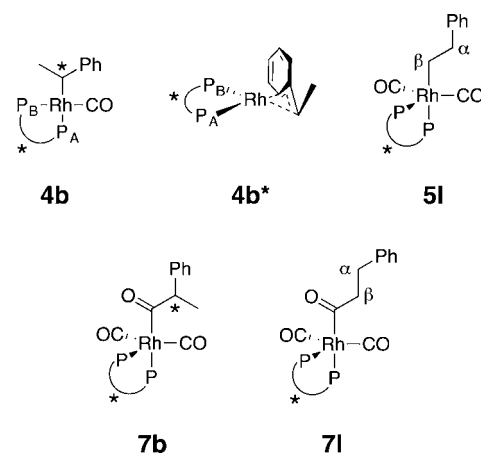
Under a narrow range of conditions (ca. 1 atm CO, 0 to –30 °C), the reaction of this rhodium hydride with 5 equiv of styrene can be monitored directly by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. A representative set of <sup>31</sup>P{<sup>1</sup>H} spectra, showing the course of the reaction at –20 °C under a CO atmosphere, is presented in Figure 2. The phosphorus signal of the hydride complex **1** (δ 83 ppm) disappears in a roughly first-order fashion, with a half-life of about 30 min. It is replaced by several



**Figure 2.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra (202.5 MHz) monitoring the reaction of [Rh(H)(CO)<sub>2</sub>(BDP)] (**1**; 83 ppm; 60 mM) with styrene under a CO atmosphere at –20 °C in CH<sub>2</sub>Cl<sub>2</sub>. Spectra show acyl complexes **7b**, **71** and alkyl complexes **4b**, **4b**\* growing in over time. Conversion to aldehydes <1%.

new ligand-containing species. The two major species are the five-coordinate linear and branched acyl complexes **71** and **7b** (see Chart 1), each of which has two distinct phosphorus

**Chart 1. Rhodium Alkyl and Acyl Complexes Generated from the Reaction of [Rh(H)(CO)<sub>2</sub>(BDP)] with Styrene<sup>a</sup>**

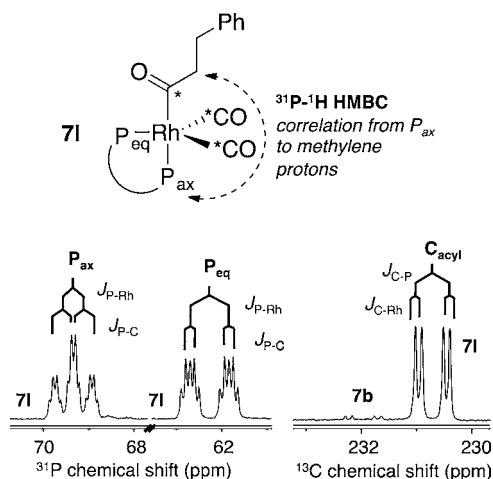


<sup>a</sup>Chiral centers denoted by (\*).

resonances at δ 69.1 and 59.3 ppm and δ 69.8 and 62.4 ppm, respectively. Each peak is a doublet of doublets; the larger coupling is <sup>1</sup>J<sub>P<sub>Rh</sub></sub>, and the smaller is <sup>2</sup>J<sub>PP</sub>.

The branched (**7b**) and linear (**71**) regioisomers are distinguished by <sup>31</sup>P–<sup>1</sup>H multiple-bond correlation experiments which show through-bond coupling from the ligand phosphorus atoms of **7b** to a methine quartet and methyl doublet, and from those of **71** to methylene protons. Acyl carbonyl signals, characterized by their far-downfield chemical shifts, confirm the assignment as acyl rather than alkyl complexes (see Figure 3). The chemical shifts and coupling constants are consistent with those reported by Brown for the five-coordinate acyl complexes of triphenylphosphine.<sup>10b</sup>

The other diastereomer of the branched acyl complex, **7b**', cannot be distinguished in the relatively crowded <sup>31</sup>P NMR



