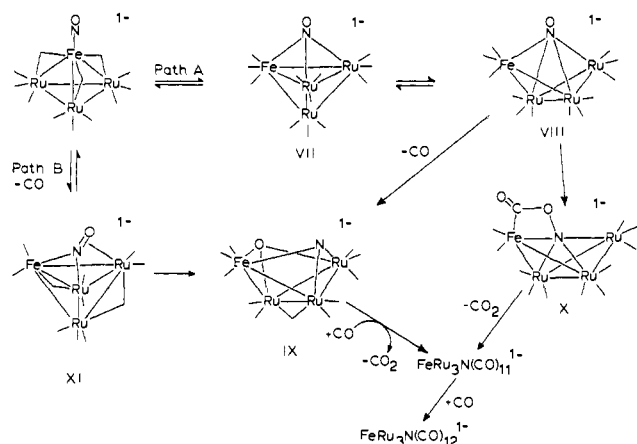


Scheme II



donated to the cluster and could result in the N–O bond cleavage.

Conclusions

In this study we have evaluated the conversion of a nitrosyl ligand to a nitrido ligand on a tetranuclear cluster. The data suggest that the conversion is intramolecular and possible mechanistic pathways have been suggested. The butterfly cluster $[\text{FeRu}_3\text{N}(\text{CO})_{12}]^-$ exists in two isomeric forms both in the solid state and in solution. The thermodynamic and kinetic parameters

for the interconversion of the isomeric forms provide the first evidence that the wing-tip and hinge positions of butterfly clusters having μ_4 -bridging atoms can interconvert.

The isolation of $[\text{FeRu}_3(\text{CO})_{12}(\text{NO})]^-$ has afforded us a unique opportunity to study in detail a complex and important reaction of a metal cluster. Studies such as this provide strong evidence supporting the idea that multiple coordination sites are valuable for activating small molecules. Further work in progress is designed toward the synthesis of new molecules that may allow us to directly observe some of the suggested reaction intermediates in Scheme II.

Acknowledgment. We wish to thank the National Science Foundation for supporting this research (Grant No. CHE-8106096) and Doyle Britton and Robert Stevens for valuable assistance with the x-ray diffraction studies. The FAB mass spectrum was obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska.

Registry No. I, 90968-63-1; I- Et_4N , 90968-65-3; I-PPN, 90968-68-6; II, 90968-66-4; II- Et_4N , 90968-67-5; II-PPN, 90968-69-7; PPN $[\text{FeRu}_3(\text{CO})_{12}(\text{NO})]$, 76791-97-4; PPN $[\text{FeRu}_4\text{N}(\text{CO})_{14}]$, 90990-44-6; PPN $[\text{Fe}(\text{CO})_3(\text{NO})]$, 61003-17-6; $\text{Et}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$, 35610-51-6; $[\text{Fe}(\text{CO})_3(\text{NO})]^-$, 15020-24-3; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{P}(\text{OCH}_2)_3$, 121-45-9.

Supplementary Material Available: A listing of the rate data for reaction II and the isomerization of I to II as well as the details of the crystallographic studies (37 pages). Ordering information is given on any current masthead page.

Coordination Chemistry of Pyridines on Ni(100)

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Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720. Received December 19, 1983

Abstract: The coordination chemistry of methyl-substituted pyridine molecules on Ni(100) is described. The position of methyl substitution had a profound effect upon pyridine surface chemistry. 4-Methylpyridine behaved analogously to pyridine and showed extensive molecular desorption. The decomposition of this pyridine yielded H_2 in three different maxima: the data suggest that the first step yields α -pyridyl and that the CH_3 C–H bonds are not cleaved at low temperatures (as is the case for 3,5-dimethylpyridine). In contrast, both 2-methylpyridine and 2,6-dimethylpyridine show CH_3 C–H bond breaking at low temperatures. These results are discussed in terms of the C_5N ring orientation with respect to the Ni(100) plane for this methylpyridine chemistry.

