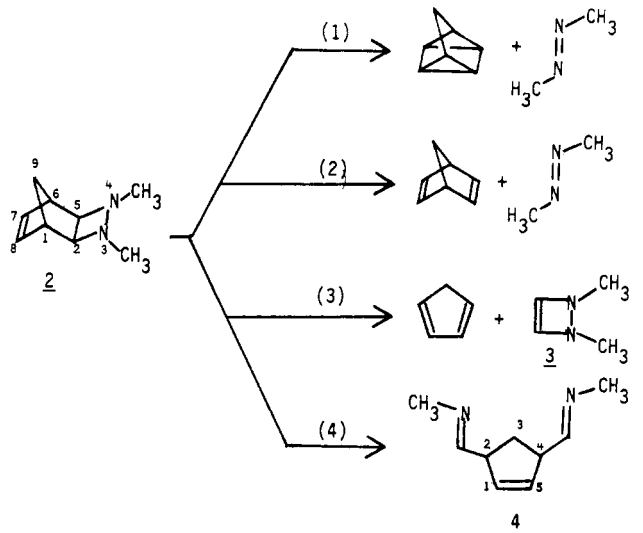
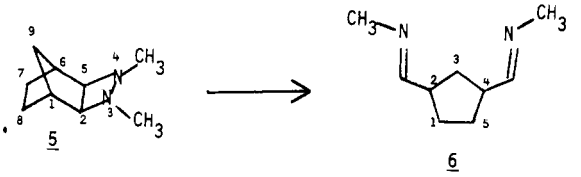


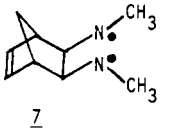
Solutions of **2** at 200 °C slowly turn black, and no characterizable product could be isolated. Since the primary product of this thermolysis was apparently unstable, **2** was then subjected to flash vacuum thermolysis[4] (FVT). FVT of **2** at 450 °C (contact time,[4b] ~0.5 s) produces diimine[5] **4** as the sole product, and thermolysis of the analogous saturated 1,2-diazetidine[3] **5** at 450 °C produces diimine **6** as the exclusive



product.[6] Integration of the ^1H NMR spectrum of the crude pyrolysate vs. CH_2Cl_2 added as an internal standard indicated an 86% recovery of **4**. Diimines **4** and **6** were identified on the basis of infrared and ^1H and ^{13}C NMR spectra.[5,6] The cis configuration at C-2, C-4 in **4** and **6**, demanded if the C-1, C-2 or C-5, C-6 bonds in **2** and **5** remain intact during the thermolysis, was indicated by spectral comparison with authentic samples of **4** and **6** prepared from the reaction of methylamine with *cis*-4-cyclopentene-1,2-dicarboxaldehyde[7] and *cis*-1,3-cyclopentanedicarboxaldehyde, respectively. The ^1H and ^{13}C NMR spectra of **4** and **6** show singlets for *N*-methyl absorptions, indicating either that both imines have the same configuration (anti) or that all possible syn and anti configurations are rapidly equilibrating at room temperature.

Thermolysis of **2** at 400 °C results in incomplete decomposition (~50% conversion of **2** into **4**), and at 600 °C **4** is the sole product. The thermolysis of **5** exhibits a temperature dependence similar to that shown by **2**: at 400 °C, incomplete decomposition of **5** (~60%) is observed; and at 600 °C, diimine **6** is still the sole product. The similarity of the product and temperature dependency of the thermolyses of **2** and **5** indicate the absence of participation of the double bond in the decomposition of **2**.

Two mechanistic extremes for the conversion of **2** to **4** are possible: (1) a concerted cycloreversion ($2\sigma_s + 2\sigma_a$ or $2\sigma_s + 2\sigma_s$);[9] or (2) a stepwise process involving initial rupture of the N-N bond producing biradical **7** that undergoes β scission to



4. A concerted cycloreversion seems unlikely since the bicyclo ring in **2** prevents the four-membered ring from adopting the skewed conformation requisite for the symmetry-allowed[9] [$2\sigma_s + 2\sigma_a$] process. A [$2\sigma_s + 2\sigma_s$] cycloreversion is also possible; however, it is difficult to understand why such a symmetry-forbidden process would be observed in preference to other possible symmetry-allowed pathways available for the thermolysis of **2** [e.g., (1) and (3)]. As a result, we propose that a two-step process involving initial rupture of the weakest (N-N) bond in **2** is operative.

