

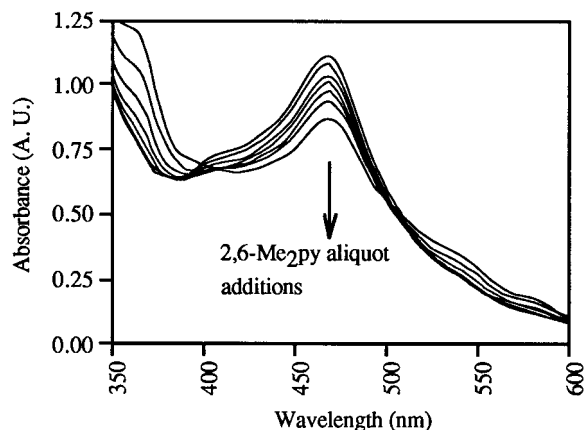
# Additions and Corrections

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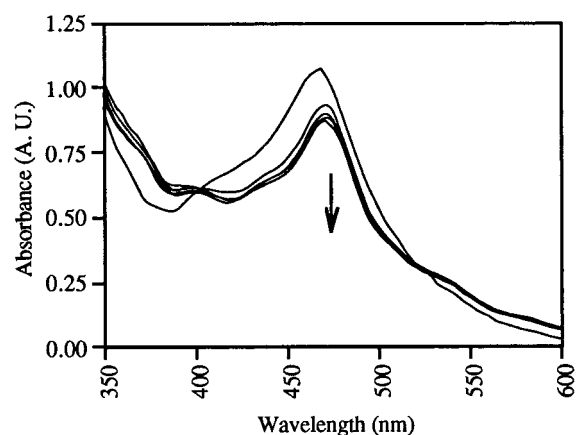
**Jeanne M. Sirovatka and Richard G. Finke\***: Coenzyme B<sub>12</sub> Axial-Base Chemical Precedent Studies. Adenosylcobinamide Plus Sterically Hindered Axial-Base Co–C Bond Cleavage Product and Kinetic Studies: Evidence for the Dominance of Axial-Base Transition-State Effects and for Co–N(Axial-Base) Distance-Dependent, Competing  $\sigma$  and  $\pi$  Effects.

Pages 1697–1707. The titrations of Co<sup>II</sup>Cbi<sup>+</sup> (generated photochemically from AdoCbi<sup>+</sup>) plus 2,6-dimethylpyridine (2,6-Me<sub>2</sub>py) and 3-methylpyridine (3-Mepy) in this paper have proven unrepeatable; the corrected, repeatable spectra are those in the revised figures provided, specifically Figures 5' and S9', which should be used to replace the original published Figures 5 (and its equivalent, S10) and S9, respectively, in the paper (S = figure in the Supporting Information). In hindsight, the original Figures 5 and S9 appear to be contaminated with an X-Cbi<sup>+</sup> (i.e., Co(III)) species, as can be seen by the increase in absorbance at 360, 500, and 550 nm, probably as a result of oxygen contamination. Since the original Figure 5 is incorrect, the possible explanation for the lack of isosbetics given on p 1702 and involving  $\alpha/\beta$  isomerism also cannot be correct (and, in any event, is itself a flawed argument, as Prof. L. Marzilli has brought to our attention, since in a quickly interconverting  $\alpha/\beta$  isomerism equilibrium, there is an equilibrium constant that allows one isomer to be expressed in terms of the other isomers' concentration and their equilibrium constant<sup>1</sup>). The flawed  $\alpha/\beta$  isomerism argument is repeated in the figure captions of Figures S7, S8, and S10 and should also be withdrawn from there.