We have previously reported¹ on the chemistry of pyridine on nickel surfaces. Through the use of specific isotope labeling, the reversible regiospecific scission of α carbon–hydrogen bonds was demonstrated for pyridine coordinated to Ni(100). However, no information about the coordination geometry of the pyridine molecule was obtained. The issue of pyridine coordination to transition-metal surfaces has been a subject of controversy with respect to the disposition of the pyridine ring relative to the surface and the primary mode of interaction. Pyridine is believed to bind to Pt(111) and -(100)² through the nitrogen atom on the basis of work function measurements. Near-edge X-ray absorption studies³ have established chemisorbed pyridine on Pt(111) to be perpendicular to the surface plane, at least for coverages above ~ 0.1 monolayer. However, recent photoemission data indicate

that either or both the nitrogen lone pair and the aromatic electrons may be involved in the bonding of pyridine to Pd(111),^{4a} Ir(111),^{4b} Cu(110),⁵ and Ag(111).⁶ Described below are thermal desorption studies of methyl-substituted pyridines on Ni(100). The variation in the hydrogen desorption due to decomposition of the methyl substituent appears to provide insight to the orientation of the ring with respect to the surface and also to the molecular motion which

(1) Wexler, R. M.; Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2034.

(2) Gland, J. L.; Somorjai, G. A. *Surf. Sci.* **1973**, *38*, 157; *Adv. Coll. Interface Sci.* **1976**, *5*, 205.

(3) Johnson, A. J.; Muetterties, E. L.; Stöhr, J. *J. Am. Chem. Soc.* **1983**, *105*, 7183.

(4) (a) Netzer, F. P.; Mack, J. U. *Chem. Phys. Lett.* **1983**, *95*, 492; *J. Chem. Phys.* **1983**, *79*, 1017.

(5) Bandy, B. J.; Lloyd, D. R.; Richardson, N. V. *Surf. Sci.* **1979**, *89*, 344.

(6) Demuth, J. E.; Christmann, K.; Sanda, P. N. *Chem. Phys. Lett.* **1980**, *76*, 201.

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† Deceased January 12, 1984.

leads to the regiospecific scission of α C-H bonds.

Experimental Section

Nickel single crystals (99.999% purity, Materials Research Corporation) were prepared as described previously⁷ except that the final chemical etching for the crystals was omitted since this often led to formation of an oxide film. The final cleaning of the single-crystal surfaces was performed in an ultrahigh vacuum chamber described previously. Clean Ni(100) surfaces were obtained by cycling of argon ion bombardment (6×10^{-5} torr, 1 kV, 10 A/cm², 700 °C, 5–15 min) and oxygen treatments (2×10^{-8} torr, 800 °C, 1 min) until sulfur was completely removed. Residual carbon was then removed by heating at 700 °C in 1×10^{-7} torr of oxygen for 1 min. Any remaining oxygen could be removed by heating to 700–800 °C.

A modified Varian flip offset manipulator was used, which allowed the crystal to be heated resistively while being continuously cooled. Heating was accomplished by passing currents of up to 20 amp through 0.010-in. diameter tantalum wires which were spot welded to the crystal. Conduction of heat through the spot welds and current passing through the crystal led to the heating of the crystal. Continuous cooling was achieved by placing a liquid air filled copper reservoir in thermal contact with the crystal via copper braids. A stainless steel shield with a $3/8$ -in. diameter circle was placed between the mass spectrometer ionizer and crystal to decrease any background desorption due to warming of cold parts of the manipulator. With the ionizer, circle in the shield, and crystal face aligned, the primary source of any observed mass signal was the crystal face. The crystal temperature was monitored by a chromel–alumel thermocouple in all experiments.

Reagent-grade chemicals were generally distilled in vacuum and degassed by three freeze–evacuate–melt cycles prior to introduction to the vacuum chamber. All samples were stored over 3- or 4-Å molecular sieves in vacuum at room temperature. The purity of each sample was judged by its mass spectrum by using either the quadrupole in the vacuum chamber or the UCB Department of Chemistry Mass Spectrometry Laboratory.

Pyridine was purchased from Mallinckrodt and pyridine-*d*₅ (99.5+%) was obtained from Merck, Sharpe & Dohme. All methyl-substituted pyridines and piperidine were purchased from Aldrich. A literature method⁸ was used to prepare *m*-xylene-*d*₆. This compound was graciously supplied by Robert Lum.

Results and Discussion

We seek a definition of the electronic and stereochemical features of the interaction of well-defined transition-metal surfaces with certain classes of organic molecules. Presently, a set of organic molecules of major interest to us is benzene and heteroaromatic molecules like pyridine, thiophene, furan, and pyrrole. A classic perturbation technique that can provide substantial insight to the surface interactions of these molecules is substitution of hydrogen by other atoms or groups at specific sites on the ring. In other studies, we have found methyl substitution to be an especially effective probe, specifically for benzene,^{9a} thiophene,^{9b} and as reported here, for pyridine.

