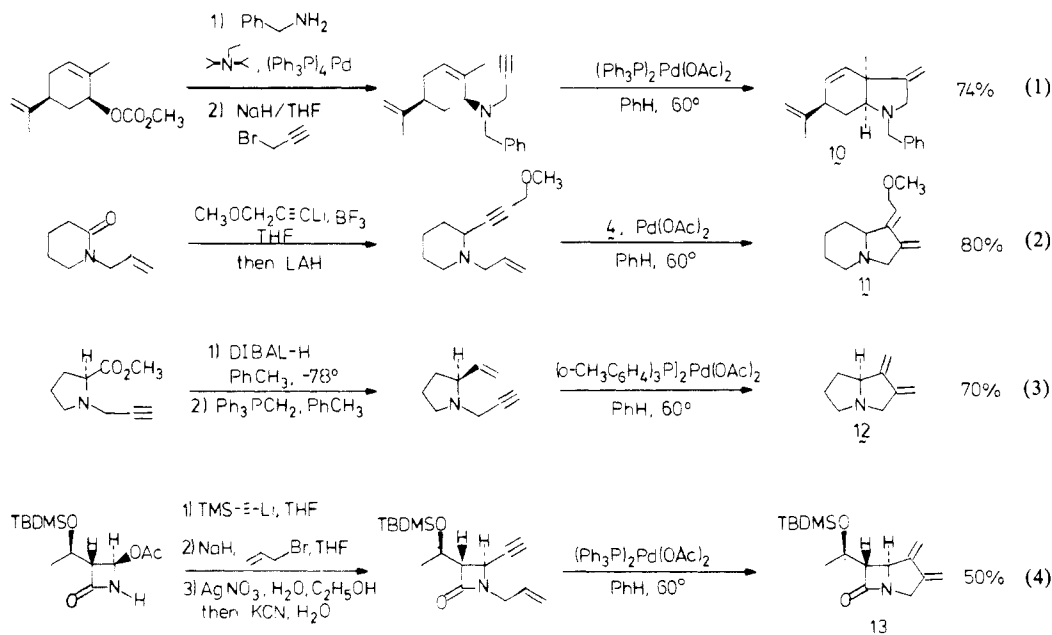
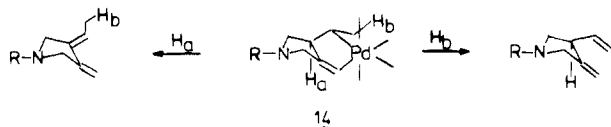


## Scheme I



the bicyclic skeleton of **10**<sup>5</sup> corresponds to the core ring of dendrobium alkaloids as represented by dendrobine itself.<sup>9</sup> The indolizidine skeleton of **11**<sup>5</sup> may represent a bicyclic nucleus of diverse alkaloids.<sup>10-13</sup> The pyrrolizidine skeleton of **12** is the ring nucleus of many alkaloids of current interest.<sup>1</sup> The mildness of the reaction conditions is highlighted by the successful formation of the carbapenem nucleus of **13**,<sup>2</sup> eq 4, by formation of the C(3)-C(4) bond.<sup>2,14</sup> This success is even more striking in light of a recent report where an attempt to form a similar carbapenem nucleus via a palladium-catalyzed addition of a vinyl bromide onto an olefin failed.<sup>14</sup>

While the mechanism of this reaction remains unknown, invoking a palladacycle such as **14** as an intermediate allows understanding of the origin of both the 1,3- and 1,4-dienes which control experiments establish as kinetic products.<sup>4a,15,16</sup> Whereas,



the allylic hydrogen  $H_a$  in **14** represents the weakest bond and therefore the most likely bond for migration, steric hindrance in inserting into a tertiary hydrogen combined with the conformational restraints of the palladacyclopentene disfavor the process leading to the 1,3-diene in favor of inserting into  $H_b$  to give the 1,4-diene. The substantial amount of 1,3-diene formed in the case of **1** with phosphine ligands compared to the previously examined carbocycles may reflect more of the intrinsic electronic bias for  $H_a$  insertion as a result of greater conformational mobility and less steric hindrance in this heterocyclic system. Nevertheless, it could be controlled by ligand manipulation. As noted, the

presence of an oxygen on the carbon bearing  $H_b$  as in **7** inhibits insertion into the C- $H_b$  bond.<sup>8</sup> It appears that this electronic effect of oxygen on the regioselectivity is general and may be conveniently exploited as a regiochemical control element. The ability to generate nitrogen heterocycles under such mild conditions greatly expands the applicability of this cyclization to five-membered rings via palladium-catalyzed isomerization especially combined with Pd(0)-catalyzed alkylations to generate the requisite substrates.

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### Asymmetric Synthesis of $\beta$ -Lactams and the Carbapenem Antibiotic (+)-PS-5

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The condensation of ester enolates with aldimines is an effective method for preparing  $\beta$ -lactams.<sup>1-8</sup> Attempts to obtain optically

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clarified before a convincing rationale for the observed asymmetric induction can be offered.

In conclusion, an encouraging step toward incorporating asymmetry into ester-imine condensations has been achieved. This approach to optically active  $\beta$ -lactam is versatile in design and its utility has been demonstrated with a synthesis of (+)-PS-5 (17). Studies with other homochiral esters are in progress.