Research on more complete elucidation of the mechanism of thermal cycloreversion of 1,2-diazetidines is in progress.

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(5) **4**: ^1H NMR ($CDCl_3$) δ 7.56 (d, J = 5 Hz, 2 H), 5.83 (br s, 2 H), 3.85–3.20 (m, 2 H), 3.29 (s, 6 H), 2.73–1.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 167.4 (C=N), 133.0 (C-1, C-5), 51.6 (C-2, C-4), 47.7 (*N*-CH_3), 30.8 (C-3); IR (CCl_4) 1670 (C=N), 1610 cm^{-1} (C=C); mass spectrum parent peak at *m/e* 150. Diimine **4** slowly polymerizes at room temperature ($t_{1/2} \sim 2$ h).
(6) **6**: ^1H NMR ($CDCl_3$) δ 7.60 (d, J = 4 Hz, 2 H), 3.26 (s, 6 H), 1.45–2.28 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 168.6 (C=N), 47.7 (*N*-CH_3), 45.4 (C-2, C-4), 33.8 (C-3), 29.2 (C-1, C-5); IR (CCl_4) 1680 cm^{-1} (C=N); mass spectrum parent peak at *m/e* 152. Like diimine **4**, **6** also slowly polymerizes at room temperature.
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Interception and Characterization of a Hydridoalkylrhodium Intermediate in a Homogeneous Catalytic Hydrogenation Reaction

Sir:

Reductive elimination of an alkane from a *cis*-hydridoalkyl metal complex (formed by olefin insertion into the corresponding dihydrido complex) has frequently been postulated as the product-forming step in the homogeneous catalytic hydrogenation of olefins.[1,2] However, failure of the proposed hydridoalkyl intermediate to accumulate in detectable concentrations generally has precluded direct observation of this step, the evidence for which has thus far been largely indirect.[3] We now report the interception and characterization of such a hydridoalkyl intermediate and the direct observation of the alkyl-hydride reductive elimination step, in a homogeneous catalytic hydrogenation reaction.

Our observations relate to the homogeneous catalytic hydrogenation of methyl (*Z*)-α-acetamidocinnamate (MAC, **1**),

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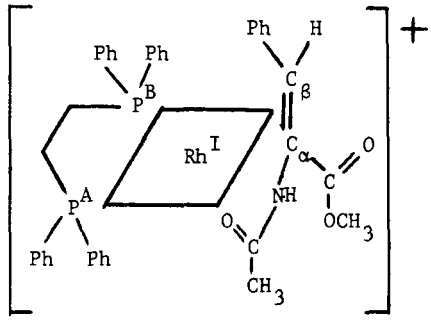
with the cationic rhodium catalyst, 1,2-bis(diphenylphosphinoethane)rhodium(I) (abbreviated $[Rh(diphos)]^+$).[6,7] This system is of particular interest since related catalysts containing chiral derivatives of diphos, e.g., $[(o\text{-}CH_3OC_6H_4)(C_6H_5)P^*CH_2CH_2P^*(C_6H_5)(o\text{-}CH_3OC_6H_4)]$ (dipamp)[9] and $[(C_6H_5)_2PC^*H(CH_3)C^*H(CH_3)(C_6H_5)_2]$ (chiraphos),[10] have been shown to be highly effective in the asymmetric catalytic hydrogenation of MAC and related substrates, yielding the corresponding optically active amino acid derivatives (e.g., *N*-acetylphenylalanine methyl ester, **3**, from MAC) in high optical yields. Characterization of the intermediates in these reactions clearly is important for an understanding of the origin of the remarkable stereoselectivity of these catalyst systems.