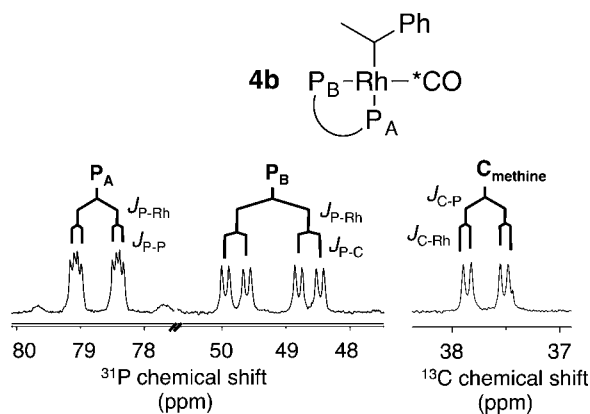
**Figure 3.** Phosphorus (left) and acyl carbon (right) signals for **71** generated using <sup>13</sup>CO. Coupling of both P<sub>ax</sub> and P<sub>eq</sub> to two distinct carbonyl ligands establishes coordination number. <sup>31</sup>P{<sup>1</sup>H} NMR, 202.5 MHz; <sup>13</sup>C{<sup>1</sup>H} NMR, 125.8 MHz; both in CH<sub>2</sub>Cl<sub>2</sub> at –20 °C. Labeled carbons are denoted in the figure by (\*).

spectrum; however, the  $^{13}\text{C}$  NMR spectrum shows a doublet 1 ppm upfield from the methine resonance of **7b** which is consistent with **7b'**.

While both four- and five-coordinate acyl complexes are possible under these conditions, the coupling pattern of the acyl complexes generated using  $^{13}\text{CO}$  rules out four-coordinate species. Figure 3 shows that  $\text{P}_A$  is coupled to three  $^{13}\text{C}$  nuclei, demonstrating that species **7b,1** are five-coordinate trigonal bipyramidal species with two terminal CO ligands.<sup>13</sup>

Similar acyl species have been observed in the reactions of **1** with allyl cyanide and vinyl acetate; details will be reported in a future publication.

Under conditions of low  $[\text{CO}]$ , three species with  $^{31}\text{P}$  resonances at  $\delta$  50 and 79 ppm,  $\delta$  73.7 and 74.4 ppm, and  $\delta$  57 and 78 ppm become more prominent. We have characterized these as the branched rhodium-alkyl monocarbonyl complex **4b** (see Figure 4),<sup>14</sup> the  $\eta^3$ -benzyl complex **4b\*** resulting from CO dissociation from **4b**, and the linear alkyl-rhodium dicarbonyl complex **5l**, respectively (see Chart 1).



**Figure 4.** Phosphorus (left) and methine carbon (right) signals for **4b** generated using  $^{13}\text{CO}$ .  $\text{P}_A$  and  $\text{P}_B$  are coupled to only one carbonyl ligand.  $^{31}\text{P}\{^1\text{H}\}$  NMR, 202.5 MHz;  $^{13}\text{C}\{^1\text{H}\}$  NMR, 125.8 MHz; both in  $\text{CH}_2\text{Cl}_2$  at  $-20^\circ\text{C}$ . Labeled carbons are denoted in the figure by (\*).

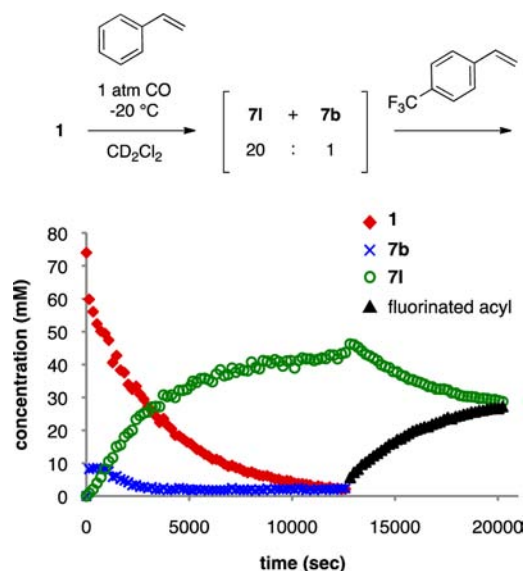
Multinuclear NMR and judicious use of  $^{13}\text{C}$ -labeled styrene (in the  $\alpha$  and  $\beta$  positions) and  $^{13}\text{CO}$  provide definitive characterization.