As reported earlier,¹ pyridine on Ni(100) at 25 °C, and at approximately monolayer coverage,^{10a} undergoes competing molecular desorption (~50%) and decomposition in a thermal desorption experiment. The only pyridine decomposition products^{10b} that desorbed from the nickel surface were hydrogen and nitrogen. Distinctive for Ni(100) were the three H₂ desorption maxima of approximate relative intensities: 1:2:2 at ~100, 235, and 335 °C, respectively. The low-temperature peak is in the region characteristic of Ni(100)–H^{11a} derived from adsorption of H₂ on a clean

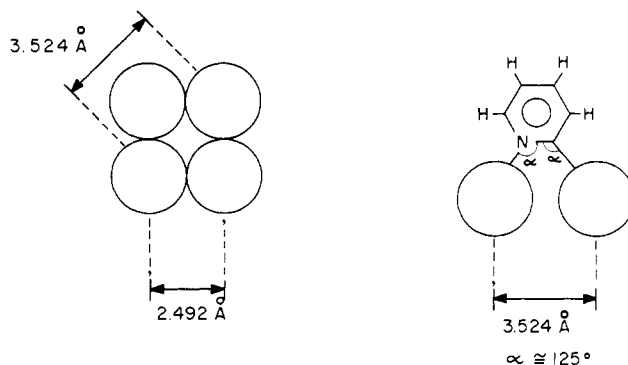


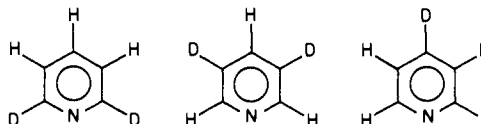
Figure 1. Nickel–nickel separation of 3.52 Å for the diagonal of the (100) unit cell and the interr ridge step of the (110) unit cell is well suited to accommodate a bridging η^2 -2-pyridyl ligand.

Table I. Short Metal–Metal Separations for the Face-Centered Cubic and Hexagonal Close-Packed Surface Planes

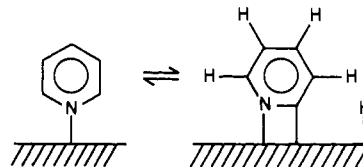
metal	bond ^a dist	separation, Å	
		(111) diag ^b – (001) diag	(110) step– (100) diag
nickel	2.492	4.316	3.524
palladium	2.751	4.765	3.891
platinum	2.746	4.757	3.883
cobalt	2.506	4.341	
ruthenium	2.650	4.590	
osmium	2.675	4.633	

^aData taken from: "Handbook of Chemistry and Physics", 55th ed.; CRC Press: Cleveland, OH, 1974–1975. At 18–25 °C. ^bLong diagonal.

Ni(100) surface (85 °C at saturation coverage to 130 °C at low coverage).^{11b} By studying the decomposition of the three deuterium labeled pyridines



it was established that the hydrogen (deuterium) that appeared in the low-temperature signature peak (~100 °C) was derived solely from one of the α -C–H(C–D) sites of the pyridines. These and related experiments defined a facile^{11c} equilibrium between molecularly bound pyridine and α -pyridyl:



The chemistry of pyridine on Ni(100) contrasts sharply with that on Ni(111) and Ni(111) × (111) where no molecular pyridine desorption occurs and only one hydrogen desorption peak is observed.¹ However, the decomposition of pyridine on Ni(110)^{11c} is similar to that on Ni(100) in that three peaks are observed in the hydrogen desorption spectrum with similar intensities to those from Ni(100). The differences in pyridine chemistry between the

(7) Friend, C. M.; Stein, J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767.

(8) Chen, T.-S.; Wolinska-Mocylarz, J.; Leitch, L. C. *J. Labelled Compds.* **1970**, *6*, 285.

(9) (a) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773; (b) unpublished results.

(10) (a) Coverage is defined as the ratio of surface non-hydrogen atoms to surface metal atoms. (b) Other potential decomposition products such as piperidine and bipyridine were not detected. Bipyridine chemisorption was not examined; probably this bifunctional molecule will undergo primarily decomposition on nickel surfaces under UHV conditions. Piperidine (at a coverage of ~0.4) exhibited competitive desorption and decomposition. Piperidine desorption began at about 65 °C and peaked at about 175 °C. H₂ from decomposition started at about 50 °C, peaked at about 170 °C, and had a small shoulder at about 290 °C.

