presence of a magnetic exchange interaction. It can be prepared either with or without one water molecule per manganese ion depending on the synthetic route, the sixth coordination site of each manganese ion in the dimer being sterically and electronically accessible to small ligand molecules. It should be noted in this respect that the oxygen oxidation of this dimer has been shown to afford a mixed-valence Mn(II)–Mn(III) complex[24] that exhibits magnetic properties related to those of the oxygen-evolving metalloprotein of photosystem II. $Mn^{II}(5\text{-}NO_2\text{-saldien})\cdot CH_3OH$ (**3**) presents extended intermolecular magnetic exchange interactions in the solid state. When dissolved in noncoordinating solvents, it exhibits dimeric properties similar to those of $Mn^{II}$(saldien).

By lengthening the bridging units between the three nitrogen donors of these pentadentate ligands from ethylene to propylene units and thus giving some more flexibility to the pentadentate ligand, it is possible to obtain monomeric pentacoordinated manganese(II) complexes (compounds **4** and **5**).

Complexes **6** and **7**, characterized by two $N_2O$ donor sets, and complexes **8**–**13**, characterized by a $N_4O_2$ donor set, have been shown to be monomeric hexacoordinated species with departures from the regular octahedral symmetry more or less marked depending on steric and/or electronic factors. These conclusions have been confirmed by an X-ray molecular structure determination for one of these complexes, $Mn^{II}[5\text{-}NO_2\text{-sal-N}(1,5,9,13)]$.

Among the complexes studied herein the monomeric compounds **4**–**13** exhibit splitting of the NH and $CH_2$ stretches and of the $CH_2$ rocking frequencies in the solid state. They also exhibit a splitting of the manganese hyperfine EPR resonances at both X-band and Q-band when examined as frozen solutions. These observations, indicative of simultaneous NH, $CH_2$, and Mn inequivalences both in the solid state and in solution, indicate that these complexes may exist in different isomeric forms. Indeed, structural determinations indicate that the $Mn^{II}[5\text{-}NO_2\text{-sal-N}(1,5,9,13)]$ crystal is built from trans isomers (this work) while the $Mn^{IV}[\text{sal-N}(1,4,7,10)](ClO_4)_2$ crystal[23] is made from cis-$\alpha$ isomers.

**Acknowledgment.** We thank the National Institutes of Health for partial support of the work at the University of Illinois through Grant HL 13652 to D.N.H. J.-P.T. and D.N.H. are thankful for a NATO grant for collaborative research. The crystal structure of complex **13** was determined by F. Dahan. Her excellent contribution to this work is gratefully acknowledged. J.-M. Savariault is to be thanked for help in obtaining the X-ray diffraction powder patterns and unit cell dimensions of complex **2**. M. D. Timken and Y. T. Hwang are acknowledged for help in fitting the magnetic susceptibility data.

**Registry No.** **1**, 69879-57-8; **2**, 101056-15-9; **3**, 101056-16-0; **3**·$CH_3OH$, 101247-86-3; **4**·$H_2O$-*trans*, 101224-27-5; **4**·$OH_2$-*cis*, 101398-95-2; **5**-*trans*, 101056-17-1; **6**-*trans*, 101143-58-2; **6**-*cis*, 84279-69-6; **7**-*trans*, 101143-59-3; **7**-*cis*, 84279-70-9; **8**-*trans*, 101056-18-2; **8**-*cis*, 101398-96-3; **9**-*trans*, 101056-19-3; **9**-*cis*, 101400-28-6; **10**-*trans*, 75058-23-0; **10**-*cis*, 101398-97-4; **11**-*trans*, 101056-20-6; **11**-*cis*, 101312-95-2; **12**-*trans*, 75061-38-0; **12**-*cis*, 101468-30-8; **13**-*trans*·$xC_2H_4Cl_2$, 101056-22-8; **13**-*cis*, 101312-96-3; salprenOH, 3694-33-5; 5-$NO_2$-saldien, 101079-16-7; 5-$NO_2$-saldpt, 88389-93-9; 5-$NO_2$-salaep, 101079-17-8; 5-$NO_2$-sal-N(1,4,7,10), 101079-18-9; 5-$NO_2$-sal-N(1,5,8,12), 101079-19-0; 5-$NO_2$-sal-N(1,5,9,13), 101079-20-3; N(1,5,9,13), 4605-14-5; N(1,4,7,10), 112-24-3; N(1,5,8,12), 10563-26-5; dpt, 56-18-8; dien, 111-40-0; aep, 2706-56-1; 1,3-diamino-2-hydroxypropane, 616-29-5; salicylaldehyde, 90-02-8; 5-nitrosalicylaldehyde, 97-51-8.

