chemical reaction presumably occurs by breaking the W–L bond, to form the intermediate $W(CO)_5$, which is then scavenged by the ethanol (in our case).[2] It is at least debatable whether the W–L bond-breaking reaction should be activated to the extent of 9 kcal mol^{-1}.

An attractive alternative is a two-state scheme in which chemical reaction occurs from a LF state lying above the emitting CT state (in our case), and in steady-state equilibrium with it. The observed E_ϕ^* is now attributed primarily to the energy difference between the two states. In this scheme, excitation leads, through the intersystem crossing, to a triplet CT state, ^3CT.[13] This state is emitting, but not highly chemically reactive. The higher lying LF state, presumably also a triplet, does react efficiently, but the overall quantum yield is small because of the competition with nonradiative relaxation of ^3CT. The detailed kinetics for such a system have been discussed.[14–16]

The above type of two-state scheme has been proposed in explanation of the photochemical behavior of $Ru(NH_3)_5L^{2+}$ complexes,[17] as well as for that of the present type of carbonyl complexes.[2,18,19] It has the appealing feature of accounting for the increase in ϕ for cases where L is such that the CT absorption band lies at higher energy than the LF one. We hope, through current solvent dependence studies, and through variations in L, to gain leverage in distinguishing between the one- and two-state types of schemes.

We can report on results with other potential quenchers. The emission is quenched by 9-methylanthracene and by 1,2-benzanthracene, but not by 1,2,5,6-dibenzanthracene or ferrocene. The respective triplet-state energies are 16.2,[20] 16.5,[20] 18.3,[20] and 18.6 kK.[21] The triplet-state energy for anthracene is 14.7 kK.[20] With the assumption that quenching occurs by energy transfer, the above results indicate that the energy of the emitting state of $W(CO)_5$(4-CNpyr) lies between 16.5 and 18.3 kK, or somewhat above the energy corresponding to the emission maximum, 15.6 kK. In terms of the two-state scheme, we would place the reactive ligand-field state at about 7.6 kcal mol^{-1} or 2.6 kK above an emitting state energy of about 17 kK, or at 19.6 kK or 510 nm. This might, for example, be assigned as the energy of the ^3E state.[22]

Quenching of emission and of photochemistry has been observed for various Cr(III) ammines,[23] and recently for $Rh(NH_3)_5Cl^{2+}$ [24] and $Rh(NH_3)_5Br^{2+}$.[25] Emission and emission quenching have been reported for rhenium tricarbonyl complexes.[26] The present case appears to be the first one involving a group 6 carbonyl complex and appears also to be novel in that quenching of photochemistry is also observed.

Acknowledgment. This investigation was supported in part by a grant from the U.S. Office of Naval Research.

Alistair J. Lees, Arthur W. Adamson*
Department of Chemistry
University of Southern California
Los Angeles, California 90007

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[13] The use of spin multiplicity designations for a heavy transition-metal complex may be questioned, but is convenient.

[14] Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

[15] Porter, G. B. In "Concepts of Inorganic Photochemistry"; Adamson, A. W.; Fleischauer, P. F., Eds.; Wiley-Interscience: New York, 1975, p 37.

[16] Kane-Maguire, N. A. P.; Toney, C. G.; Swiger, B.; Adamson, A. W.; Wright, R. E. *Inorg. Chim. Acta* **1977**, *22*, L11.

[17] Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601.

[18] See references in ref 2 and 3; also Wrighton, M., private communication.

[19] Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154.

[20] Birks, J. B. "Photophysics of Aromatic Molecules", Wiley-Interscience: New York, 1970; p 182.

[21] See: Wrighton, M. S.; Pdungsap, L.; Morse, D. L. *J. Phys. Chem.* **1975**, *79*, 66.

[22] This is merely an indicative calculation. Detailed analysis would require knowledge of $E_{\phi'}^*$, the activation energy of reaction from the LF state, for example, as well as the temperature dependence of all other rate processes that affect the coupled system. We are indebted to P. J. Wagner for pointing this out.