(11) (a) Accordingly, the first pyridine C–H bond-breaking process occurs at measurable rates at 100 °C or below. (b) Any hydrogen desorption peaks occurring at higher temperatures are the result of reaction-limited steps. (c) This equilibrium is established^{11d} rapidly at 100 °C. Rates are probably high below this temperature. Our data provide no measure of the magnitude of the equilibrium constant at 100 °C. (d) Thermal desorption of pyridines following reaction of hydrogen or deuterium with the species derived from adsorption of each of the three deuterium-labeled pyridines displayed hydrogen incorporation into only pyridine-2,6-*d*₂ and deuterium incorporation into pyridine-3,5-*d*₂ and pyridine-4-*d* but not pyridine-2,6-*d*₂. (e) Friend, C. M.; Muetterties, E. L., unpublished results.

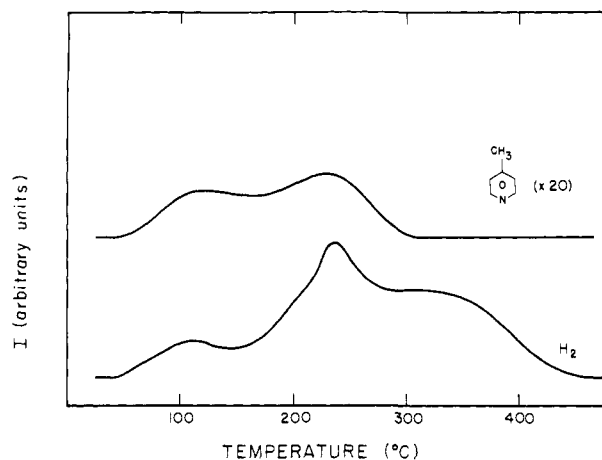


Figure 2. Thermal desorption of 4-methylpyridine and hydrogen desorption resulting from its decomposition on Ni(100) closely mimics the behavior of pyridine.¹ The increased intensity of the two high-temperature peaks of the hydrogen spectrum relative to the pyridine decomposition spectrum indicates that C–H bond scission in the methyl group occurs in the high-temperature region.

close-packed nickel surface and the nickel(100) and -(110) surfaces may be due to a geometric factor. The optimal Ni–Ni separation for a μ - η^2 -2-pyridyl interaction is ~ 3.3 Å using 1.91 Å Ni–N and 1.85 Å Ni–C distances.¹² However, the two Ni–Ni separations on a Ni(111) surface that could be used for a μ - η^2 -2-pyridyl bonding are 2.49 and 4.29 Å. Hence there would be substantial internal ring strain were the 2-pyridyl species to bridge either the edge or the diagonal of the Ni(111) unit cell (the 2-pyridyl species could be centered over a single nickel atom¹³ but the ring strain in such a three-membered ring system would be even more pronounced than for the bridging positions on the (111) nickel surface). In sharp contrast to Ni(111), the Ni(100) and Ni(110) surfaces, which do exhibit regiospecificity for C–H bond breaking in pyridine, have virtually ideal separations: the nickel–nickel separation is 3.52 Å for the diagonal nickel atoms on the Ni(100) unit cell and for the “step” atoms in the interr ridge or repeating step of the Ni(110) surface (Figure 1). Thus, both Ni(111) and Ni(100) can support a μ - η^2 -2-pyridyl species without significant bond angle distortions. Based on these purely geometric features of a μ -pyridyl ground state, Co(001) should not exhibit extensive regiospecificity in the initial C–H bond breaking of pyridine. Also, the degree of regiospecificity in the nickel group should follow the trend Ni > Pd \approx Pt, and rhodium and iridium should be analogous to Pd and Pt¹⁴ (see Table I). Experimentally, the former trend has been confirmed.¹⁵ Note that these projections ignore electronic factors that could be substantial in changing groups or in going from a 3d to a 4d or a 5d metal.

With this basic background for pyridine, we now consider the results for the methyl-substituted pyridines. Introduction of one methyl group at the 4-position should not significantly perturb the nickel(100) surface chemistry of pyridine because the methyl hydrogen atoms would be directed away from the surface and should not electronically alter the pyridine surface binding energy to a significant degree. This was the experimental observation.

