solid state, none of these resonances appears to arise from the N–N stretching as $\mathbf{1}$-^{15}N exhibits a virtually identical spectrum.

The coordination of N_2 is quite robust and only traces of nitrogen were pumped-off from a solution of **1** in THF, during several evacuation cycles carried out in a high-vacuum line equipped with a Toepler pump. However, complex **1** exhibited a quite promising chemical reactivity because replacement of (μ-N_2) can be achieved with a number of reagents including CO, acetylenes, and other unsaturated organic substrates. An extensive study to delineate the chemistry of this complex is in progress at the moment.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and an extensive list of bond distances, angles, and torsion angles (19 pages); tables of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

Formation of NH_x(a) Species by Hydrogenation of c(2×2)-N on Pd(100)

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Neither dissociative adsorption of N_2 on palladium metal surface nor formation of bulk nitride of palladium has been observed. So far, only adsorption of nitrogen stimulated by electron bombardment on polycrystalline Pd,[1] Pd(331),[2] Pd(110),[3] or enrichment or accumulation of nitrogen through dissociative adsorption of NO on Pd(331)[2] or during reaction of NO with CO or H_2 nitrogen on polycrystalline Pd[4] has been reported in the literature. The catalytic reduction of NO with hydrogen or carbon monoxide, NO + H_2 or CO → N(a) + H_2O or CO_2, on a Pd(100) surface yielded the ordered adsorption of N in a c(2×2) structure.[5] In this paper, NH_x intermediates were detected during hydrogenation of N(a) on a Pd(100) surface by high-resolution electron energy loss spectroscopy (HREELS).

Experiments were performed in an ultrahigh vacuum chamber attached with a small-volume, high-pressure reactor of which details were reported elsewhere.[6] A clean surface was obtained by Ar ion bombardment and oxidation at a 10^{-7} Torr of O_2 at 700–900 K followed by annealing in vacuum. The clean Pd(100) surface was exposed to a 1:1 mixture of NO and H_2 or NO and CO at a total pressure of 2–4 Torr and 550–600 K for 5 min. The gas phase was evacuated, and the crystal was rapidly cooled to room temperature. The crystal was then heated to 450 K for a few seconds to remove molecularly adsorbed species. By this procedure, a clean Pd(100) surface only with adsorbed nitrogen in a relatively large amount, N(KLL)/Pd(MNN) = 0.02, was obtained.[5]

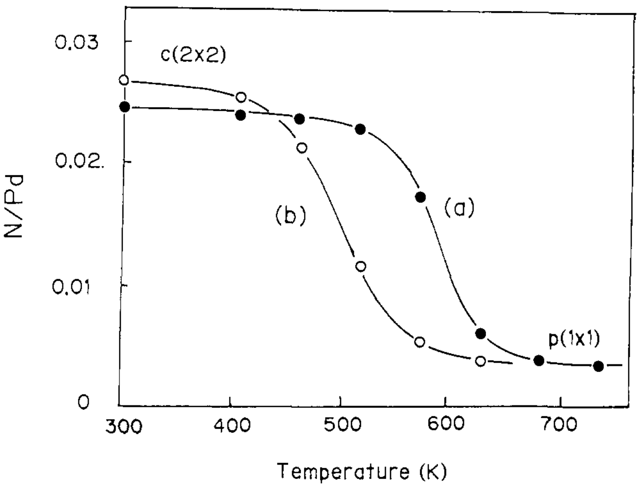

Figure 1. Change of N(KLL)/Pd(MNN) AES ratio when c(2×2)-N on the Pd(100) surface was heated in vacuum (curve a) and in H_2 of 1 × 10^{-6} Torr (curve b).

