

In order to examine the kinetics of the NO insertion reaction, we have generated the alkyl complex **2a** at low temperature in the probe of an NMR spectrometer, in the presence of varying (excess) concentrations of triphenylphosphine. After warming to 10 °C, the conversion of **2a** to alkylnitroso complex **3a** was monitored by integration of the Cp resonances against ferrocene added as internal standard. Both the disappearance of **2a** and the appearance of **3a** exhibited good pseudo-first-order kinetics (Table I), giving rate constants within experimental error of one another in each case. Inspection of these data show that large changes in phosphine concentration produce only a very weak response in k_{obsd} . This requires rate-determining formation of an intermediate, which is trapped by phosphine faster than it returns to starting material. It seems most reasonable that the intermediate is the coordinatively unsaturated (or possibly THF-solvated) complex **4** (Scheme II).

In summary, these observations demonstrate that (a) a low-valent cobalt nitrosyl anion can be prepared; (b) this material is nucleophilic enough to undergo rapid alkylation with organic electrophiles; (c) the alkyl complexes formed in this way undergo NO migratory insertion under very mild conditions to give η^1 -RNO complexes; (d) the mechanism of this reaction involves initial formation of a coordinatively unsaturated (or solvated) RNO complex, followed by rapid reaction of this intermediate with phosphine. We conclude that the process of NO migratory insertion is not inherently difficult and the small number of examples

uncovered to date is probably a result only of the relatively few alkylnitrosyl complexes which are known.⁷ We are presently attempting to expand this class of reactions and also to find methods for efficient release of the organic ligand from the RNO complexes.

Acknowledgment. We acknowledge financial support of this work from the National Institute of Health (Grant GM-25459). The crystal structure analysis was performed by Dr. F. J. Holander, staff crystallographer at the UC Berkeley College of Chemistry X-ray Crystallographic Facility (CHEXRAY). Funds for the analysis were also provided by NIH Grant GM-25459.

Supplementary Material Available: Additional data from the X-ray diffraction study, including (a) two figures (S-1 and S-2) showing ORTEP drawings of each of the two molecules of complex **3b** in the unit cell, (b) seven tables of data (S-1 through S-7), covering crystal and data collection parameters, positional and thermal parameters, interatomic distances and angles, torsional angles, root-mean-square amplitudes of thermal vibration, and observed and calculated data points (36 pages). Ordering information is given on any current masthead page.

(7) For leading references, see: (a) Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317. (b) Connelly, N. G. *Inorg. Chim. Acta*, **1972**, *6*, 47. (c) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

Additions and Corrections

Stereochemistry of an Enzymatic Baeyer–Villiger Reaction. Application of Deuterium NMR [*J. Am. Chem. Soc.* **1981**, *103*, 1876]. JOHN M. SCHWAB, Department of Chemistry, Catholic University of America, Washington, D.C. 20064.

Scheme I. ^aBr₂, CCl₄. ^bEt₃N, CCl₄. ^cHOCH₂CH₂OH, *p*-TsOH, benzene, reflux. ^d*n*-BuLi, THF, -76 °C. ^e²H₂O. ^f(COOH)₂, CH₂Cl₂, H₂O. ^g*Beauveria sulfurescens* ATCC 7159.

Scheme II. ^aMCPBA, CHCl₃. ^bDIBAL, THF, -76 °C. ^c(Ph₃P)₃RhCl, benzene, reflux. ^d(-)-Camphanyl chloride, pyridine.

Conformations of Six *N*-Methylated Diketopiperazines in Solution [*J. Am. Chem. Soc.* **1980**, *102*, 5999]. W. RADDING,* B. DONZEL, N. UYAMA, and M. GOODMAN,* Department of Neurological Surgery College of Physicians and Surgeons, Columbia University, New York, N.Y. 10032, and Department of Chemistry, University of California, San Diego, La Jolla, California 92093.

On page 6004 the caption to Figure 11 should read as follows: (a) *c*-(L-NMePhe)₂ in Me₂SO and in the solid state. (b) *c*-(L-NMePhe)₂ with $B > 0$. (c) and (d) of the caption are correct as published.

In the first paragraph on page 6004, third sentence: TFA/CCl₃ should be changed to TFA/CDCl₃.

In the second paragraph on page 6004, second sentence: in both instances CCl₃ should be changed to CDCl₃.

In the last paragraph on page 6004, second sentence: Figure 8d should be changed to Figure 11d.

On page 6005, first sentence, second line: pseudoequatorial should be changed to pseudoaxial; the end of the sentence, "even in this $\beta > 0^\circ$ situation" should be deleted.

On page 6005, first paragraph, first sentence: Figure 8b should be changed to Figure 11b.

On page 6005, the entire second paragraph should be replaced and should read as follows: Given the NMR-determined rotamer populations, an explanation for the fact that *c*-(L-NMePhe)₂ apparently exists in the pseudoaxial conformation in solution might be that the side chains can be arrayed in various correlated

conformations. If the NMR rotamer populations of both side chains are considered to be uncorrelated in CDCl₃ and Me₂SO, the two side chains would be in contact approximately 25% of the time (Table III). It seems likely that some effect, perhaps ring–ring interactions, obviates the tendency of steric side chain repulsion to force the molecule into the $\beta > 0$ conformation. This view of folded rotamer contrasts with calculations which arrive at an energy minimum for $\chi = 60^\circ$ without the introduction of special inter-ring forces^{38,39} although a simple van der Waals exclusion model could not predict the side-chain energy minimum.⁴⁰

The Solution Conformational Preferences of the Sugar and Sugar Phosphate Constituents of RNA and DNA [*J. Am. Chem. Soc.* **1980**, *102*, 7433]. JOHN A. GERLT* and A. VIRGINIA YOUNGBLOOD, Department of Chemistry, Yale University, New Haven, Connecticut 06511.

Page 7437, column 2: The sentence beginning in line 13 should read: If this description of the sugar pucker is correct, the protons on C₂ can be assigned, with the pro-*R* proton being *upfield* of the pro-*S* proton.

We thank Professor Frank Hruska, University of Manitoba, for pointing out the stereochemical assignment error. This change does not affect the conclusions reached in the article.

Effect of Photoelectrode Crystal Structure on Output Stability of Cd(Se,Te)/Polysulfide Photoelectrochemical Cells [*J. Am. Chem. Soc.* **1980**, *102*, 5962–5964]. GARY HODES, JOOST MANASSEN, and DAVID CAHEN,* Weizmann Institute of Science, Rehovot, Israel.

Page 5963, reference 20 should read as follows: (20) These comparisons show preferred orientation of the (111) plane in the sphalerite phases, and of the crystallographically similar (0001), or of the (10 $\bar{1}$ 0) planes in the wurtzite phases.

This mistake does not affect our argument, as can be easily seen by reading the relevant part of the communication.