[23] See: Zinato, E. In "Concepts of Inorganic Photochemistry"; Adamson, A. W.; Fleischauer, P. D.; Eds.; Wiley-Interscience: New York, 1975; p 143.

[24] Adamson, A. W.; Fukuda, R. C.; Larson, M.; Mäcke, H.; Puaux, J. P. *Inorg. Chim. Acta* **1980**, *44*, L13.

[25] Larson, M.; Adamson, A. W.; Rumfeldt, R. C., submitted for publication in *J. Am. Chem. Soc.*

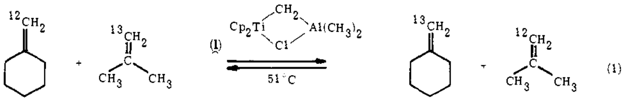
[26] Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

Titanium Metallacarbene–Metallacyclobutane Reactions: Stepwise Metathesis

Sir:

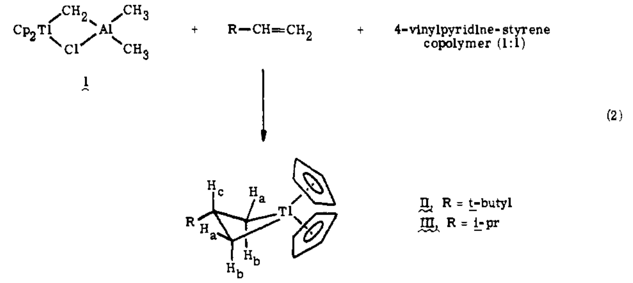
The mechanism of the olefin metathesis reaction[1] has been examined through model and labeling studies. These studies support a mechanism involving the interconversion of metal–olefin–carbene complexes and metallacyclobutanes.[2] Numerous questions concerning the structure of the intermediates, the factors controlling the stereochemistry of the reaction,[3] and the role of the cocatalyst in the active systems remain to be answered.

Parshall and Tebbe[4] recently reported a slow but well-defined catalyst (I) for the degenerate metathesis of isobutene and methylenecyclohexane (eq 1). Reaction was extensive after 47 h and was selective for exchange of terminal methylene groups. Ethylene and propylene were reported to undergo a methanation reaction instead of metathesis.[5]



As part of a study of the factors controlling the stereochemistry of metathesis with unsymmetrical analogues of I,[6] $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCH_2\cdot AlClMe_2$ and $(\eta^5\text{-}1,2,4\text{-}C_5Me_3H_2)(\eta^5\text{-}C_5H_5)TiCH_2\cdot AlClMe_2$, the methanation reaction was reexplored. We have now isolated a metallacyclobutane[7] from the true metathesis system I,[4] which provides answers to a few of the questions mentioned above.

The reaction of the "Tebbe" reagent (I) with neohexene in THF gave intractable products. However, when the reaction was run in benzene containing 1 equiv of pyridine, there was produced a near quantitative yield of a single metallocene product (II) and the pyridine–dimethylchloroaluminum adduct (eq 2). The two products could be separated with difficulty by repeated recrystallization from hexane–THF. It was subsequently found that



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[1] Grubbs, R. H. *Prog. Inorg. Chem.* **1979**, *24*, 1.

[2] Herisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

[3] (a) Casey, C. P.; Tuinstra, H. E. *J. Am. Chem. Soc.* **1978**, *100*, 2271. (b) Basset, J. M.; Bilhou, J. L.; Martin, P.; Theider, A. *Ibid.* **1975**, *97*, 7376. (c) Katz, T. J.; McGinnis, J. *Ibid.* **1975**, *97*, 1572.

[4] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Cp = $\eta^5\text{-}C_5H_5$.

[5] Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074.

[6] deBoer, E. J. M.; Grubbs, R. H., unpublished results.

[7] Other metallacyclobutanes isolated are limited to Pt,[a,b] Mo, W,[c] and Ru:[d] (a) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, 626. (b) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (c) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, *1131*. (d) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *Ibid.* **1978**, 446.