Figure 1 shows the change of the N/Pd Auger peak ratio when the c(2×2)-N on the Pd(100) surface was heated up step by step in vacuum (curve a) and in 1 × 10^{-6} Torr of H_2 (curve b). It is clear that the N/Pd ratio started to decrease at about 550 K in vacuum but at 430 K in H_2. HREELS was used to follow the surface reaction of c(2×2)-N with hydrogen. A c(2×2)-N overlayer was prepared on the Pd(100) surface and was examined by in situ HREELS experiments while exposing the surface to 1 × 10^{-7} Torr of H_2 at 400 K for 50 min. The N–H stretching vibration was seen at 3190 cm^{-1}. The deformation frequencies of the NH_x (x = 1, 2, 3) species were observed between 1140 and 1600 cm^{-1} for NH_3(a),[7] 1560 cm^{-1} for NH_2 in an amido(NH_2) complex of Co,[8] and 1414 cm^{-1} for NH in a imido(NH) complex of Os.[9] Our spectra do not have sufficient resolution (about 20 meV during this experiment) to identify the specific value of x, and a very weak band which might correspond to Pd–N was recognized in some cases at 720 cm^{-1}. Figure 2 shows the time dependent change of the HREELS spectra of the c(2×2)-N Pd(100) surface in the presence of 10^{-7} Torr of H_2 at 375 K. The heating current through the sample during measurement of the energy loss spectrum may be responsible for the poor S/N ratio of the spectrum. The loss peak for the NH_x species grew for 16 min (spectrum 2). When the H_2 was replaced with D_2 at 19 min, the peak for ND_x appeared immediately (spectrum 4) and became the major peak at 41 min (spectrum 5). A large inverse isotope effect in the synthesis of ammonia on a doubly promoted Fe catalyst[10] and a large normal isotope effect in the decomposition of ammonia on W-filament, powder, and polycrystalline foil[11] have been observed. In the case of the hydrogenation reaction of c(2×2)-N on the Pd(100) surface, when the ambient gas was replaced with a 1:1 mixture of H_2 and D_2 (1 × 10^{-7} Torr) at 53 min, peaks for NH_x and ND_x were observed simultaneously (spectra 6 and 7). The S/N ratio was rather poor, but no appreciable isotope effect was observed for the equilibrium amounts of the NH_x species on the Pd(100) surface. The LEED pattern of c(2×2) did not change when the surface was exposed to H_2 at around 400 K, and there was no great difference from the c(2×2) of pure N(a) by visual observation of the "I-V" function. When the surface with NH_x was heated up to 450 K in vacuum, the peak at 3190 cm^{-1} disappeared, but no appreciable decrease of N(a) by AES was observed. It is therefore likely that N(a) is still the dominant species and NH_x is a small part on the surface,

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and the formation of NH_x intermediates is reversible on Pd(100) surface. When a c(2×2)-N Pd(100) surface was subjected to a temperature-programmed reaction in a flow of H_2 at 1 × 10^{-6} Torr, a peak of NH_3 appeared at 460 K which was coincident with the temperature for the decrease of N(a) in Figure 1. We conclude that the c(2×2)-N is an intermediate in the NH_3 formation reaction, and its hydrogenation reaction proceeds at the boundaries of islands of c(2×2)-N on Pd(100).

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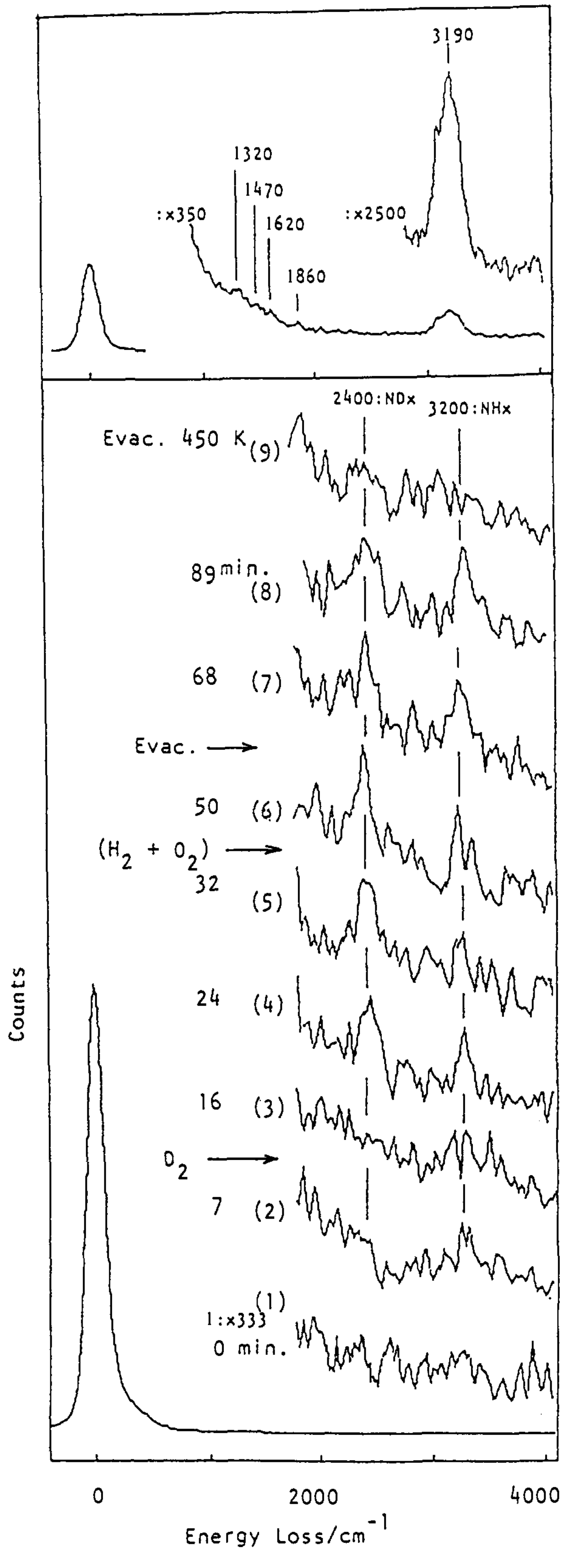