4-Methylpyridine chemisorbed on Ni(100) to give a state that on heating produced molecular desorption and thermal decom-

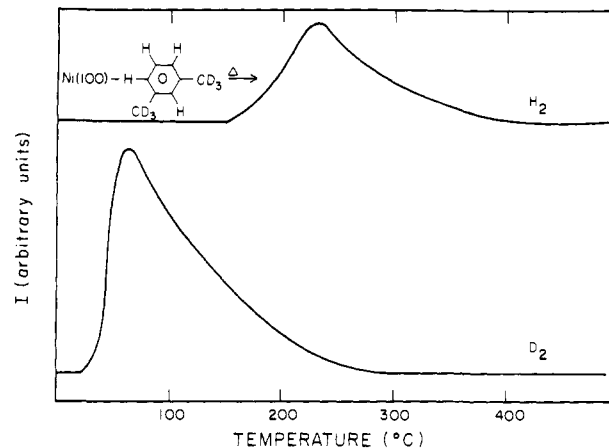


Figure 3. As indicated by the H₂ and D₂ evolution from thermal decomposition of *m*-xylene-*d*₆ on Ni(100), the methyl group carbon–hydrogen bonds are broken prior to scission of aromatic carbon–hydrogen bonds. Due to the presence of background hydrogen and the temperature overlap of C–D and C–H bond breaking, HD was also observed with two overlapping peaks at 60 and 225 °C. The intensities of the HD peaks were comparable (second peak slightly more intense) to the intensity of the H₂ peak.

position to degrees comparable to the parent pyridine molecule (Figure 2). Molecular desorption of 4-methylpyridine began at ~ 50 °C and reached a plateau at ~ 200 °C. The rate then increased and peaked at 240 °C. The hydrogen desorption spectrum (Figure 2) from the fraction of pyridine that decomposed consisted of three peaks, as for pyridine itself, at ~ 110 , 235, and 325 °C; even the temperature maxima were similar to those for pyridine.¹ The third peak was broad and appeared as a shoulder on the 235 °C peak. The ratio of the 110 °C peak intensity to the combined intensities of the 235 and 335 °C peaks was approximately 1:6. Clearly, it must be the α -C–H bond that is first cleaved in Ni(100)–4-methylpyridine. This is consistent again with a facile equilibrium between molecularly bound 4-methylpyridine and the α -pyridyl species derived from this methylpyridine. The absence of attack of the methyl C–H hydrogen atoms at low temperatures is also a very significant observation. Had 4-methylpyridine been wholly or partially bound, as the molecule, on this surface with an orientation in which the C₅N ring plane were nearly parallel to the surface plane, the methyl C–H bonds probably would have been cleaved first (compare below the behavior of 2-methylpyridine and 2,6-dimethylpyridine). Accordingly, the chemisorption process probably would have been irreversible or at least less reversible than for pyridine.

There is the possibility that pyridine could bond to a flat metal surface in an η^6 -fashion (parallel to the surface plane)—e.g., under conditions of low coverage or if the pyridine nitrogen atom were made relatively inaccessible by bulky substituents at the 2-position or 2- and 6-positions. Accordingly, it is informative to compare pyridine chemistry with arene chemistry since the arenes do bind in an η^6 -fashion on flat metal surfaces. Of special relevance is the effect of methyl substituents on the nickel surface chemistry of benzene.

Benzene reversibly (partially) chemisorbs on nickel surfaces under UHV conditions.^{9a,16,17} However, methyl-substituted benzenes irreversibly chemisorb on Ni(111) or Ni(100). Specifically studied have been toluene, the isomeric xylenes, and mesitylene.^{9a,15} In the decomposition of these methylbenzene

(12) Unperturbed pyridine ring parameters were used and obtained from: Mootz, D.; Wussow, H.-G. *J. Chem. Phys.* **1981**, *75*, 1517. The distances used for Ni–N and Ni–C were 1.91 and 1.85 Å, respectively.

(13) A nonbridging η^2 -2-pyridyl configuration is reported for (C₅H₅)₂Ti(6-NC₅H₃(CH₃)) (Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *214*, 53) and for [η^2 -C₅(CH₃)₃]Lu(NC₅H₄) (Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337). The latter has been crystallographically confirmed, unpublished data.

