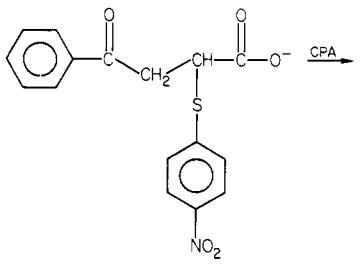
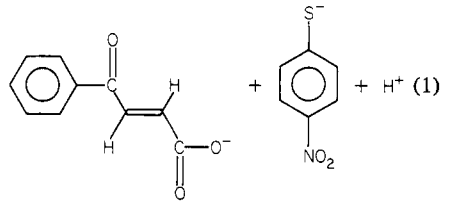
elimination of *p*-nitrothiophenol from (+)-**2**, a reaction which was followed spectrophotometrically at 412 nm (see eq 1 below).



2



3

When the enzyme concentration was much greater than the substrate concentration, pseudo-first-order kinetics were observed for the liberation of 1 equiv of *p*-nitrothiophenol from (+)-**2** under anaerobic conditions. The dependence of the observed first-order rate constant on the concentration of the enzyme yielded the kinetic parameter k_{cat}/K_m which had a value of 4.97 ± 0.34 M^{-1} s^{-1} under the conditions mentioned above. The CPA-catalyzed elimination of *p*-nitrothiophenol from (+)-**2** was completely inhibited upon the addition of 2.37 mM of *dl*-benzylsuccinic acid. Since *dl*-benzylsuccinic acid is a potent inhibitor of the hydrolytic action of CPA (K_i = 1.1 μM),[8] the inhibition observed for the elimination reaction provides strong evidence that the latter process occurred at the active site. On the other hand, CPA does not catalyze the elimination of *p*-nitrothiophenol from (−)-**2** even though (−)-**2** binds to the enzyme active site. Compound (−)-**2** is a competitive inhibitor for the CPA-catalyzed hydrolysis of *O*-(*trans*-*p*-chlorocinnamoyl)-L-β-phenyllactate with a K_i value of 640 ± 40 μM at pH 7.5, 0.5 M NaCl, 0.05 M Tris–HCl buffer, 3% acetonitrile and 25.0 °C. From kinetic experiments under substrate in excess conditions using (+)-**2**, the kinetic parameters K_m = 420 ± 10 μM and k_{cat} = (1.4 ± 0.1)10^{-3} s^{-1} were obtained at pH 7.5, 0.5 M NaCl, 0.05 M Tris–HCl buffer, 6.3% acetonitrile at 25.0 °C. Thus it appears that both enantiomers of **2** bound to the active site of the enzyme approximately equally, but only (+)-**2** is a substrate, consistent with the enzymic nature of the elimination reaction. Because *p*-nitrothiophenol readily adds to the unsaturated acid **3** in organic solvents, the product analyses which we performed on the elimination reactions of **2** were carried out in the presence of 1 mM potassium ferricyanide which oxidizes the *p*-nitrothiophenol produced in the α,β-elimination reaction to bis(*p*-nitrophenyl)disulfide. Control experiments showed that the presence of potassium ferricyanide up to a concentration of 1.5 mM in the reaction mixture does not affect the rate of the enzymic or nonenzymic elimination reactions carried out at pH 7.5. The disulfide formed by the oxidation of *p*-nitrothiophenol precipitates from the reaction mixture under these conditions and was removed by filtration. Then, the filtrate was acidified to pH 2 by using cold HCl and extracted immediately with ether three times. Subsequently, the organic layer was dried over $MgSO_4$, and the solvent was evaporated by using a rotary evaporator in the cold. A 270-MHz ^1H NMR spectrum showed that the residue contained only carboxylic acid **3** as the product obtained in either the enzymic or nonenzymic elimination reactions of (+)-**2** or (±)-**2**. The cis isomer of **3** can be distinguished from *trans*-**3** by NMR spectroscopy.[9]

(8) Byers, L. D.; Wolfenden, R. *Biochemistry* **1973**, *12*, 2070.
(9) Sugiyama, N.; Kataoka, H.; Kashima, C.; Yamada, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1353.