**Supplementary Material Available:** Figure 10, showing the KBr pellet infrared spectra of 5-$NO_2$-sal-N(1,5,8,12) (- - -) and $Mn^{II}[5\text{-}NO_2\text{-sal-N}(1,5,8,12)]$ (—), Figures 11–13 and 17, showing magnetic susceptibility data and least-squares fits for complexes **4**, **5**, **1**, and **9**, respectively, Figures 14a–c and 15a–c, showing X-band powder EPR spectra for complexes **12**, **7**, **6**, **9**, **13**, and **10**, respectively, Figure 16a,b, showing X-band DMF/toluene glass EPR spectra for complexes **10** and **7**, respectively, Tables IX and X, listing analytical data for Schiff base ligands isolated as solids and manganese(II) complexes, respectively, Tables XI–XIII, listing observed and calculated structure factors, final thermal parameters, and hydrogen atomic positional and thermal parameters, respectively, for $Mn^{II}[5\text{-}NO_2\text{-sal-N}(1,5,9,13)]\cdot 0.65CH_2H_4Cl_2$, Tables XIV–XXVII, listing experimental and calculated magnetic susceptibility data, and Tables XXVIII–XXX, listing intermolecular hydrogen contacts, crystallization solvent bond lengths and angles, and deviations of atoms from their least-squares plane, respectively, for $Mn^{II}[5\text{-}NO_2\text{-sal-N}(1,5,9,13)]\cdot 0.65CH_2H_4Cl_2$ (42 pages). Ordering information is given on any current masthead page.

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Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

# Atom Transfer and Chelate Fragmentation Reactions of Bis(cyclopentadienyl)titanium Thiophosphoryls[1]

Gregg A. Zank and Thomas B. Rauchfuss*

*Received June 28, 1985*

The compound $(RCp)_2TiS_4(PAn)_2$ (**1**; RCp = $\eta^5$-$RC_5H_4$, R = H, Me; An = 4-$MeOC_6H_4$) reacts with 1 or 2 equiv of oxygen to give the six- and seven-membered heterocycles $(RCp)_2TiOS_4(PAn)_2$ (**2**) and $(RCp)_2TiO_2S_4(PAn)_2$ (**3**). These reactions appear to involve the dissociation of **1** to give $(RCp)_2TiS_3(PAn)$ and $[AnPS]_3$, followed by the oxygenation of the latter to give $[AnPSO]_n$ and insertion of an AnPSO fragment into $(RCp)_2TiS_3(PAn)$ to give **2**. In a similar way $(RCp)_2TiS_3(PAn)$ adds $[AnPS_2]_2$ to give $(RCp)_2TiS_5(PAn)_2$ (**4**), an all-sulfur analogue of **2**. Compound **4** converts organic carbonyls into thiocarbonyls concomitant with the formation of **2**. The structure of **3** was determined by single-crystal X-ray diffraction. $(CH_3C_5H_4)_2TiO_2S_4(P(C_6H_4OCH_3))_2$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.458$ (3) Å, $b = 10.611$ (3) Å, $c = 15.975$ (5) Å, $\alpha = 94.96$ (2)°, $\beta = 109.34$ (2)°, and $\gamma = 105.38$ (2)°. With use of 7288 unique reflections with $I > 3.00\sigma(I)$, the structure was solved by direct methods and refined to a final $R = 0.037$ and $R_w = 0.048$. The structure consists of a $(MeCp)_2Ti$ moiety incorporated into a seven-membered Ti–O–P(S,An)–S–S–P(An,S)–O ring (each phosphorus atom maintaining a terminal sulfide and an anisole group). The reaction of **1** or **4** with organic carbonyls gives $(MeCp)_2TiO_2S_3(PAn)_2$, which exists as cis and trans isomers.