(14) We have established that there is some regiospecificity for Ru(001)–NC₅H₃ and Os(001)–NC₅H₃, but it is difficult to quantitatively compare these with palladium and platinum. Shanahan, K. L.; Muettterties, E. L., unpublished results.

(15) Unpublished observations from our laboratory.

(16) Benzene molecularly chemisorbs on flat metal surfaces with the ring plane parallel to the surface plane.^{17a–h}

(17) (a) Kelemen, S. R.; Fischer, T. E. *Surf. Sci.* **1981**, *102*, 45. (b) Avouris, P.; Demuth, J. E. *J. Chem. Phys.* **1981**, *75*, 4783. (c) Lehwald, S.; Ibach, H.; Demuth, J. E. *Surf. Sci.* **1978**, *78*, 577. (d) Bertolini, J. C.; Rousseau, J. *Ibid.* **1979**, *89*, 467. (e) Hofmann, P.; Horn, K.; Bradshaw, A. M. *Ibid.* **1981**, *105*, L260. (f) Lloyd, P. R.; Quinn, C. M.; Richardson, N. V. *Solid State Commun.* **1977**, *23*, 141. (g) Fischer, T. E.; Kelemen, S. R.; Bonzel, H. P. *Surf. Sci.* **1977**, *64*, 157. (h) Koel, B. E.; Somorjai, G. A. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *28*, 287.

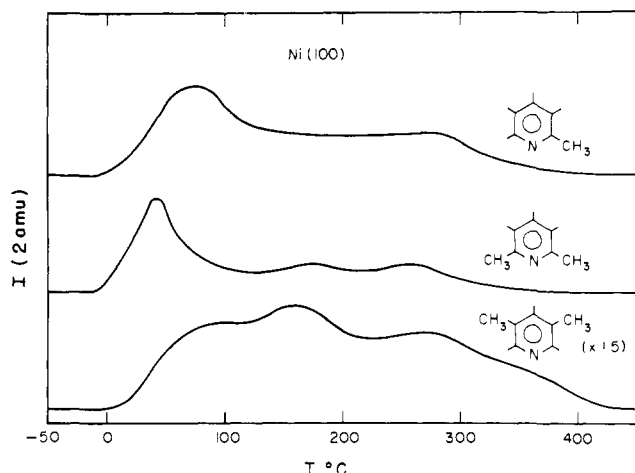


Figure 4. Molecular hydrogen desorption arising from decomposition of 2-methylpyridine and 2,6-dimethylpyridine indicates that methyl groups α to the nitrogen undergo C–H bond scission prior to aromatic C–H bond breaking. The H_2 desorption spectrum from 3,5-dimethylpyridine decomposition on Ni(100) shows a lack of intensity variations that is found for other methyl-substituted aromatic molecules. Thus, it is likely that the pyridine ring is oriented at an acute angle relative to the surface although not parallel to the surface plane.

molecules, the hydrogen, H_2 , product typically desorbs with two maxima, and it is the methyl hydrogen atoms that appear in the low-temperature peak. Thus, the methyl C–H bonds are broken first. For toluene¹⁸ on atomically flat nickel surfaces, this feature is dominant, and the C–H bond breaking is fully regiospecific as shown in experiments with $CD_3C_6H_5$ and $CH_3C_6D_5$.^{9a} To probe the regiospecificity further, as background information to compare with the dimethylpyridine systems, the decomposition of 1,3-xylene on Ni(100) was studied. In this system, the hydrogen desorbs with two maxima, one at 90 °C and the other at 200 °C (compared with toluene where the maxima were at ~ 110 and 230 °C) with a respective intensity ratio of $\sim 6:4$. Illustrated in Figure 3 are the hydrogen and deuterium desorption spectra for the decomposition of Ni(100)–1,3-(CD_3)₂C₆H₄.¹⁹ Here, the distribution of D_2 and H_2 clearly show that the hydrogen atoms from the two methyl groups are responsible for the low-temperature hydrogen desorption and that the aromatic C–H hydrogen atoms appear only in the high-temperature peak.

The chemistry of pyridine molecules containing one or two methyl groups α to the nitrogen atom is much different than that observed for pyridine and 4-methylpyridine. After adsorption to monolayer coverage at -60 or 25 °C, neither 2-methylpyridine nor 2,6-dimethylpyridine detectably desorbed from Ni(100). In addition, the character of the hydrogen evolution due to decomposition of the respective pyridines (Figure 4) was distinctively different from those of pyridine and 4-methylpyridine. The hydrogen desorption spectra for both molecules was characterized by a low-temperature peak (50–100 °C) followed by a less intense (by a factor of 2) broad desorption, which ceased at approximately 430 °C. In the case of 2-methylpyridine, this broad desorption exhibited no distinct peak maximum while 2,6-dimethylpyridine decomposition exhibited weak maxima at 170 and 290 °C in this broad-desorption region.