Although the absolute configuration of (+)-**2** is not known yet, it would be reasonable from the above data to assume that (+)-**2** binds to the active site of the enzyme in a fashion similar to that observed for (−)-**1**. In that event, the *p*-nitrothiophenyl group would be placed in a hydrophobic pocket, the carboxylate anion of the substrate with its negative charge interacting with the positively charged side chain of Arg-145, the carbonyl oxygen of **2** coordinated to the reactive site zinc ion, and a hydrogen of the α-methylene group within striking distance from the γ-carboxylate group of Glu-270.[10] According to this proposal, either the γ-carboxylate group of Glu-270 or a water molecule assisted by this residue acting as a general base catalyst would be the species removing the hydrogen from the α-methylene position of (+)-**2**.

In summary, in this communication we have demonstrated that CPA can catalyze an α,β-elimination reaction with an appropriately designed ketone substrate containing a labile group β to the ketone function. The k_{cat}/K_m value for the catalytic action of CPA on (+)-**2** is comparable to the second-order rate constant for the hydroxide ion catalyzed elimination of *p*-nitrothiophenol from **2** (k_{OH^-} = 4.7 ± 0.1 M^{-1} s^{-1} at 30.0 °C) and at least 10^5 greater than the rate constant observed with acetate ion (k_{OAc^-} = (2.6 ± 0.2)10^{-5} M^{-1} s^{-1} in 33% ethanol (v/v), 30.0 °C). The possibility that elimination reactions can be employed as the basis for the design of "suicide" substrates for the action of the hydrolytic enzyme CPA is under active investigation in our laboratory.

Acknowledgment. We are grateful to the National Institute of Arthritis, Metabolic and Digestive Diseases for support of this research.

(10) One question which must be raised with regard to this suggestion is whether the *p*-nitro substituent of the *p*-nitrothiophenyl moiety can fit in the hydrophobic pocket of CPA. We are probing this point by examining the reactivity of a variety of substrates related to **2** in which there is a considerable range in the size of the para substituent attached to the thiophenyl ring.

Direct Observation of Alkyl/Nitrosyl Migratory Insertion in an Organotransition Metal Complex

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Migratory insertion of CO into metal carbon bonds (eq 1) is one of the most ubiquitous and well-studied reactions in organotransition metal chemistry. In addition to its fundamental importance, CO migratory insertion is a critical step in many important carbon–carbon bond-forming processes involving homogeneous transition-metal catalysts.[1] In contrast, migratory insertion of NO into metal–carbon bonds (eq 2) is much less

$$R\text{–}M(CO) + L \rightarrow R\text{–}CO\text{–}M(L) \quad (1)$$

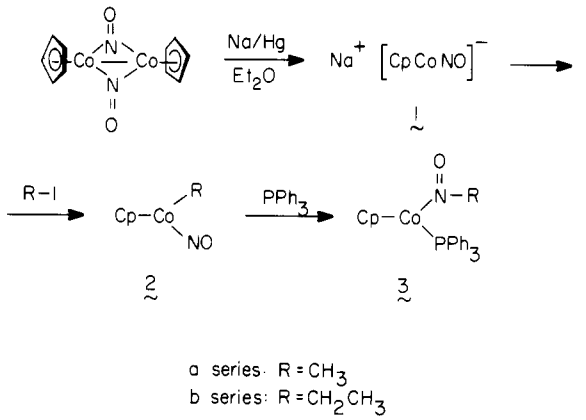
$$R\text{–}M(NO) + L \rightarrow (RNO)M(L) \quad (2)$$

* To whom correspondence should be addressed at the University of California, Berkeley.

(1) For reviews, see: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Parshall, G. W. "Homogeneous Catalysis",; Wiley: New York, 1980; p 77ff. (c) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.
(2) See, for example: (a) Klein, H.; Karsch, H. *Chem. Ber.* **1976**, *109*, 1453. (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155. (c) Schoonover, M. W.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880. (d) Middleton, A. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1888.