## Introduction

Monoorganophosphorus sulfides have an extensive chemistry and are of considerable importance as synthetic intermediates and reagents.[2] Aryl derivatives of the phosphorus sulfides have been intensively studied, and five structural types are now characterized, three of the formula $[ArPS]_n$[3-5] ($n$ = 3, 4) and two of the formula $[ArPS_2]_n$[4-6] = 1, 2). The dimeric compounds $[ArPS_2]_2$ have received the greatest attention because of their utility in organic chemistry,[7] and their transition-metal derivatives have been the

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(1) This is the second of a two-part series; for part 1 see ref 10.

(2) Maier, L. *Top. Phosphorus Chem.* **1970**, *2*, 43–131; **1978**, *10*, 129–69.

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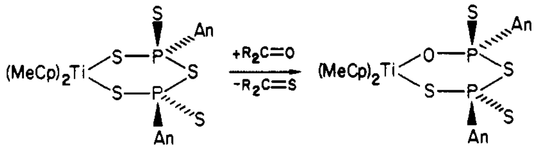
**Table I.** Selected Bond Distances (Å) and Angles (deg) for $(CH_3C_5H_4)_2TiO_2S_4(PAn)_2$[a]

| | | | |
|---|---|---|---|
| Ti–$O_a$ | 1.969 (1) | Ti–$O_b$ | 1.985 (1) |
| Ti–$C_{ga}$ | 2.067 | Ti–$C_{gb}$ | 2.070 |
| $O_a$–$P_a$ | 1.539 (2) | $O_b$–$P_b$ | 1.531 (2) |
| $S_{a1}$–$P_a$ | 1.944 (1) | $S_{b1}$–$P_6$ | 1.950 (1) |
| $S_{a2}$–$P_a$ | 2.119 (1) | $S_{b2}$–$P_6$ | 2.108 (1) |
| $S_{a2}$–$S_{b2}$ | 2.070 (1) | | |
| $P_a$–$C_{a1}$ | 1.807 (1) | $P_b$–$C_{b1}$ | 1.798 (2) |
| Ti–$O_a$–$P_a$ | 147.65 (9) | Ti–$O_b$–$P_b$ | 151.04 (9) |
| $O_a$–$P_a$–$S_{a1}$ | 120.93 (6) | $O_b$–$P_b$–$S_{b1}$ | 119.04 (7) |
| $O_a$–$P_a$–$S_{a2}$ | 106.70 (6) | $O_b$–$P_b$–$S_{b2}$ | 107.48 (6) |
| $O_a$–$P_a$–$C_{a1}$ | 105.31 (9) | $O_b$–$P_b$–$C_{b1}$ | 105.42 (9) |
| $S_{a1}$–$P_a$–$S_{a2}$ | 102.74 (3) | $S_{b1}$–$P_b$–$S_{b2}$ | 103.54 (4) |
| $P_a$–$S_{a2}$–$S_{b2}$ | 105.47 (3) | $P_b$–$S_{b2}$–$S_{a2}$ | 102.04 (3) |

[a] Atoms are labeled in agreement with Figure 1.

subject of three recent reports.[8-10] Chelates containing both RP(S) and S atoms are of interest because of their relationship to polysulfide compelxes.[11] Our previous paper[9] described the synthesis and interconversions of the compounds $(RCp)_2TiS_3(PAr)$ and $(RCp)_2TiS_4(PAr)_2$. The latter compound and its relative $(RCp)_2TiS_5(PAr)_2$ have been found to be highly labile and reactive toward oxygen-containing substrates (eq 1 and 2, An = 4-$C_6H_4OMe$). In contrast $(RCp)_2TiS_5$ is kinetically inert and