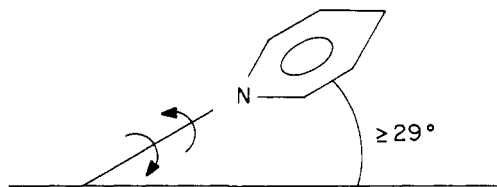
(18) High-resolution electron energy loss studies of Pt(111)–toluene at 20 °C are consistent with an η^6 -toluene ligand with the toluene in a plane parallel to the surface plane. Grassian, V. H.; Muettterties, E. L., unpublished results. Also, near-edge X-ray absorption fine structure studies³ indicate that toluene is in a plane parallel to the surface plane.

(19) The discrepancies in peak temperatures for the D_2 and H_2 observed from *m*-xylene-*d*₆ and the two H_2 peaks from *m*-xylene are probably the result of the following differences in the two experiments. Since the low-temperature peak is desorption limited, differences in initial xylene coverages would lead to variable peak temperatures. For the high-temperature peak, peak overlap leads to an increase in the amount of hydrogen desorption on the low-temperature edge for the unlabeled xylene relative to the labeled xylene, where overlap leads to formation of HD. Thus, the high-temperature peak for unlabeled *m*-xylene is skewed toward a lower temperature.

It appears that the placement of the methyl groups near the nitrogen atom of the pyridine ring substantially alters the surface chemistry of the pyridine moiety. The initial molecular bonding of the α -methylpyridines may have the ring plane far from normal to the surface plane. Steric factors introduced by the α -methyl groups could be sufficient to alter the relative stabilities of an η^1 -pyridine ligand and an η^6 -pyridine ligand on the flat Ni(100) surface. In any case, the intense low-temperature H_2 peak from 2,6-dimethylpyridine must be due to breaking of the α -methyl group C–H bonds. This characterization is similar to that proposed for the behavior of *m*-xylene on Ni(100), discussed above, where the methyl groups in the ground-state configuration are very close to surface metal atoms.

Once the initial C–H bond breaking has occurred in 2-methylpyridine and 2,6-dimethylpyridine, it would appear that the nitrogen lone pair may still be involved in bonding to the surface in the intermediate(s) leading to breaking of the aromatic C–H bonds since the high-temperature H_2 desorptions from 2-methylpyridine and 2,6-dimethylpyridine extend to much higher temperatures and are not well-defined peaks as observed for the *m*-xylene decomposition.

The behavior of 3,5-dimethylpyridine appears to be intermediate between those of the pyridine and 4-methylpyridine systems and the 2-methylpyridine and the 2,6-dimethylpyridine systems. As with the α -substituted pyridines, no 3,5-dimethylpyridine desorbed from Ni(100). However, the molecular hydrogen desorption (Figure 4) resulting from the decomposition of this pyridine molecule does not resemble that of any other methyl-substituted aromatic molecules, (*vide supra*) as a very broad desorption with weak maxima at about 60, 160, and 270 °C was observed. Since the low-temperature H_2 peak that seems to be prevalent in π -bonded methyl-substituted aromatic hydrocarbons and α -methyl-substituted heteroaromatics was not observed from 3,5-dimethylpyridine, it is unlikely that the methyl group C–H bonds are involved in the initial bond breaking. This would indicate that the pyridine ring is bonded to Ni(100) such that the methyl hydrogen atoms in the 3,5-dimethylpyridine are not interacting strongly with the nickel surface atoms below ~ 25 °C. With this proposed constraint of noninteraction, a geometric analysis using average bond distances from low-valent nickel complexes containing hydrogen²⁰ (Ni–H = 1.45 Å) and nitrogen²¹ ligands leads to a lower limit of 29° for the angle between the surface plane and the plane of the pyridine ring (1).



