$\tau_{1/2}$ of 120 μsec which are speculated to correspond to the absorption of the metastable triplet state.[1,2] Taking into account the differences in temperature and the fact that the different cell environments may influence the detailed triplet dynamics, our dynamic data, with decay times on the order of 500 μsec, are consistent with the optical measurements of Parson et al.[2] The measurements of Dutton and Leigh would seem to best be explained as due to processes other than those associated with triplet intersystem crossing kinetics.

One of the most interesting features of the zero field spectra is that a single dominant set of triplet signals are observed with narrow, symmetrical line widths. Whatever models of cooperativity or delocalization among bacteriochlorophyll and bacteriopheophytin are used to describe the photochemical reaction center in the photosynthetic cells, the models must include the fact that the zero field triplet spectra are unique, sharp, and structureless at low temperatures. Further studies on other cells, as well as on isolated bacteriochlorophyll and bacteriopheophytin molecules, are presently underway to determine the influence of temperature and local cell structure on the triplet intersystem crossing rates for in vivo systems.

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The Tetrakis(*N,N*-dimethyldithiocarbamato)tantalum(V) Cation. A Stereochemically Rigid Eight-Coordinate Complex

Sir:

Stereochemical nonrigidity is a pervasive feature of the chemistry of eight-coordinate complexes and, despite several low-temperature studies,[1-6] no tetrakis chelates have been reported which are stereochemically rigid on the NMR time scale.[7-9] We have now identified several tetrakis chelates which exhibit inequivalent site environments in low-temperature ^{1}H NMR spectra.[10] We present herein a preliminary account of our ^{1}H NMR and x-ray crystallo-

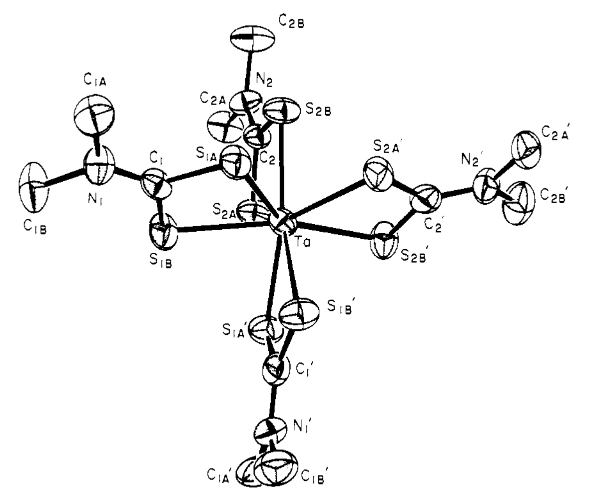

Figure 1. A view of the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation in crystals of $[Ta(S_2CN(CH_3)_2)_4]Cl{\cdot}CH_2Cl_2$.

graphic studies of the eight-coordinate, dodecahedral tetrakis(*N,N*-dimethyldithiocarbamato)tantalum(V) cation, $[Ta(S_2CN(CH_3)_2)_4]^+$.

Air sensitive, yellow crystals of composition $Ta(S_2CN(CH_3)_2)_4Cl{\cdot}CH_2Cl_2$ (**1**) and orange crystals of composition $Ta(S_2CN(CH_3)_2)_2Cl_3{\cdot}0.25CH_2Cl_2$ (**2**) have been isolated following reaction of tantalum(V) chloride with anhydrous sodium *N,N*-dimethyldithiocarbamate (1:5.1 molar ratio) in refluxing dichloromethane. Both new compounds are 1:1 electrolytes in dichloromethane, and both exhibit a single methyl resonance at τ 6.60 in ^{1}H NMR spectra of dichloromethane solutions at 37°. Compound **1** shows the following characteristic ir bands: ν(C$\stackrel{...}{-}$N) 1557, ν(C$\stackrel{...}{-}$S) 992, and ν(Ta$\stackrel{...}{-}$S) 358 cm^{-1} (Nujol mull). The ir spectrum of compound **2** is closely similar except that additional strong bands attributable to $TaCl_6^-$ are observed at 316 and 328 cm^{-1}. These data suggest that compounds **1** and **2** should be formulated as $[Ta(S_2CN(CH_3)_2)_4]Cl{\cdot}CH_2Cl_2$ and $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]{\cdot}0.5CH_2Cl_2$, respectively, in accord with a previous study of the analogous *N,N*-diethyldithiocarbamate complexes.[11]