1 3 (1)



4 2 (2)

resilient to a variety of oxo compounds. These transformations are described in this paper with attention to their mechanism, their scope, and the structure of one of the products. These reactions likely proceed via fragments that possess monoorganophosphorus moieties multiply bonded to oxygen atoms. Unlike compounds containing P=S bonds mentioned earlier and those with P=P linkages, which have recently been extensively studied,[12] the reactions of low-coordinate phosphorus oxides are not well characterized.[13,14]

## Results and Discussion

Reaction 1 occurs within seconds when solutions of $(MeCp)_2TiS_4(PAn)_2$ (**1**; An = 4-$C_6H_4OMe$) are exposed to air. The reaction time is lengthened to hours when only stoichiometric quantities of oxygen are employed. The conversion of **1** to the dioxo complex also occurs upon treatment with dimethyl sulfoxide, affording dimethyl sulfide as the coproduct in quantitative yield. The dioxo complex **3** was characterized by spectroscopy as well as by single-crystal X-ray diffraction (Figure 1). Important bond distances and angles are presented in Table I. The structural analysis revealed that **3** is a chiral molecule of approximate $C_2$ symmetry. The key parameters for the seven-membered $TiO_2P_2S_2$ ring are the open Ti–O–P angles of 149 ± 2°, Ti–O distances of 1.97 ± 0.01 Å (for comparison, a Ti–O–C angle of 133.2° and Ti–O distance of 1.86 Å are found for $Cp_2Ti(OC_2H_5)Cl$[15]), and a normal S–S distance of 2.07 Å.[16] A spirocyclic $C(O_2P_2S_2)_2$ structure has been proposed for the product of $[AnPS_2]_2$ and $C(CH_2OH)_4$.[17] Both the $^1H$ and the $^{31}P$ NMR studies indicate that the trans configuration observed for **3** in the solid state is retained in solution.

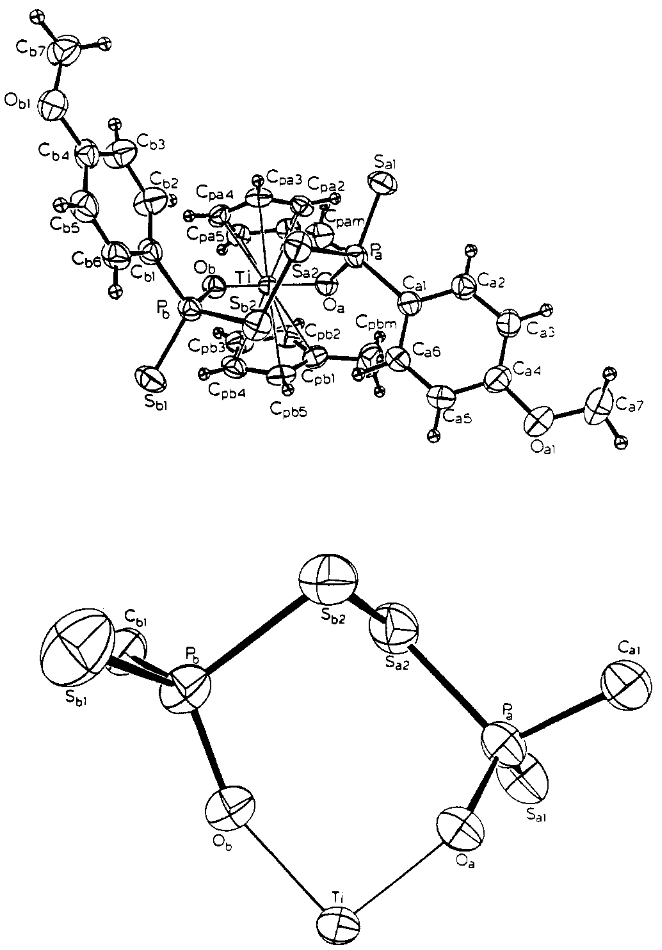


**Figure 1.** ORTEP view of $(MeCp)_2TiO_2S_4(PAn)_2$ (**3**) showing the labeling scheme for all non-hydrogen atoms and a drawing nearly normal to the seven-membered ring. The ellipsoids are drawn with 35% probability boundaries and the hydrogen atoms assigned small arbitrary isotropic thermal coefficients.