An initial binding of pyridine to nickel(100) through the nitrogen lone pair with the plane of the ring substantially tipped toward the surface may have implications concerning the uniqueness of the 3,5-dimethylpyridine decomposition and the molecular motion which leads to α -C–H bond breaking. The 3,5-dimethylpyridine is capable of undergoing the regiospecific α -C–H bond breaking established for pyridine and 4-methylpyridine. However, with the plane of the ring tilted with respect to the surface, α -C–H bond scission could be closely followed by scission of one or two methyl C–H bonds on the same side of the ring as the initially broken α -C–H bond. Rotation about the metal–nitrogen bond vector which would lead to the α -C–H bond breaking also would bring one methyl group closer to the surface. This could account for the initial hydrogen evolution, which is comparable in intensity to the remainder of the H_2 thermal desorption spectrum. While one methyl group is brought closer to the surface, this rotation of the ring takes the other methyl group

(20) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(21) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Oxford University Press: London, 1975; and references therein.

away from the surface. This would provide an explanation for the absence of a very intense peak at low temperatures in the H₂ spectrum from 3,5-dimethylpyridine decomposition. If the α -pyridyl species were nearly perpendicular to the surface, the intensity of the low-temperature region of the hydrogen spectrum would be low. This is because both methyl groups would still be far removed from the surface and would likely undergo C-H bond scission at higher temperatures causing much higher intensity in the high-temperature region of the spectrum. In addition, it might be expected that 3,5-dimethylpyridine oriented perpendicular to the surface would be capable of the same reversible α -C-H bond breaking process that preceded pyridine desorption. However, the lack of 3,5-dimethylpyridine molecular desorption and the relatively flat profile of the H₂ desorption as a function of temperature suggest that the pyridine ring and the α -pyridyl ring are oriented at an acute angle with respect to the surface and that the regioselective bond breaking is brought about through rotation

about the nitrogen-nickel bond rather than bending of this bond (1).

We plan temperature-dependent studies of this methylpyridine chemistry on Ni(100) by near-edge X-ray absorption fine-structure spectra (NEXAFS). These studies may establish accurate dihedral angles formed by the metal surface plane and the ring plane of the pyridines.

Acknowledgment. This research was supported by the National Science Foundation and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098. We are also indebted to the Fannie and John Hertz Foundation for a graduate fellowship (R.M.W.).

Registry No. Ni, 7440-02-0; pyridine, 110-86-1; 4-methylpyridine, 108-89-4; 2-methylpyridine, 109-06-8; 2,6-dimethylpyridine, 108-48-5; 3,5-dimethylpyridine, 591-22-0.

Intramolecular Influence of a Carboxylic Function on Platinum Blue Synthesis. A Systematic Study of Complexes Originating from Acid Amides

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Abstract: The use of acid amide as ligand for obtaining platinum blue has been investigated. While blue compounds are generally obtained by using the hydrolysis product of *cis*-dichlorodiammineplatinum(II) as platinum source, with such ligands the reaction occurs very readily using potassium tetrachloroplatinate(II). The role of the carboxylic function which offers here a primary ligating site to platinum is evidenced. The compounds obtained have been characterized by UV-visible spectral measurements, Ce(IV) oxidative titration, ESR spectroscopy, and magnetic properties. Antitumor activity toward leukemia L1210 and sarcoma 180 is reported for two of these compounds. As a first step for this antitumor study, these compounds have been found to be inactive toward Leukemia while they present interesting activity toward Sarcoma.

Interest in the blue platinum complexes has been recently raised by the discovery that *cis*-dichlorodiammineplatinum(II) (*cis*-DDP) displays antitumor properties probably related to its interactions with DNA.¹⁻⁷ An important outcome of the study of these interactions was the isolation of a new type of platinum complexes, "the platinum-pyrimidine blues", which seemed to be very promising with regard of their high index of antitumor activity associated with a low nephrotoxicity.^{8,9}

Independent of their pharmacological properties, the blue species raise many fundamental problems among which the most important was underlined by Lippert since 1979 and is related to the origin of their paramagnetic behavior.¹⁰ It is noteworthy that

the blue complexes retain their characteristics (color and paramagnetism) in solution while other mixed-valence compounds such as the violet Krogmann salts lose their color and paramagnetism in solution.

In spite of these physiological and physicochemical properties, a restricted number of blue platinum compounds has been described. Beside acetamide blue and other related amide complexes,^{11,12} interest has been essentially focused on pyrimidine blues and on the α -pyridone blue, which is the only species to be obtained as monocrystal and therefore extensively studied.¹³⁻¹⁸

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