We have previously reported that the $[Rh(diphos)]^+$-catalyzed homogeneous hydrogenation of olefins, including MAC, in methanol solution at *ambient temperatures* proceeds by the mechanistic sequence depicted by eq 1 and 2.[6,11] The inter-

$$[Rh(diphos)]^+ + \underset{\mathbf{1}}{\text{H(Ph)}C_\beta{=}C_\alpha(\text{COCH}_3)(\text{NHCCH}_3{=}\text{O})} \rightleftharpoons \mathbf{2} \quad \text{(rapid equilibrium)} \quad (1)$$

$$\mathbf{2} + H_2 \xrightarrow{k_2} [Rh(diphos)]^+ + \underset{\mathbf{3}}{\text{PhCH}_2\text{CH}(\text{COCH}_3)(\text{NHCCH}_3{=}\text{O})} \quad \text{(rate-determining)} \quad (2)$$

mediate $[Rh(diphos)(MAC)]^+$ (**2**) has been characterized in solution by ^1H, ^{31}P, and (for the adduct of MAC labeled with



2

^{13}C at the C=C α-carbon atom) ^{13}C NMR spectroscopy and isolated as the BF_4^- salt whose structure has been determined by single-crystal X-ray crystallography.[11]

The equilibrium constant of reaction 1, determined by spectral titration,[6] was found to be $5.3 \times 10^3\ M^{-1}$, this high value presumably reflecting the additional contribution to binding of the chelating amide carbonyl group. Thus, even at moderate concentrations of MAC (typically $\gtrsim$0.1 M) the conversion of $[Rh(diphos)]^+$ into the MAC adduct, **2**, is essentially complete. Kinetic measurements over the temperature range 0–50 °C confirmed that reaction 2 obeyed the second-order rate law (eq 3), with $k_2 = 1.0 \times 10^2\ M^{-1}\ s^{-1}$ at 25 °C, $\Delta H_2^{\ddagger} = 6.3$ kcal/mol, and $\Delta S_2^{\ddagger} = -28$ cal mol^{-1} deg^{-1}.

$$-d[H_2]/dt = k_2[\mathbf{2}][H_2] \quad (3)$$

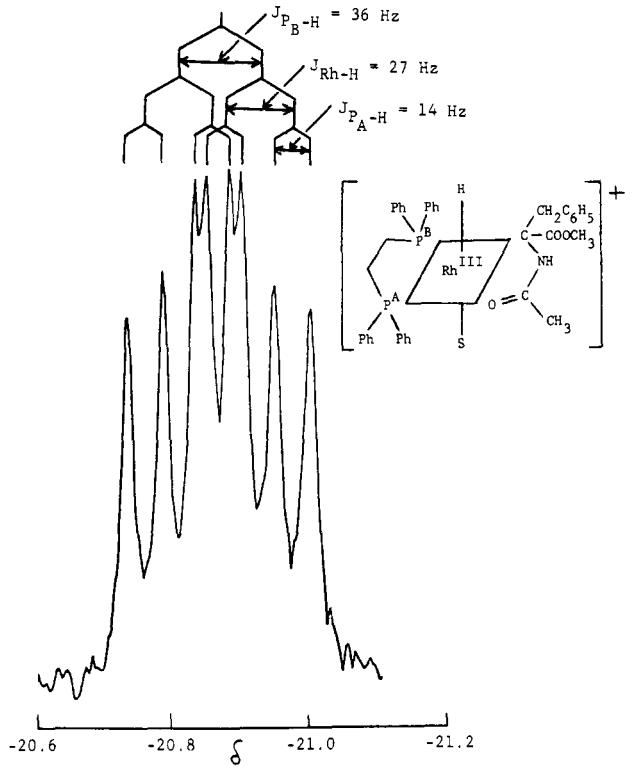
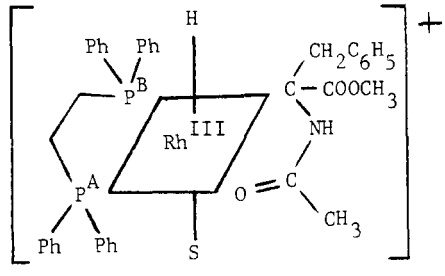


Figure 1. 270-MHz FT ^1H NMR spectrum (Rh-H region) of **4a** in CD_3OD at −78 °C.