When solutions of **1** are supplied with only 1 equiv of oxygen (with $O_2$ or $Me_2SO$), a monoxide is formed. The new compound $(MeCp)_2TiOS_4(PAn)_2$ (**2**) exists as a mixture of cis and trans isomers, each of which exhibits a similar AB quartet in the $^{31}P\{^1H\}$ NMR spectrum. The $^1H$ NMR spectrum of **2** also supports the presence of two asymmetric isomers in a 9:1 ratio (eq 3). The diastereoisomers of **2** are apparently intermediates in the transformation shown in eq 1 as evidenced by the fact that they react further with oxygen or $Me_2SO$ to give the single diastereoisomer of **3** (Figure 2). We have not proven that $(MeCp)_2TiOS_4(PAn)_2$ is an intermediate in the conversion of **1** into **3** since the con-

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(7) For an early report see: Hoffman, H.; Schumacher, G. *Tetrahedron Lett.* **1967**, *31*, 2963-6. For a review see: Pedersen, V.; Yde, B.; Andersen, T.; Thorsen, M.; Clausen, K.; Lawesson, S.-O. *Phosphorus Sulfur* **1983**, *18*, 381-4

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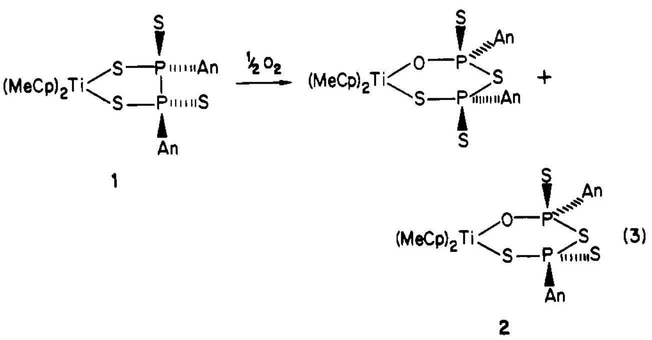


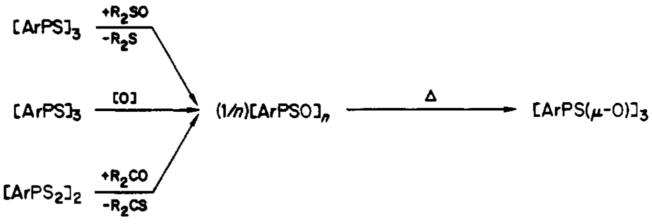
(3)

proportionation of **1** and **3** occurs faster than the oxygenation of **2**.

Our investigation of the mechanism of the conversion of **1** to **2** evolved into a study of the chemistry of the trimers of the type $[ArPS]_3$ (Ar = Ph, An). The latter exists in equilibrium with **1** according to eq 4.[10] The compound $[PhPS]_3$[18] is quite oxophilic,

$$(MeCp)_2TiS_4(PAn)_2 \rightleftarrows (MeCp)_2TiS_3(PAn) + {}^1/_3[AnPS]_3 \quad (4)$$

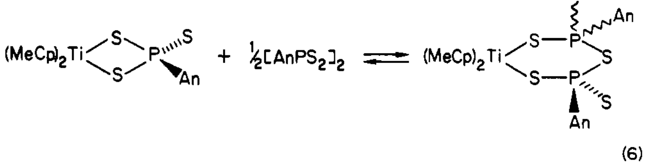
and its solutions react quantitatively with $Me_2SO$ to give dimethyl sulfide and a soluble form of $[PhPSO]_n$. The same oligomer can also be prepared by treatment of $[PhPS]_3$ with dry oxygen, and a spectroscopically similar material is formed through the reaction of $[AnPS_2]_2$ with acetamide (eq 5).[19] Aerobic workup of solutions