Fortunately, the major conclusions in the paper are *not* changed by these results (the Co<sup>II</sup>Cbi<sup>+</sup>BF<sub>4</sub><sup>-</sup> titrations were done



**Figure 5'**. Repeated titration of  $\sim 1 \times 10^{-4}$  M Co<sup>II</sup>Cbi<sup>+</sup>BF<sub>4</sub><sup>-</sup> in degassed ethylene glycol with neat, degassed, 2,6-Me<sub>2</sub>py. After each aliquot of 2,6-Me<sub>2</sub>py was added, the cuvette was shaken for  $\sim 60$  s to ensure complete dissolution of the base into solution, and then the sample was equilibrated in the spectrometer for  $\sim 5$  min. A control was also done showing that the same result as above is obtained if Co<sup>II</sup>Cbi<sup>+</sup>BF<sub>4</sub><sup>-</sup> is generated by the photolysis of AdoCbi<sup>+</sup>BF<sub>4</sub><sup>-</sup> in the presence of TEMPO nitroxide, a control which suggests that the presence of photolysis byproducts is not the source of the irrepeatability in the published Figure 5 (or S9). (The expected photolysis byproducts are primarily the cyclic product 8,5-anhydroadenosine and H<sub>2</sub>, plus some 5'-deoxyadenosine and, initially, HOCH<sub>2</sub>CH(OH)<sup>•</sup> radical from Ado<sup>•</sup> abstraction of H<sup>•</sup> from the glycol solvent.<sup>4</sup>)



**Figure S9'**. Titration of photochemically generated Co<sup>II</sup>Cbi<sup>+</sup> with 3-Mepy at 25 °C, done exactly as described in the Experimental Section of our original paper. After each aliquot of 3-Mepy was added, the cuvette was shaken for  $\sim 60$  s to ensure complete dissolution of the base into solution, and then the sample was equilibrated in the spectrometer for  $\sim 5$  min.

only to provide independent evidence that bulky bases could bind to Co<sup>II</sup>Cbi<sup>+</sup>BF<sub>4</sub><sup>-</sup>, as an energetic model for the [Ado-Co<sup>II</sup>Cbi<sup>+</sup>•Base]<sup>‡</sup> homolysis transition state; that conclusion is still *probably* true, *vide infra*). However, to be rigorous the conclusion in the original paper that “sterically hindered bases do bind to Co<sup>II</sup>Cbi<sup>+</sup>BF<sub>4</sub><sup>-</sup>” should be changed to “sterically hindered bases do react with photochemically generated Co<sup>II</sup>Cbi<sup>+</sup>BF<sub>4</sub><sup>-</sup>, but the following will be required to prove that this reaction is, or is not, a simple axial-base coordination reaction: a clean synthesis of isolated, crystalline Co<sup>II</sup>Cbi<sup>+</sup>X<sup>-</sup> followed by EPR and other direct measurements of the reaction of that Co<sup>II</sup>Cbi<sup>+</sup>X<sup>-</sup> with sterically hindered bases.”

Typically, we carry out control experiments using Co<sup>II</sup>Cbl (or, if needed, the extremely air-sensitive Co<sup>II</sup>Cbl) to check the ability of our Schlenk cuvettes to maintain air-free conditions. However, it appears that the Schlenk cuvettes used in this particular work had developed an undetected leak after they were tested. Of course trace oxygen contamination is a very old—but obviously still prevalent—issue in working with air-sensitive organometallics,<sup>2</sup> the literature teaching that others have had to work hard to avoid artifacts when working with Co(II) cobamides over longer periods of time.<sup>3</sup>

- (1) Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: New York, 1992; Chapter 4, pp 103–106.
- (2) A textbook example is eq 4.25, p 263, of the following: Collman, J. P.; Hegedus, L. S.; Norton, R. N.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987.
- (3) Kratky, C.; Kräutler, B. X-Ray Crystallography of B<sub>12</sub>. In *Chemistry and Biochemistry of B<sub>12</sub>*; Banerjee, R., Ed.; J. Wiley and Sons: New York, 1999; Chapter 2; see p 26, where problems with air sensitivity of Co<sup>II</sup>Cbl impeding its crystal structure analysis are described.
- (4) Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *7*, 1469.

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