The presence of the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation in both crystalline salts has been confirmed by x-ray diffraction. Crystal data: $[Ta(S_2CN(CH_3)_2)_4]Cl{\cdot}CH_2Cl_2$ (**1**), M = 782.2; monoclinic, space group $C2/c$ ($C_{2h}{}^6$, No. 15); a = 12.055 (5), b = 18.473 (8), c = 12.794 (5) Å; β = 94.71 (3)°; d_{measd} = 1.83 g cm^{-3}, Z = 4, d_{calcd} = 1.829 g cm^{-3}; $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]{\cdot}0.5CH_2Cl_2$ (**2**), M = 1098.0; monoclinic, space group $C2/c$; a = 30.97 (1), b = 9.537 (4), c = 25.95 (1) Å; β = 117.17 (3)°; d_{measd} = 2.11 g cm^{-3}, Z = 8, d_{calcd} = 2.139 g cm^{-3}. The structures have been solved by straightforward application of the heavy-atom technique using data (Mo Kα radiation) collected with a Picker FACS-I automated diffractometer. The structure of **1** has been refined (anisotropically for the atoms in the cation) to an unweighted R_1 value of 0.063 for the 2458 observed reflections. For compound **2**, refinement (anisotropic for the heavy atoms Ta, S, and Cl) has resulted in an R_1 value of 0.096 for the 3317 observed reflections.

A perspective view of the eight-coordinate $[Ta(S_2CN(CH_3)_2)_4]^+$ cation in the more accurately determined structure (compound **1**) is shown in Figure 1. The bidentate dithiocarbamate ligands span the m edges of an idealized D_{2d}-$\bar{4}2m$ dodecahedron to give the $mmmm$-D_{2d} stereoisomer.[12,13] The cation is located on a crystallographic twofold axis which passes through the midpoints of the opposite dodecahedral b edges defined by atoms S_{1B} and

Table I. Averaged Dimensions of the Dodecahedral Coordination Polyhedra[a]

	$[Ta(S_2CN(CH_3)_2)_4]^+$ Compd 1	Compd 2	$Ti(S_2CN(C_2H_5)_2)_4$[b]
Bond (Å)			
$M-S_A$	2.590	2.591	2.606
$M-S_B$	2.521	2.515	2.522
Edge (Å)			
a	2.974	3.007	3.00
b	3.648	3.642	3.64
m	2.843	2.843	2.84
g	3.276	3.263	3.30
Angles (deg)[c]			
θ_A	35.0	35.4	35.1
θ_B	77.4	76.6	77.5

[a] Reference 12. [b] Reference 14. [c] θ_A and θ_B are the averaged angles which the $M-S_A$ and $M-S_B$ bonds, respectively, make with the $\bar{4}$ axis of the idealized $D_{2d}-\bar{4}2m$ dodecahedron.[13]

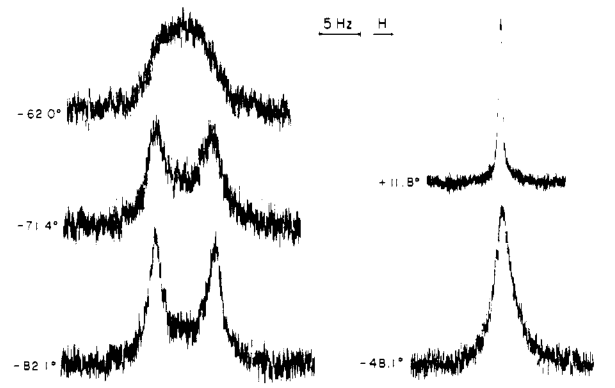

Figure 2. Methyl proton resonances of $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]$, 2.8×10^{-3} *M*, in $CH_2Cl_2-CD_3CN$ (10-15% CD_3CN by weight).

S_{1B}' and by atoms S_{2B} and S_{2B}'. The interpenetrating trapezoidal planes (defined by atoms Ta, S_{1A}, S_{1B}, S_{2A}', and S_{2B}', and by atoms Ta, S_{1A}', S_{1B}', S_{2A}, and S_{2B}) are nearly perpendicular (89.4°), with the metal atom and the atoms which define an individual trapezoid being planar to within 0.04 Å. In the hexachlorotantalate salt (compound **2**) the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation occupies a position of no site symmetry, and packing relations are, of course, different. Nevertheless, the cation maintains the same stereochemistry. Averaged dimensions of the coordination polyhedra in the two salts (Table I) are almost identical, and little different from those in the analogous titanium(IV) complex, $Ti(S_2CN(C_2H_5)_2)_4$.[14] As is expected for molecules of this geometry,[13] complexing bonds to the dodecahedral A sites are longer (by ~0.07 Å) than bonds to the B sites.

Proton NMR spectra of the more soluble salt (compound **2**) in a $CH_2Cl_2-CD_3CN$ solvent mixture were recorded over the temperature range +37 to −94°; typical spectra are presented in Figure 2. The single, time-averaged methyl resonance characteristic of the higher temperatures splits into two lines of equal intensity below the coalescence temperature of −62°. The frequency separation in the slow-exchange limit is 7.20 Hz at 60 MHz, and the minimum line width below coalescence is ~2.0 Hz (at −84°); below −84° the line width increases due to viscosity broadening.