0002-7863/81/1503-3612$01.25/0

Scheme I



well-known and in most cases has only been inferred as one step in a more complicated overall transformation.[2] Because of the fundamental importance of C–N bond-forming reactions, as well as their potential utility in organic chemistry, we have initiated a program to examine the scope and mechanism of NO insertion reactions. In this communication we report the preparation of an NO-containing anionic cobalt complex and the rapid alkylation of this material to give a series of alkylnitrosyl complexes. These complexes are quite sensitive thermally, but in the presence of phosphines they undergo directly observable migratory insertion, leading to isolable alkylnitroso complexes, one of which we have characterized by X-ray diffraction. It has been possible to study this NO insertion reaction kinetically and thus obtain information about its reaction mechanism.

Our system is outlined in Scheme I. After several trial experiments, we found it possible to successfully reduce Brunner's dimer[3] $[CpCo(NO)]_2$ to sodium η^5-cyclopentadienylnitrosylcobaltate (**1**) by carrying out the reduction in diethyl ether. The salt precipitates from the reaction solution as a pink, pyrophoric solid in 70% yield. The ^1H NMR spectrum of **1** in THF-d_8 exhibits a cyclopentadienyl resonance at δ 4.1. The salt shows two IR absorptions in the M–NO region in THF (1560, 1530 cm^{-1}) but only one (1570 cm^{-1}) in acetonitrile. Addition of 1 equiv of CH_3I or methyl *p*-toluenesulfonate to a solution of **1** in THF at room temperature led rapidly to decomposition products. However, when this reaction was carried out at −40 °C in the presence of at least 1 equiv of PPh_3, a much cleaner reaction took place. Alkylation occurred immediately, leading to a new complex which exhibited a higher frequency M–NO absorption at 1780 cm^{-1} and two singlets in the NMR spectrum, one at δ 5.15 (5 H) and the other at δ 1.93 (3 H). On the basis of these data, we assign to this material the structure of the nitrosylalkyl complex **2a**. It is stable in solution below −30 °C but decomposes rapidly upon attempted isolation or warming above this temperture in the absence of phosphines. However, when the solution of **2a** was warmed above 0 °C in the presence of 1 equiv of PPh_3, the complex was transformed into a new material having an absorption in the IR spectrum at 1310 cm^{-1} and resonances in the ^1H NMR spectrum at δ 4.52 (5 H, s) and 2.63 (3 H, d, J = 3 Hz), consistent with its formulation as the phosphine-induced NO insertion product **3a**. This material was isolated from the reaction mixture in analytically pure form as dark green, slightly air-sensitive crystals (mp 115 °C dec) in 80% yield.

Similar observations were made using ethyl iodide or ethyl trifluoromethanesulfonate as alkylating agents. In this case, complex **3b** was observed as the ultimate product, formed in ca. 90% yield by NMR spectroscopy. No evidence for free or bound ethylene was observed, indicating that β elimination, a common decomposition route for *n*-alkyl complexes,[4] does not in this case compete with NO insertion. Isolation and recrystallization from toluene/hexanes gave **3b** as dark green, analytically pure, air-stable crystals in 27% yield, mp 125 °C dec.

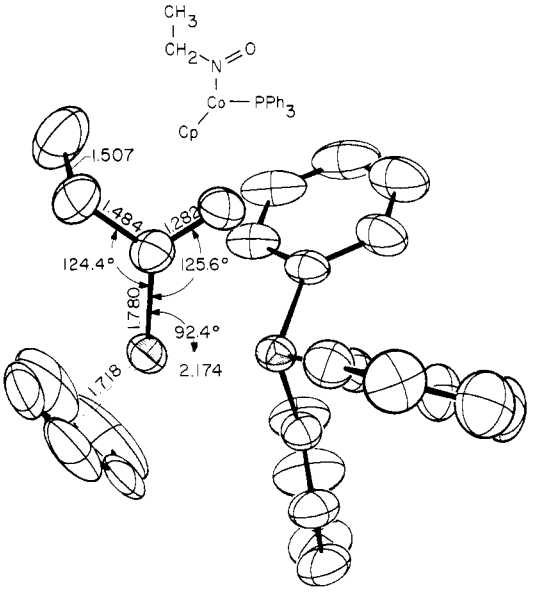
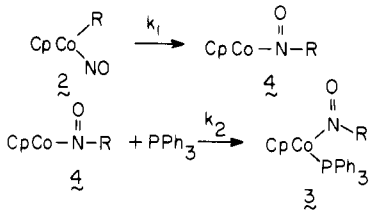


Figure 1. ORTEP drawing of **3b**.

