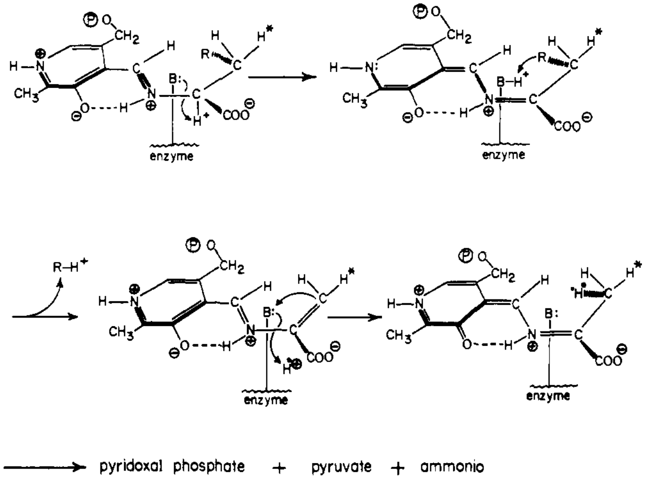
Scheme I



A plausible mechanism which incorporates these features is shown in Scheme 1. It appears that the enzyme obeys the minimal base number rule proposed by Hanson and Rose.[12]

Acknowledgments. We thank Professor H. Eggerer, Regensburg, for reference samples of authentic *R*- and *S*-acetate-*2-d*$_1$-*2-t*$_1$ and Professor R. Somerville, Lafayette, for *E. coli* strain A2/F′A2. This work was supported by U.S. Public Health Service Research Grant GM 18852 and by a postdoctoral fellowship (to E.S.) from the Max-Kade-Foundation, New York.

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Bis(2,6-dimethylpyridine)chromium. A π-Heterocyclic Complex

Sir:

Heterocyclic compounds are known to act as 5- or 6-electron ligands to form π-complexes with transition metals. Thus pyrrole,[1] pyridine,[2] indole,[2a] carbazole,[2a] and thiophene[3] nuclei are reported to form π-complexes to metal carbonyl moieties; the iron atom in azaferrocene, which is isomorphous with ferrocene, carries both pyrrole and cyclopentadienyl as π-complexed ligands.[1,4] We wish to report the synthesis and structure of bis(2,6-dimethylpyridine)chromium.

Table I. Crystallographic Data

	Form A	Form B
a (Å)	7.307 (1)	9.421 (1)
b (Å)	8.242 (2)	10.496 (2)
c (Å)	6.316 (2)	12.725 (2)
α (deg)	112.50 (3)	90
β (deg)	104.01 (2)	90
γ (deg)	102.46 (2)	90
Space group	$P\bar{1}$	*Pbcn*
No. of molecules per crystallographic asymmetric unit	1/2	1/2
Crystallographic site symmetry occupied by molecule	$\bar{1}(C_i)$	$2(C_2)$
Final $R(=\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.087	0.045

Bis(2,6-dimethylpyridine)chromium was prepared by co-condensing chromium atoms with the ligand at 77 K, the latter substance being present in excess; the apparatus employed is essentially that described by Timms.[5,6] The frozen matrix of ligand containing metal atoms undergoes the typical color change observed in other syntheses of this type (colorless → dark) as it warms to room temperature. The final reaction mixture is a red-brown solution in excess ligand containing dispersed unreacted metal. Excess ligand was removed in high vacuum, and the dark residue was sublimed to give a red-brown substance, as the sole product, in 2% yield (based upon chromium) which proved to be bis(2,6-dimethylpyridine)chromium (mp 79–80 °C). The product sublimes readily at 65 °C (10^{-3} Torr) and exhibits a molecular ion peak in the high resolution mass spectrum at 266.0877 mass units consistent with the expected molecular composition ($C_{14}H_{18}N_2{}^{52}Cr$ = 266.0875). The proton magnetic resonance spectrum of the substance shows a singlet at δ 2.38 and a complex multiplet centered at δ 4.40; the free ligand exhibits resonances at δ 2.52, assigned to CH_3, and δ 6.97 and 7.45 which are assigned to ring protons. The upfield shifts in the proton resonances are typical of those observed for analogous bisarenechromium compounds.[6] The proton magnetic resonance spectrum of bis(2,6-dimethylpyridine)chromium in toluene-d_8 is consistent with free rotation of the complexed rings down to −65 °C. The pure compound is unstable in air, decomposing to a nonvolatile green substance (Cr_2O_3?). Bis(2,6-dimethylpyridine)chromium is soluble in deoxygenated benzene, pyridine, tetrahydrofuran, hexane, acetone, and water; these solutions appear to be stable. The compound decomposes rapidly in carbon tetrachloride and carbon disulfide.

In order to obtain definitive proof of structure by x-ray crystal structure analysis, crystals were grown by vacuum thermal gradient sublimation. Crystals exhibiting two different morphologies were obtained: one form (A) grew as parallelepipeds, for the most part twinned, and proved to be triclinic; the other, plate-like form (B) was orthorhombic. X-Ray crystal structure studies have been carried out on both forms. In all cases, the crystal was mounted in an atmosphere of N_2 and then quickly transferred to a Syntex P2$_1$ diffractometer. During the course of all diffraction experiments[7] the data crystal was maintained in an environment of N_2 ca. −35 °C. Relevant crystal data are presented in Table I.