The spectrum in the slow-exchange limit is most simply interpreted in terms of the *mmmm*-D_{2d} stereoisomer found in the solid state, A- and B-site methyl groups (Figure 1) being inequivalent by symmetry. Among the square antiprismatic and dodecahedral stereoisomers enumerated by Hoard and Silverton[13] are several others which are consistent with the limiting low-temperature spectrum, viz., *ssss*-D_2, *gggg*-D_2, *gggg*-S_4, as well as the unlikely *aabb*-D_2. However, in view of the short bite of the dithiocarbamate ligand,[13,15] the similar geometry of the cation in the different crystalline environments of compounds **1** and **2**, and the close similarity of solid state and solution state ir spectra of **2**, we consider it unlikely that there is a change in stereochemistry on going from the solid state to solution.

Total line-shape analysis of the NMR spectra at 15 temperatures between −39.4° (where $k = 200$ sec^{-1}) and −77.6° (where $k = 1.8$ sec^{-1}) has afforded the following activation parameters for exchange of methyl groups between the A and B sites: $\Delta H^* = 10.4 \pm 0.4$ kcal/mol, $\Delta S^* = -3.1 \pm 2.0$ eu, and $\Delta G^*(-62°) = 11.05 \pm 0.08$ kcal/mol. The exchange process is intramolecular; the rates are independent of the concentration of the complex, and intermolecular exchange of $S_2CN(CH_3)_2^-$ ligands between the complex and $NaS_2CN(CH_3)_2$ is slow on the NMR time scale at 37°.

Two kinds of mechanisms for methyl group exchange might be considered: (1) intramolecular metal-centered rearrangement and (2) restricted rotation about the C⩦N bond.[16] Comparison of the C⩦N stretching frequencies in $[Ta(S_2CN(CH_3)_2)_4]^+$ (1557 cm^{-1}) and the methyl ester $CH_3SC(S)N(CH_3)_2$ (1498 cm^{-1})[17] indicates that C⩦N bond rotation should be appreciably slower in the cation than in the ester. Since C⩦N bond rotation in the ester is slow on the NMR time scale below about −25°,[17] the observed coalescence process for $[Ta(S_2CN(CH_3)_2)_4]^+$ may be assigned to metal-centered rearrangement.

Previous work[4-6] has shown that the analogous $M(S_2CNR_2)_4$ (M = Ti or Zr) complexes are stereochemically nonrigid at very low temperatures (down to at least −140°[5]). Consequently, the relatively high coalescence temperature for $[Ta(S_2CN(CH_3)_2)_4]^+$ (−62°) is somewhat surprising, especially in view of the nearly identical dimensions for the coordination polyhedra of $[Ta(S_2CN(CH_3)_2)_4]^+$ and $Ti(S_2CN(C_2H_5)_2)_4$ (Table I). It is evident that the charge on the tantalum complex plays a dominant role in slowing the rate of rearrangement. We are commencing studies of complexes with unsymmetrical dithiocarbamate ligands in an effort to obtain information about the rearrangement mechanism.

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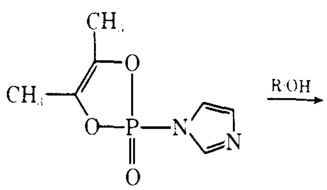
One-Flask Synthesis of Unsymmetrical Phosphodiesters. Selective Amine Catalysis of Phosphorylations of Primary vs. Secondary Alcohols

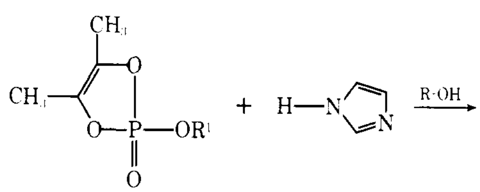
Sir:

We wish to describe a new procedure for the direct conversion of two different alcohols into an unsymmetrical phosphodiester without the isolation of any intermediate ("one-flask" reaction).

An acetonitrile solution of R^1OH is added to a solution of *N*-(1,2-dimethylethenylenedioxyphosphoryl)imidazole[1] (**1**) in the same solvent, and the mixture is stirred for 45 min (20°, 0.6 *M*). R^2OH is introduced, and the solution is stirred at 20° for periods which vary with the structure of the alcohols; reaction times are conveniently ascertained by ^1H NMR spectrometry. The solution is diluted with acetonitrile, mixed with twice its volume of water (final molarity ~0.1), treated with 2 mol equiv of triethylamine, and stirred at 70° for ca. 10 hr. The acetonitrile is evaporated, and the aqueous solution is treated with sodium carbonate, extracted with dichloromethane to remove by-products, acidified, and reextracted with dichloromethane. The phosphodiester, **4**, is obtained in high degree of purity and is converted into a crystalline amine salt, **4a**, for characterization.