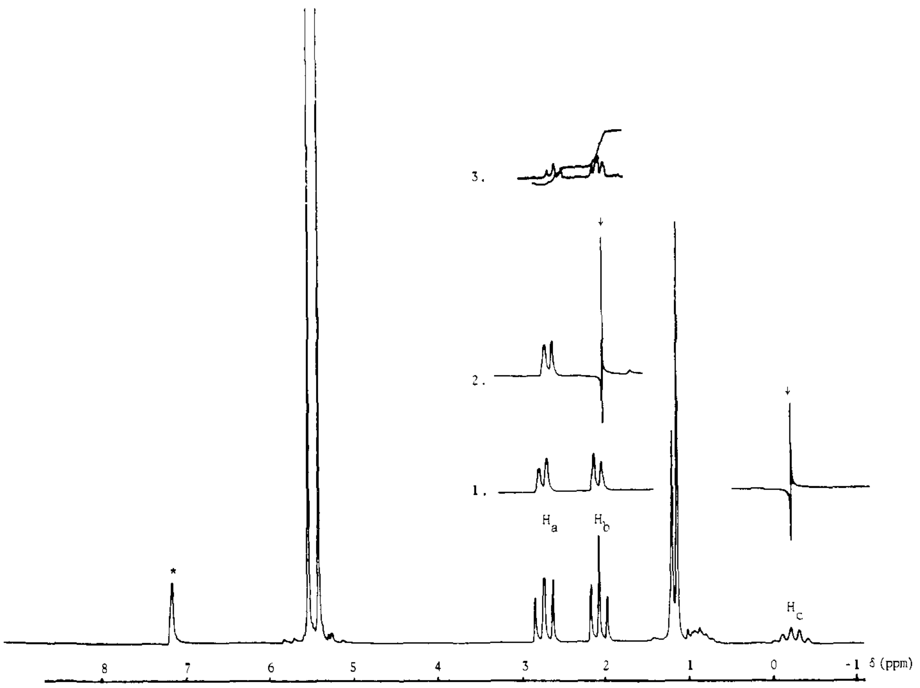


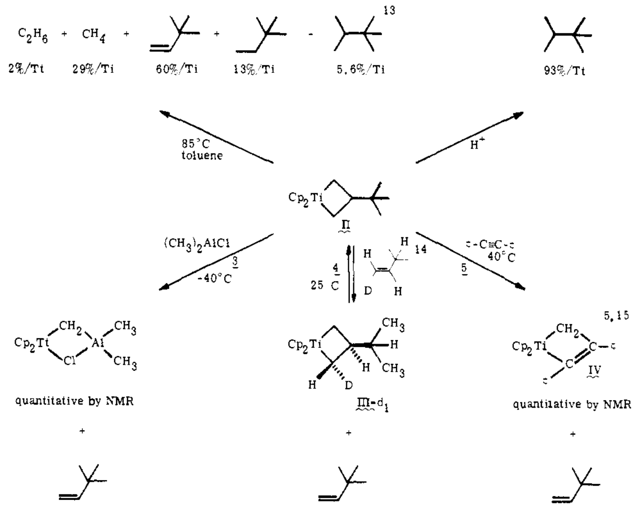
Figure 1. ^1H NMR spectrum of III in benzene-d_6 (*), 90 MHz at 34 °C. 1. and 2. show the H_a and H_b regions in selective homodecoupling of H_c and H_b, respectively. ↓ indicates the position of the decoupling power. 1. AB quartet, $J_{AB} = 8.1$ Hz. 2. $J_{AC} = 8.0$ Hz. 3. III-d_1; see reaction scheme for the structure, H_a (-d).

the 4-vinylpyridine–styrene copolymer (1:1)[8] served as a more convenient Lewis base. In a typical reaction, 0.6 mL (4.7 mmol) of neohexene was mixed with 1 g (3.5 mmol) of I, in 15 mL of toluene. The polymer (1 g) was then added, and the mixture was stirred for 3.5 h at room temperature. After filtration, the solvent was removed, and the crude product was recrystallized from *n*-hexane to give a 64% yield of analytically pure[9] red needles of II.