By extending these studies to lower temperatures we have been able to intercept a further intermediate (i.e., the hydridoalkylrhodium complex, **4a**) in reaction 2, which can now be



4a, S = CH_3OH

b, S = CH_3CN

written as the sequence of steps (4 and 5). We report here the results of measurements of the kinetics of reaction 4 and 5 and the characterization of the intermediate **4a** by ^1H, ^{31}P and ^{13}C NMR spectroscopy.

$$\mathbf{2} + H_2 \xrightarrow{k_2} \mathbf{4a} \quad (4)$$

$$\mathbf{4a} \xrightarrow{k_5} [Rh(diphos)]^+ + \mathbf{3} \quad (5)$$

Passing H_2 through a methanol solution of **2** at −78 °C for ~3 h resulted in discharge of the red color and the formation of a new species identified as **4a** on the basis of its ^1H, ^{31}P, and ^{13}C NMR spectra: ^1H NMR (Figure 1), Rh-H, δ −20.9 ($J_{Rh-H} = 27$, $J_{PB-H} = 36$, $J_{PA-H} = 14$ Hz); ^{31}P NMR, P^A, δ 44.3, P^B, 58 ($J_{Rh-PA} = 96$, $J_{Rh-PB} = 141$, $J_{PA-PB} = 17$ Hz); ^{13}C NMR (measured on the complex derived from MAC 50% ^{13}C enriched at C_α; see Figure 2), C_α, δ 71.2 ($J_{Rh-^{13}C} = 21$, $J_{PA-^{13}C} = 84$, $J_{PB-^{13}C} = 4$ Hz) (confirmed by corresponding ^{31}P NMR spectrum).[12]

Reaction 4, leading to the formation of **4a**, presumably in-

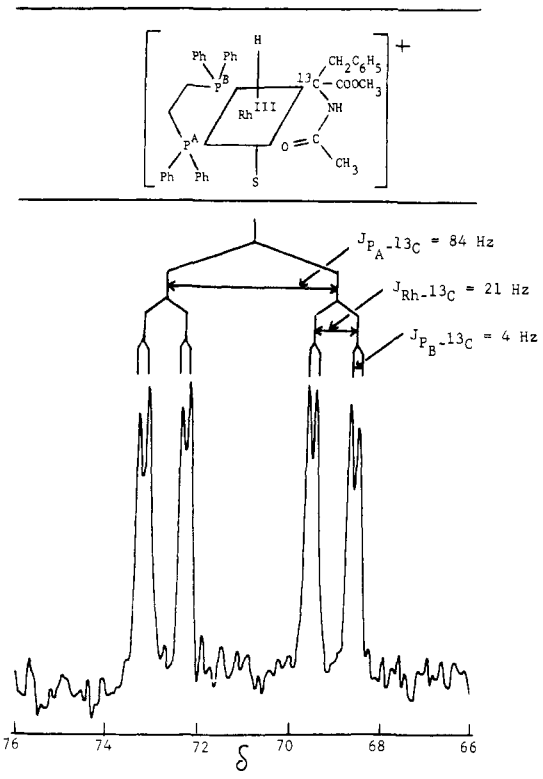


Figure 2. 22.63-MHz FT ^{13}C NMR spectrum (broad band proton decoupled) of **4a**, enriched with 50% ^{13}C at C_α, in CD_3OD at −78 °C.

volves the familiar oxidative addition–migratory insertion sequence depicted by eq 6. The NMR measurements on the ^{13}C-labeled compound clearly reveal that H transfer during the migratory insertion step occurs to the β-carbon atom of the C=C, bond while the α-carbon atom becomes bonded to the rhodium.

$$\mathbf{2} + H_2 \xrightarrow{k_2} [RhH_2(diphos)(MAC)]^+ \xrightarrow[\text{fast}]{S} \mathbf{4a} \qquad (6)$$