Both crystal structure determinations support the formulation of the molecule as the sandwich complex bis(2,6-dimethylpyridine)chromium. In crystal modification A (Figure 1), the molecule occupies a crystallographic inversion center, and thus the pyridine rings are strictly parallel. In

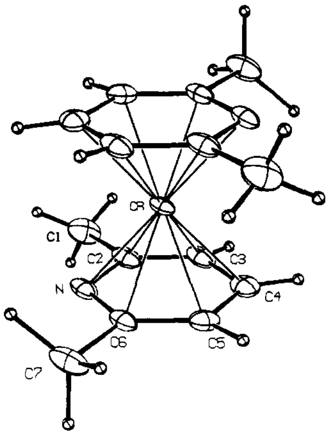

Figure 1. A view of the triclinic form (A) of $(C_7H_9N)_2Cr$. The Cr atom resides at a site of C_i symmetry. Selected bond lengths (Å): Cr-N = 2.151 (6), Cr-C(2) = 2.129 (8), Cr-C(3) = 2.128 (7), Cr-C(4) = 2.161 (8), Cr-C(5) = 2.130 (9), Cr-C(6) = 2.116 (8).

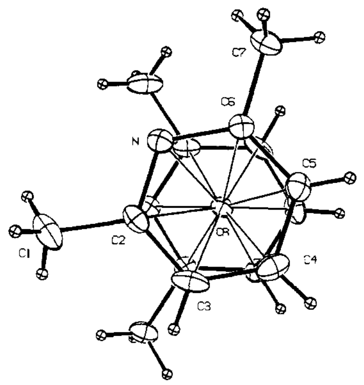

Figure 2. A view of the orthorhombic form (B) of $(C_7H_9N)_2Cr$ normal to the pyridine rings and to the C_2 axis which contains Cr. Note the staggered disposition of methyl carbons C(1) and C(7). Selected bond lengths (Å): Cr-N = 2.131 (3), Cr-C(2) = 2.126 (4), Cr-C(3) = 2.137 (3), Cr-C(4) = 2.134 (4), Cr-C(5) = 2.164 (4), Cr-C(6) = 2.125 (3).

crystal form B, the molecule resides on a twofold rotation axis that passes through the Cr atom and is parallel to the N-C(4) line. Hence, the rings are again strictly parallel, but now, as shown in Figure 2, methyl groups C(1) and C(7) are staggered.

Corresponding geometrical features of the complex in forms A and B are in good agreement.[8] For example, the mean Cr to ring atom distances are 2.136 (15) Å in A and 2.136 (10) Å in B. For sake of comparison, the mean Cr-C distances in dibenzenechromium[9] and benzenechromium tricarbonyl[10] are 2.142 (2) and 2.243 (14) Å, respectively. The least-squares planes calculated through the pyridine atoms show that these rings are planar in A, but slightly boat-shaped in B with atoms N and C(4) disposed (by 0.025 (3) and 0.033 (4) Å) toward Cr. In A methyl carbons C(1) and C(7) lie out of the pyridine planes (by 0.03 (1) Å) and away from Cr, but in B such displacements of atoms C(1) and C(7) are not apparent.

N-Methylpyrrole does not react with chromium atoms under the conditions of our experiment. However, pyridine, 2,6-difluoropyridine, and borazine react with chromium using the metal atom synthesis technique. In these cases, the products have not yielded to characterization using conventional methods; they possess low volatility and appear to be marginally stable. Further experiments are underway to prepare and characterize heterocyclic π-complexes of other transition metals, which will be reported elsewhere.

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On the Energy Threshold and Population Mechanism of One Metastable Methane Ion

Sir:

We wish to give detailed information about a metastable transition as observed from CH_4^+, under electron impact, in a double focusing mass spectrometer used in the defocusing mode.[1] The process which has been studied in both the normal and perdeuterated forms of the molecule is:

$$CH_4\cdot^+ \rightarrow CH_3^+ + H\cdot$$

A counting technique has been used for the energy threshold determinations. The thresholds are obtained at low source pressure (2×10^{-6} Torr) by the vanishing current method. The vanishing currents observed for ions of several of the noble gases are used as a calibration of the electron energy scale. The results are as follows. (a) The metastable ion decay has been observed to be an essentially unimolecular process. (b) The metastable peak observed for this process exhibits a thermal kinetic energy distribution (about 5 meV energy release, measured from the width at half-height). A weak component of width corresponding to an energy release of about 100 meV is only detectable at source pressures higher than 1×10^{-5} Torr. The peak widths are not in disagreement with more detailed values recently published by Solka, Beynon, and Cooks.[2] (c) The appearance potential (AP) of the fragments formed from metastable ions (16.0 ± 0.5 eV) is much higher than the AP for CH_3^+ ions formed by a fast process (14.25 ± 0.02 eV).[3] See Figure 1. (d) By using the ion source of the mass spectrometer in the Čermăk mode,[4] we have been able to detect charge transfer processes, as reported in Table I.

Intensities are expressed as the ratio of the peak height observed with the charge exchange gas present and absent. The table shows evidently that a metastable peak, corresponding to a process which is not observed under electron impact, is weakly induced by charge exchange between Kr^+ and CH_4. On the other hand charge exchange does not lead to production of metastable ions in the energy range corresponding to the AP of metastable ions observed under electron impact (i.e., with Ar^+, N_2^+, H_2^+).

These observations induce us to interpret the situation as follows. (a) Under electron impact, the metastable transition remains undetected near the threshold energy corre-