The ^1H and ^{13}C NMR[10] spectra were invaluable in characterizing these complexes. Figure 1 shows the ^1H NMR spectrum of III. The key features in the spectrum are the barely resolved AB quartets for protons H_a and H_b and the high-field shift of H_c. The latter may be a result of H_c being forced into the shielding environment of the $[Cp_2Ti]$ fragment due to the puckering of the metallacycle ring.[11] Spectra showing analogous features were obtained on mixing I with ethylene, propylene, styrene, cyclopentene, and norbornene in the presence of pyridine.[12]

The important reactions of II are given in Scheme I. These reactions, in combination with the spectral data, provide firm evidence for the structure of the adducts. It is significant that cyclopropanes are not produced in any of the reactions.

Scheme I



Reaction 3 suggests the role of the cocatalyst in metathesis reactions. The Lewis acid cocatalyst facilitates the carbene–metallacycle equilibrium. Pyridine (or its derivatives) removed Me_2AlCl from I, and the reactive $[Cp_2TiCH_2]$ fragment was trapped immediately by the olefin to form the metallacycle. The formation of II, coupled with reaction 3, provides the necessary steps for this metathesis system. Complex *trans*-II-d_1, isolated by the above technique, from the reaction with *trans*-neohexene-*1*-d_1, gave a mixture of I and I-d_1 on treatment with Me_2AlCl in toluene.[16a] Thus, the required metathesis cycle is completed.

In the presence of 1 equiv of PhC≡CPh at 40 °C, II-d_1 afforded the metallacyclobutenes IV and IV-d_1.[16b] A free carbene intermediate need not be involved in this and the related olefin reaction,

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(8) The copolymer was prepared from 4-vinylpyridine and styrene in THF with AIBN as an initiator.

(9) Anal. Calcd for $C_{17}H_{24}Ti$ (II): C, 73.91; H, 8.76; Ti, 17.34; mol wt, 276. Found: C, 73.88; H, 8.81; Ti, 17.44; mol wt, 292 (cryoscopic in benzene). Both II and III were thermally stable in the solid state at ambient temperature for long periods of time.

(10) Both ^1H and ^{13}C NMR spectra were measured in benzene-d_6 on a JEOL FX-90Q spectrometer operated at 90 and 22.50 MHz, respectively. Measurements made from C_6D_5H, δ 7.15 for ^1H NMR, δ 128 for ^{13}C NMR. II: ^1H NMR δ 5.61 (5 H, s, Cp), 5.43 (5 H, s, Cp), 2.24 (2 H, d of d, H_a, $J_{AB} = 8.5$ Hz), 1.92 (2 H, d of d, H_b, $J_{AB} = 8.5$ Hz), 0.93 (9 H, s, CMe_3), -0.02 (1 H, m, H_c). III: ^1H NMR δ 5.50 (5 H, s, Cp), 5.37 (5 H, s, Cp), 2.63 (2 H, d of d, H_a, $J_{AB} = 8.1$ Hz, $J_{AC} = 8.0$ Hz), 1.99 (2 H, d of d, H_b, $J_{AB} = 8.1$ Hz, $J_{BC} = 8.0$ Hz), 1.05 (6 H, d, C–Me_2, $J = 5.5$ Hz), 0.78 (1 H, m, C–H), -0.27 (1 H, m, H_c). II: $^{13}C\{^1H\}$ NMR δ 110.6, 110.1 (Cp), 67.6 (2 C_α), 18.4 (C_β). III: $^{13}C\{^1H\}$ δ 110.3, 109.4 (Cp), 75.2 (2 C_α), 13.2 (C_β).

(11) X-ray structure for II in progress.

(12) The mono- and disubstituted titanacycles are now being investigated in detail and will be reported later.