The remaining aspect of the characterization of **4a** involves determination of the number and position of coordinated solvent molecules (S), which are not directly revealed by the NMR spectra when S = CH_3OH. This was accomplished by titrating a methanol solution of **4a** with CH_3CN. Using ^{31}P NMR to monitor the change resulting from incremental addition of CH_3CN, it was found that **4a** reacted stoichiometrically with exactly *one* molecule of CH_3CN to yield a new species (**4b**) whose ^1H and ^{31}P NMR spectra resembled those of **4a** with slightly modified parameters: ^1H NMR, Rh-H, δ −16.5 (J_{Rh-H} = 19, J_{P^B-H} = 30, J_{P^A-H} = 11 Hz); ^{31}P NMR, P^A, δ 50, P^B, 61 (J_{Rh-P^A} = 92, J_{Rh-P^B} = 140, $J_{P^A-P^B}$ = 16 Hz). The presence of a coordinated CH_3CN ligand was confirmed by preparing a solution of **4b** using $CH_3C^{15}N$. The additional large $^{15}N-H$ coupling ($J_{^{15}N-H}$ = 29 Hz) in the resulting ^1H NMR spectrum and the absence of detectable $^{31}P-^{15}N$ coupling (expected for trans-related atoms) in the resulting ^{31}P NMR spectrum both are consistent with structure **4b** in which the H and $CH_3C^{15}N$ ligands are trans related.

Measurements of the kinetics of reaction 4 at −78 °C yielded a rate constant, 0.13 M^{-1} s^{-1}, in excellent agreement with the value of k_2 (0.14 M^{-1} s^{-1}), extrapolated from kinetic measurements on reaction 2 over the temperature range 0–50 °C. This supports the conclusion that reaction 4, leading to the formation of the intermediate **4a**, also is the rate-determining step of reaction 2, i.e., of the $[Rh(diphos)]^+$-catalyzed hydrogenation of MAC at ambient temperatures.

The species **4a**, generated as described above, was stable in methanol solution at −78 °C for at least 1 day. Warming to temperatures above −65 °C resulted in decomposition at measurable rates, according to eq 5, to yield *N*-acetylphenylalanine methyl ester (**3**) and $[Rh(diphos)]^+$, thus completing the catalytic cycle for the $[Rh(diphos)]^+$-catalyzed hydrogenation of MAC. Reaction 5, monitored by ^{31}P and ^1H NMR, obeyed the first-order rate law $-d[\mathbf{4a}]/dt = k_5[\mathbf{4a}]$, with values of k_5 ranging from 6.0 × 10^{-4} s^{-1} at −56.4 °C to 5.9 × 10^{-3} s^{-1} at −43.4 °C, corresponding to $\Delta H_5^{\ddagger}$ = 17.0 kcal/mol and $\Delta S_5^{\ddagger}$ = 6.0 cal mol^{-1} deg^{-1}. The temperature dependencies of k_2 and k_5 are such that, at 1 atm of H_2, the rates of reactions 2 and 5 are comparable at about −40 °C, the former reaction being rate determining at higher temperatures and the latter at lower temperatures (where the intermediate **4a** can, accordingly, be intercepted).

Although hydridoalkyl complexes, analogous to **4a**, have been postulated as intermediates in many other homogeneous catalytic hydrogenation reactions,[1,2] in no other case to our knowledge has such an intermediate been intercepted and characterized. Comparison of the kinetic parameters of the present system with those of other catalytic hydrogenation reactions [e.g., the $Rh(PPh_3)_3Cl$-catalyzed hydrogenation of olefins][13] and of other hydridoalkyl reductive elimination reactions (e.g., the intramolecular reductive elimination of CH_4 from *cis*-$[PtH(CH_3)(PPh_3)_2]$)[5] suggests that the distinctive circumstances permitting the interception of **4a** are associated, not with unusual kinetic stability of the latter, but rather with an unusually high rate of the migratory insertion step (i.e., the second step of eq 6). This system thus is distinctive in that the steps leading to the formation of the intermediate **4a** occur at sufficiently low temperatures to permit the latter to be intercepted. The reasons for this are not clear and are being further investigated.

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