1



2

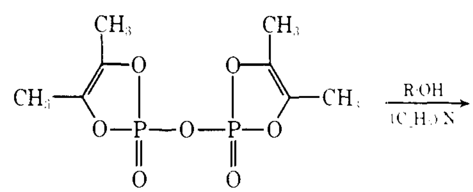
$(R^1O)(R^2O)P(O)OCH(CH_3)COCH_3 \xrightarrow{H_2O}$
3
$(R^1O)(R^2O)P(O)(OH) + HOCH(CH_3)COCH_3$
4

The following dicyclohexylammonium dialkyl phosphates,[2] **4a**, were isolated in 75–80% yield (based on R^1OH) by the above procedure: $(C_2H_5)_2CH$, $(CH_3)_2CHCH_2$; (±)3-*p*-menthanyl, $C_6H_5CH_2$; c-C_6H_{11}, $(CH_3)_2CH$; c-C_5H_9, $(CH_3)_2CHCH_2$.[3,4]

The phosphorylimidazole, **1**, can also be utilized for the conversion of the two alcohols into the acyclic triester, **3**, in one laboratory operation; **3** is then hydrolyzed[4a] to the diester, **4**, with or without an intervening purification step. The reaction is carried out as in the first procedure, but in dichloromethane solution; the latter is extracted with dilute hydrochloric acid to yield the virtually pure triester, **3**. The following dialkyl(1-methylacetonyl) phosphates,[2] **3**, were obtained in 92–96% yield (based on R^1OH): $(C_2H_5)_2CH$, $C_6H_5CH_2$; (±)3-*p*-menthanyl, $C_6H_5CH_2$; c-C_6H_{11}, $(CH_3)_2CH$; $[(CH_3)_2CH]_2CH$, $C_6H_5CH_2$; c-C_5H_9, $(CH_3)_2CHCH_2$.[3]

The syntheses are possible because alcohols react much faster with the phosphorylimidazole, **1**, than with the alkyl cyclic enediol phosphates, **2**. Imidazole[5] autocatalyzes the reaction of R^1OH with **1**, and is also an excellent catalyst for the reactions of primary and secondary alcohols (R^2OH) with the cyclic triesters, **2**. For example, when R^2 = $(CH_3)_2CHCH_2$, and R^1 = c-C_5H_9, $t_{1/2}$ for the phosphorylation is reduced from 8 hr to 2 min in 0.2 *M* $CDCl_3$, and from 12 hr to 30 min in 0.2 *M* CD_3CN by imidazole (equimolar amounts of reagents, at 25°). The rates of phosphorylation by the cyclic triesters **2** decrease significantly as the polarity of the solvent, and the size of R^1 and R^2, increase; therefore, the imidazole effect is essential for the success of the syntheses.

Triethylamine is an effective catalyst for the reaction of alcohols with the cyclic triesters, **2**, and the following procedure can also be used to prepare the acyclic triesters, **3**, in one flask. A dichloromethane solution of R^1OH containing 1 mol equiv of triethylamine is added to a solution of di(1,2-dimethylethenylene) pyrophosphate[4a] (**5**) in the same solvent, and the mixture is stirred for 30 min (20°, 0.6 *M*). R^2OH, together with 1 mol equiv of triethylamine, is introduced, and the mixture is stirred for the appropriate period of time (ca. 10 hr at 20°, in 0.5 *M* solutions, when R^1 = secondary alkyl and R^2 = primary alkyl). The dichloromethane solution is extracted with hydrochloric acid and sodium carbonate to yield the virtually pure acyclic triester **3**. The following triesters **3** were obtained in 92–95% yield (based on R^1OH): c-C_5H_9, $(CH_3)_2CHCH_2$[4a]; c-C_5H_9, $C_6H_5CH_2$.[4a] Without triethylamine these phosphorylations require ca. 30 hr for completion.[4a]



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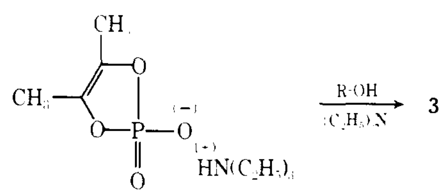
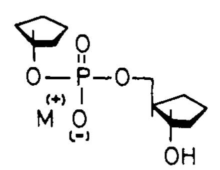


Triethylamine catalyzes the reactions of primary alcohols (R^2OH) with the cyclic triesters **2**, *but it does not catalyze the reactions of secondary alcohols with* **2**. This remarkable specificity can be exploited for the synthesis of compound **6** (M = $C_6H_{11}NH_3^{(+)}$) from cyclopentanol (R^1OH) and unprotected *trans*-2-hydroxymethylcyclopentanol (R^2OH). The selectivity in the phosphorylation of the pri-



6