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### Direct Evidence for Spillover of Hydrogen from Ruthenium to Copper in Supported Cu-Ru/SiO<sub>2</sub> Catalysts: A Study by NMR of Chemisorbed Hydrogen

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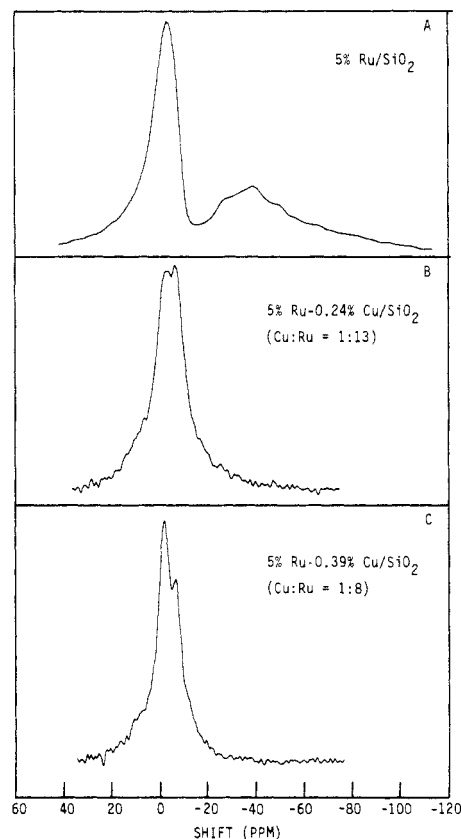
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Bimetallic catalysts have received intense attention, both because of their industrial utility for catalytic reforming and the possibility of using them as model systems in fundamental investigations of catalytic phenomena.<sup>1-5</sup> Hydrogen chemisorption has been used to characterize these systems. Specifically, on supported Cu-Ru catalysts, the number of surface Ru atoms has been inferred from titration with hydrogen under the assumption that hydrogen does not dissociatively adsorb on copper. The bases for the use of this experiment lie both in experiment and theory: the activation energy for dissociative chemisorption of hydrogen on Cu has been found experimentally to be about 5 kcal mol<sup>-1</sup>.<sup>6</sup> The activation energy for dissociative adsorption of hydrogen on Cu is a multivalued function of the orientation and vibrational-translational-rotational state of the hydrogen molecule as it approaches the surface and of the surface plane of the metal involved. Theoretical calculations have led to values both much less and much greater than that quoted above, depending upon the above-mentioned parameters, but having an average value of 5 kcal mol<sup>-1</sup>.<sup>7</sup> Hydrogen does not dissociatively chemisorb on pure copper at room temperature.<sup>8</sup> Spillover of hydrogen from Ru to Cu would invalidate this method of quantifying surface Ru.<sup>9,10</sup>

Studying the (0001) surface of single-crystal Ru having varying amounts of Cu deposited on the surface, various researchers<sup>11-17</sup>



**Figure 1.** NMR of hydrogen under a single pulse excitation for hydrogen on (a) 5% Ru/SiO<sub>2</sub>, (b) 5% Ru-0.24% Cu/SiO<sub>2</sub>, and (c) 5% Ru-0.39% Cu/SiO<sub>2</sub>. Liquid water was used as reference and all spectra were normalized to the height of the highest peak.

have found that hydrogen does not spill over on Cu at temperatures below 150 K, but Goodman et al.<sup>17</sup> have found evidence for spillover of atomic H onto Cu in such a bimetallic single-crystal system at 230 K.

Studies of supported Cu-Ru catalysts have not demonstrated spillover of hydrogen from Ru to Cu. The present work makes this demonstration for a number of Cu-Ru catalysts supported on SiO<sub>2</sub>, using nuclear magnetic resonance (NMR) of hydrogen on the substrates. The NMR spectroscopy of chemisorbed hydrogen on supported Ru has shown that the chemical shift of the hydrogen does not depend upon coverage and that the isotropic shift of hydrogen on Ru is found to be about 50 ppm upfield from the proton resonance in Me<sub>4</sub>Si.<sup>18</sup>

The home-built NMR spectrometer, similar to one previously described,<sup>19</sup> was operated at 220 MHz for proton resonance. Proton  $Q$ s were set between 50 and 200, depending upon the desired experimental response. A  $Q$  of 50, corresponding to a proton ringdown time of approximately  $21Q/3f_0 = 1.8 \mu\text{s}$  and having a receiver dead time of 500 ns,<sup>20</sup> was used to determine that no line broader than 20 kHz was present in the samples under study. The 90° broadcast pulse at probe  $Q$  of 50 was 2.5  $\mu\text{s}$  long, corresponding to a broadcast bandwidth of 200 kHz at the 3-dB point. A Biomation 2805 transient recorder was used for digitization of the NMR signal. The minimum dwell was 0.2  $\mu\text{s}$ , which was used for initial experiments to determine the spectral width of the sample under investigation. A dwell of 5  $\mu\text{s}$  and  $Q$  of 200 were used for experiments on hydrogen on the supported bimetallic Cu-Ru catalyst, in which the signal-plus-noise to noise ratio was

<sup>†</sup> Operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82.

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