Table I. Rate Constants for Reaction of $CpCo(NO)CH_3$ with Varying Concentrations of PPh_3 in THF at 10 °C

[1], M	$[PPh_3]$, M	$k_{obsd} \times 10^4$, s^{-1}
0.10	0.60	5.79
0.08	0.796	5.24
0.07	0.40	5.30
0.02	0.226	4.22
0.02	0.098	4.07
0.0049	0.029	4.06

Scheme II



The crystals of **3b** were suitable for characterization by X-ray diffraction. An ORTEP drawing of the structure of this complex is shown in Figure 1, along with some of the more important bond distances and angles determined in the diffraction study.[5] This is one of a very small group of η^1-alkylnitroso complexes which has been characterized crystallographically.[6] The Co–N bond length is very similar to that reported for a different cobalt complex by Evrard and co-workers[6a] and somewhat shorter than the Co–N and Pd–N bond distances in the RNO complexes studied by Doedens' group.[6b] The N–O bond distance is longer than those found in previous studies. The dihedral angle of the planes defined by the centroid of the Cp ligand, Co, and nitrogen atom, and that defined by the nitrogen, oxygen, and CH_2 group, is 8.6°, indicating an almost planar coordination geometry at cobalt.

(3) (a) Brunner, H. *J. Organomet. Chem.* **1968**, *12*, 517. (b) Brunner, H.; Wachsmann, H. *Ibid.* **1968**, *15*, 409.

(4) (a) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Ibid.* **1976**, *76*, 219.

(5) Crystal data for complex **2b**: triclinic crystals; space group *P1* with a = 9.779 (2), b = 10.685 (3), c = 21.721 (4) Å; α = 81.9, β = 79.8, γ v 82.8°; M = 890.78 amu; d = 1.345 g/cm^3; μ v 9.0 cm^{-1}. The structure was solved by Patterson and difference Fourier methods; of the 5754 unique reflections collected, 4001 were used in the least-squares analysis $[\sum\omega(|F_o| - |F_c|)^2]$. Refinement converged with R = 4.17%. The final R factor for all 5754 reflections was 7.71%. The ORTEP drawing in the text illustrates one of the two crystallographically distinct molecules in the unit cell; data for both are given in the supplementary material.

(6) (a) Evrard, G.; Thomas, R.; Davis, B. R.; Bernal, I. *J. Organomet. Chem.* **1977**, *124*, 59. (b) Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, *12*, 537. (c) Sams, D. B.; Doedens, R. J. *Ibid.* **1979**, *18*, 153. (d) Mansuy, D.; Dreme, M.; Chottard, J. C. *J. Organomet. Chem.* **1978**, *161*, 207. See also: Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336.

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. Hollander, 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. [a]Br_2, CCl_4. [b]Et_3N, CCl_4. [c]$HOCH_2CH_2OH$, *p*-TsOH, benzene, reflux. [d]*n*-BuLi, THF, −76 °C. [e]^2H_2O. [f]$(COOH)_2$, CH_2Cl_2, H_2O. [g]*Beauveria sulfurescens* ATCC 7159.

Scheme II. [a]MCPBA, $CHCl_3$. [b]DIBAL, THF, −76 °C. [c]$(Ph_3P)_3RhCl$, 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. UEYAMA, 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 Me_2SO 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/CCl_3 should be changed to TFA/$CDCl_3$.

In the second paragraph on page 6004, second sentence: in both instances CCl_3 should be changed to $CDCl_3$.

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 $\beta > 0°$ 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 $CDCl_3$ and Me_2SO, 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 $\chi = 60°$ 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 C_2 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.