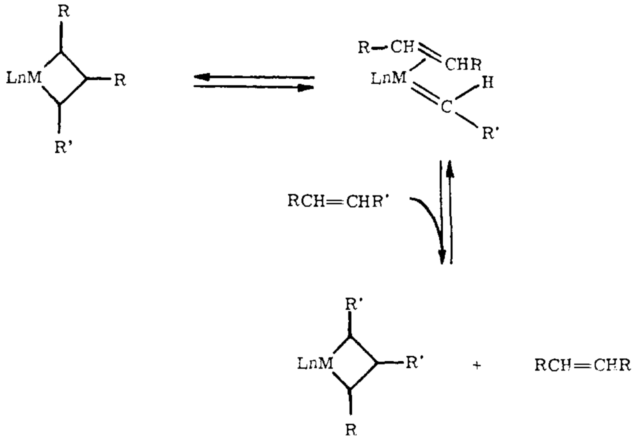
(13) Products were identified by GC–MS. CH_4 was collected via a Toepler pump. Yields for C_6 and C_7 were determined by response relative to an internal standard by gas chromatography. Response factors were obtained from authentic samples.

(14) Deuterated olefins were prepared from $Cp_2Zr(H)Cl$ and the corresponding acetylenes according to: Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. The exchange reaction was stereoselective up to 50 h at 25 °C.

(15) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.*, **1980**, *102*, 6149.

(16) Products were identified by ^1H, ^2H, and ^{13}C NMR. (a) Ratio of I-d_1 to I is ca. 1:1 by ^1H NMR. The recovered olefin was a mixture of *cis*- and *trans*-neohexene-*1*-d_1 and neohexene-d_0. (b) The reaction of diphenylacetylene with II-d_1 gave a 1:1 mixture of IV-d_1 and IV, and the deuterated olefin (50%) was pure *trans*-neohexene-*1*-d_1.

Scheme II



4. An attractive mechanism for metallacycle exchange with olefin or acetylene and therefore olefin metathesis is shown in Scheme II.

Whether the reaction proceeds through a diolefin–carbene or a free metal–carbene complex is not yet clear; this question will require further work. However, the former complex is formally a 20 e^- species. Thus, there may be two classes of metathesis catalysts, those involving metal–carbene complexes[17] and those in which metallacyclobutanes are the chain-carrying species. Each class of catalyst would be expected to show different kinetic parameters and stereoselectivities.

Although previous work has provided evidence supporting a metal carbene mechanism, the above reactions give detailed structural information about the intermediates and provide evidence for two classes of catalysts. Reaction 3 is a model of the anticipated mechanism while 4 and 5 provide a new mechanistic pathway.

Acknowledgment. Support from the National Science Foundation (CHE-7904814) and helpful suggestions of F. Tebbe are gratefully acknowledged.

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(17) Wengrouins, J. H.; Schrock, R. R.; Churchill, M. R.; Wissert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

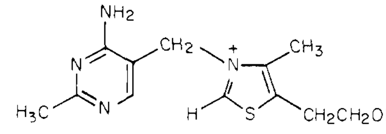
T. R. Howard, J. B. Lee, R. H. Grubbs*

Contribution No. 6255 from the Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

Received June 16, 1980

A Model for Coenzyme–Metal Ion–Apoenzyme Interactions: Crystal Structure of the Ternary Complex [(Thiamine pyrophosphate)(1,10-phenanthroline)aquacopper]-Dinitrate-Water

Sir:



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Thiamine pyrophosphate (1) (the cofactor form of vitamin B_1) is a coenzyme for a number of enzymatic processes catalyzing the decarboxylation of α-keto acids and the transfer of aldehyde or acyl groups. There is strong evidence suggesting that coenzyme thiamine pyrophosphate binds to the apoenzyme in a way where the thiamine ring moiety of the thiamine pyrophosphate molecule stacks with the indole moiety of the tryptophan residue in the active center of the apoenzyme.[1] Additionally, it has also been recognized that divalent metal ions such as Mg(II) and Mn(II) ions are also required as cofactor for the holoenzyme formation as well as the catalytic activity,[2] but their detailed roles and binding modes in their interactions with the coenzyme and apoenzyme are not as well-known. In this regard, of special interest is the observation that the charge-transfer complex between the tryptophan residue in yeast apopyruvate decarboxylase and thiochrome chromophore in thiochrome pyrophosphate, a competitive inhibitor with thiamine pyrophosphate, could be formed only in the presence of Mg(II) ions.[3] Sigel and co-workers have extensively demonstrated that metal ions could stabilize the aromatic ring stacking between nucleotide bases and heterocyclic amines by forming a metal–phosphate bridge; otherwise, such charge-transfer interactions would usually be weak.[4] In the present enzyme system, metal ions could, therefore, be expected to play such a role since thiamine pyrophosphate involves both the phosphate and ring moieties, and a proposed hypothetical structure of such a ternary adduct is shown in Figure 1.[5] In order to substantiate the formation of such a metal ion bridged stacking adduct and to elucidate its stereochemistry, we have undertaken X-ray investigations of the ternary complexes containing thiamine pyrophosphate, divalent metal ions, and aromatic heterocyclic amines such as 1,10-phenanthroline (phen), 2,2′-bipyridyl, and 2,2′-dipyridylamine which are known as useful models for aromatic amino acids.[4] We have reported here the preparation and the structure of the ternary thiamine pyrophosphate–Cu(II)–phen complex, which involves a metal–pyrophosphate bridge that connects the two constituents, as a possible model for coenzyme–metal ion–apoenzyme interactions. The possibility of the structural change from the unstacked opened structure found in the present complex to the stacked folded structure is also shown in terms of the conformational change about the ethyl ester pyrophosphate ($C5\alpha$–$C5\beta$–$O5\gamma$–$P5\delta$) side chain of the thiamine pyrophosphate molecule.

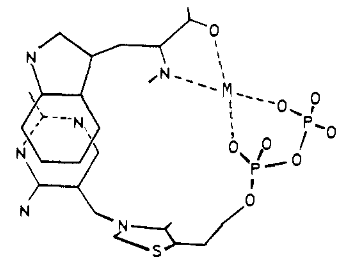

Figure 1. A proposed hypothetical structure of the M(thiaminine pyrophosphate)(tryptophan) ternary complex in the active center of the enzyme.

The complex was prepared from thiamine pyrophosphate, phen, and $Cu(NO_3)_2 \cdot 2H_2O$ in an equimolar (0.1 mmol) ratio. The mixture (pH ca. 3) was allowed to stand at room temperature. Pale blue thin plates formed after ca. 3 weeks. They were collected, washed with a little water, and air dried. Precession and Weissenberg photographs indicated that the crystals were monoclinic with the systematic absence of $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$), consistent with space group $P2_1/n$. Cell constants of $a = 11.005$ (2), $b = 43.984$ (12), $c = 6.775$ (3) Å, and $\beta = 92.59$ (3)° were determined from 13 high-order reflections ($20° < 2\theta < 29°$) on a Rigaku four-circle automated diffractometer ($T = 23$ °C, $\lambda = 0.71069$ Å). The unit-cell volume is

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(1) Kochetov, G. A.; Usmanov, R. A.; Mevkh, A. T. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 1619–1626. Kochetov, G. A.; Usmanov, R. A. *Ibid.* **1970**, *41*, 1134–1140. Heinrich, C. P.; Moack, K.; Wiss, O. *Ibid.* **1971**, *44*, 275–279.

(2) Gallo, A. A.; Hansen, I. L.; Sable, H. Z.; Swift, T. J. *J. Biol. Chem.* **1972**, *247*, 5913–5920.

(3) Wittorf, J. H.; Gubler, C. J. *Eur. J. Biochem.* **1970**, *14*, 53–60.

(4) See, for example: Chaudhuri, P.; Sigel, H. *J. Am. Chem. Soc.* **1977**, *99*, 3142–3150.

(5) This model can also be shown to be compatible with a similar complex with thiochrome pyrophosphate by the use of space-filling models (CPK atomic models by Ealing Corp.), although thiochrome has a planar tricyclic structure.

0002-7863/80/1502-6878$01.00/0