For **4b** the methyl and methine carbons appear at  $\delta$  37.7 and 20.3 ppm, respectively. The characterization of **4b\*** as a formally 3-coordinate  $\eta^3$ -benzyl species is supported by the observation of strong (38 Hz)  $^{31}\text{P}$ - $^{13}\text{C}$  coupling when  $\alpha$ - $^{13}\text{C}$ -labeled styrene is used, the nearly identical  $^{31}\text{P}$  chemical shifts of the two ligand phosphorus atoms as seen in rhodium allyl bis(phosphine) complexes,<sup>15</sup> and the absence of additional splitting in the  $^{31}\text{P}$  NMR spectrum when  $^{13}\text{CO}$  is used. The methine carbon shows a measurable (9.8 Hz) carbon-rhodium coupling in addition to carbon-phosphorus coupling. In **5l**, the  $\beta$ -methylene carbon (*trans* to phosphorus) is upfield-shifted to  $\delta$  10.3 ppm, and is coupled to phosphorus (60.4 Hz) and rhodium (13.8 Hz). To the best of our knowledge, this is the first direct observation of alkyl intermediates for any rhodium hydroformylation catalyst.<sup>16</sup> (See Supporting Information for selected spectroscopic data for **7b**, **7l**, **4b**, **4b\***, and **5l**.)

The characterization of linear and branched acyl and alkyl complexes provides unique insights into kinetic and thermodynamic influences in hydroformylation. *The branched acyl*

*complex is kinetically favored* (consistent with the conclusion of earlier studies that insertion to form a branched alkyl is fastest), *but isomerizes to the thermodynamically favored linear acyl complex* ( $[\text{7l}]:[\text{7b}] \approx 35:1$ ).<sup>17</sup> Moreover, **7b** appears to be favored over diastereomeric **7b'** by a ratio of 18:1. Equilibration between the acyls **7b** and **7l** must occur via the alkyls **4b** and **5l**. Thus, **4b** and **5l** must also be equilibrated under conditions where the acyls are in equilibrium; they appear in a ratio of  $[\text{4b}]:[\text{5l}] \approx 9:1$ . Although monocarbonyl **4b** and dicarbonyl **5l** differ in the number of terminal CO ligands, *these data demonstrate a thermodynamic preference for the branched alkyl regioisomer*<sup>18</sup> (and facile coordination of CO to the minor species **4l**).

The isomerization of **7b** to **7l** must involve  $\beta$ -hydride elimination to give an olefin hydride complex (**3** in Scheme 2). Does isomerization proceed with styrene dissociation<sup>9</sup> or is it intramolecular? To address this question, we added *p*- $\text{CF}_3$ -styrene to an equilibrated mixture of **7b** and **7l** (see Figure 5).



**Figure 5.** Reaction of **1** with styrene at  $-20^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ , followed by reaction (time = 12500 s) of the equilibrated mixture of **7b** and **7l** with *p*- $\text{CF}_3$ -styrene. Concentrations calculated from  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra.

The rate of formation of the  $\text{CF}_3$ -containing linear acyl complex (which requires olefin dissociation, followed by branched acyl formation and subsequent isomerization) is comparable to the rate of isomerization of **7b** to **7l**. Such results are consistent with a pathway for **7l** to **7b** isomerization that proceeds with olefin dissociation—that is, through rhodium hydrido carbonyl species **2**.

In conclusion, we have characterized five-coordinate rhodium acyl and four- and five-coordinate alkyl complexes of Rh(BDP) catalysts. To the best of our knowledge, this is the first example of characterization of an alkyl intermediate for any rhodium hydroformylation catalyst and the first example of detailed characterization of an acyl complex for an enantioselective hydroformylation catalyst. All data point to a strong kinetic preference for formation of the branched alkyl and acyl species. In contrast, thermodynamics appear to favor the linear isomer at the acyl stage but the branched isomer at the alkyl stage. These observations indicate that a delicate balance of rates and thermodynamics leads to the common observation of strong

dependence of regioselectivity upon reaction conditions for styrene hydroformylation.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and NMR spectra for **1**, **4b,b\***, **5I**, and **7b,l**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

landis@chem.wisc.edu

### Notes

The authors declare no competing financial interest.

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- (13)  $P_{A,ax}$  has an 80-Hz coupling to the acyl carbon, consistent with a *trans* arrangement (making the gross structure a pseudo triplet, since the coupling to rhodium is also approximately 80 Hz); it is coupled more weakly to the carbonyl ligands (ca. 15 Hz).  $P_{B,eq}$  has only moderate phosphorus–carbon coupling constants of 38 and 20 Hz, both to the carbons of the carbonyl ligands, consistent with a *cis* arrangement. Its coupling to the acyl carbon is not resolved.
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