Figure 2. HREELS of the c(2×2)-N surface exposed to 10^{-7} Torr of H_2 at 400 K for 50 min (wide range spectrum) and growth of N–H stretching vibration peak at 3190 cm^{-1} in the presence 10^{-7} Torr of H_2 at 375 K: (1) starting c(2×2)-N surface (N/Pd = 0.0216, O/Pd = 0.0039), (3) ambient H_2 was replaced with 1 × 10^{-7} Torr D_2 between (2) and (3) at 10 min, (6) ambient gas was replaced with 5 × 10^{-8} Torr of H_2 + 5 × 10^{-8} Torr of D_2 between (5) and (6) at 44 min, (7) ambient gas was evacuated between (6) and (7) at 55 min, (8) AES of the surface gave N/Pd = 0.016, O/Pd = 0.004, (9) flashed surface at 450 K in vacuum (N/Pd = 0.016, O/Pd = 0.005).

Glycosylation of Unreactive Substrates

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In spite of the advances that have been made in carbohydrate chemistry in recent years, efficient glycosylation of unreactive substrates remains a significant problem. Hindered alcohols[1a] and derivatives of phenol[1b] present particular difficulties, and in many instances none of the available glycosylation methods work well.[2] We report a new method for rapid glycosylation of unreactive substrates in high yield under mild conditions (Scheme I).[3] In a dramatic illustration of the efficacy of the method, we describe the first direct glycosylation of an amide nitrogen.

This investigation grew out of our interest in glycosylating deoxycholic acid derivative **1** (Table I). The C-7 hydroxyl in this compound is extremely hindered due to an unfavorable 1–3 diaxial interaction with the C-4 methylene in the A ring and available glycosylation procedures require extended reaction times and give poor yields (0–30%).[2] By contrast, our method glycosylates the C-7 hydroxyl rapidly and in good yield. In a typical reaction, 2 equiv of sulfoxide **6** (0.3 mmol) were added in toluene (1 mL) to triflic anhydride (0.3 mmol) in toluene (2 mL) at −78 °C followed by an acid scavenger (0.225 mmol, 2,6-di-*tert*-butyl-4-methylpyridine in toluene) and sterol **1** (0.15 mmol in 0.5 mL of toluene). After warming to −60 °C the reaction was poured into aqueous bicarbonate and a single steroid adduct was isolated in 86% yield after chromatography on silica gel.[4] The stereochemistry was assigned to be α(axial) by NMR. An X-ray crystal structure of the debenzylated ($Pd(OH)_2$-H_2-MeOH, 50 psi, 12 h, 93%) glucosteroid (Figure 1) confirmed the stereochemical assignment[5] as well as the severe steric interaction between the

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(3) The sulfoxide is obtained by mCPBA oxidation of the corresponding sulfide (equiv, 0.1 mM, CH_2Cl_2, −60 °C to room temperature, 85%). O-Glycosylation based on activation of 1-thioglycosides has been studied extensively. Inter alia: (a) Ferrier, R. J.; Hay, R. W.; Vethaviyasar, N. *Carbohydr. Res.* **1973**, *27*, 55. (b) Mukaiyama, T.; Nakatsuka, T.; Shoda, S. *Chem. Lett.* **1979**, 487. (c) Van Cleve, J. W. *Carbohydr. Res.* **1979**, *70*, 161. (d) Hanessian, S.; Bacquet, C.; Lehong, N. *Ibid.* **1980**, *80*, C17. (e) Garegg, P. J.; Henrichson, C.; Norberg, T. *Ibid.* **1983**, *116*, 162. (f) Nicolaou, K. C.; Seitz, S. P.; Papahatjis, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 2430. (g) Lonn, H. *Carbohydr. Res.* **1985**, *139*, 105, 115. (h) Sato, S.; Mori, M.; Ito, Y.; Ogawa, T. *Ibid.* **1986**, *155*, C6. (i) Pozsgay, V.; Jennings, H. J. *J. Org. Chem.* **1987**, *52*, 4635. (j) Murata, S.; Suzuki, T. *Chem. Lett.* **1987**, 849.

(4) Ratio determined by HPLC (resolve silica μm, 8 mm × 10 cm, flow rate 1.8 mL/min, CH_2Cl_2–ethyl acetate 98:2, UV 254 nm, retention time: α = 10.7 min, β = 15.3 min). The stereochemical outcome of glycosylation is independent of the stereochemistry of the starting sulfide. All new compounds were characterized by ^1H and ^{13}C NMR, IR, and high-resolution mass spectral analysis.

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