(5)

of these oligomers eventually leads to the formation of the known trimeric $[AnP(S)(\mu\text{-}O)]_3$,[19] but this species is *not* observed when these sulfur-transfer reactions are conducted under mild conditions. Solutions of the metastable form of $[ArPSO]_n$ were found to react rapidly with $(MeCp)_2TiS_3(PAn)$, giving high yields of $(MeCp)_2TiOS_4(P_2AnAr)$ (Ar = Ph, An). Significantly, the known trimer $[PhP(S)(\mu\text{-}O)]_3$ does *not* react with $(MeCp)_2TiS_3(PAn)$; therefore, $[AnP(S)(\mu\text{-}O)]_3$ is probably not the primary organophosphorus product in the S-transfer reactions of $[AnPS_2]_2$.[21]

In the same way that $(MeCp)_2TiS_3(PAn)$ reacts with $[AnPSO]_n$, we observe that a similar reaction occurs for $AnPS_2$. The latter, a three-coordinate phosphorus(V) compound,[7] exists as a minority species in solution equilibrium with the well-known dimer $[AnPS_2]_2$.[19] Treatment of $(MeCp)_2TiS_3(PAn)$ with $[AnPS_2]_2$ indeed gives a high yield of $(MeCp)_2TiS_5(PAn)_2$ (**4**), which was isolated in an analytically pure form. The NMR spectrum of this $S_5(PAn)_2$ chelate indicates the presence of a pair of isomers, presumably cis and trans with one isomer possessing a symmetry plane and the other a twofold rotational axis (eq 6). The two



(6)

isomers occur in nearly equal abundance unlike the corresponding isomer distribution for **2**. $^{31}P$ NMR studies also show that in solution the $(MeCp)_2TiS_5(PAn)_2$ isomers exist in equilibrium with $(MeCp)_2TiS_3(PAn)$ and $[AnPS_2]_2$ such that the relative concentrations of these species are comparable. As expected, $(MeCp)_2TiS_5(PAn)_2$ reacts readily with ketones (70 °C) or amides (25 °C) to initially give the thiocarbonyl compound and **2**. We propose that this transformation involves the sequence of events

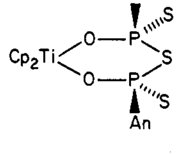
$$(MeCp)_2TiS_5(PAn)_2 \rightleftarrows (MeCp)_2TiS_3(PAn) + (1/2)[AnPS_2]_2$$

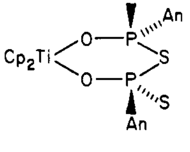
$$[AnPS_2]_2 \rightleftarrows 2AnPS_2$$

$$AnPS_2 + R_2CO \rightleftarrows (1/n)(AnPSO)_n + R_2CS$$

$$(MeCp)_2TiS_3(PAn) + (1/n)(AnPSO)_n \rightleftarrows (MeCp)_2TiOS_4(PAn)_2$$

Prolonged reaction of **4** with acetamide or benzophenone afforded substantial quantities of a new orange material that exhibits two $^{31}P$ absorptions at 86.8 and 83.8 ppm in the approximate ratio of 3:1. The $C_5H_5$ derivative of this same compound can be prepared (in 50% yield) more easily from the reaction of $Cp_2TiPS_4(PAn)_2$ and acetamide in hot THF. This compound is formulated as $Cp_2TiO_2S_3(PAn)_2$ on the basis of the microanalytical and mass spectroscopy results. The isomers of this compound are assigned the structures shown





on the basis of the 200-MHz $^1H$ NMR spectrum (Figure 3), which shows splitting patterns expected for both $C_2$ (equivalent Cp groups) and $C_s$ symmetry (nonequivalent Cp groups).

## Conclusions

The thiophosphoryl chelates $(RCp)_2TiS_4(PAn)_2$ and $(RCp)_2TiS_5(PAn)_2$ are highly labile in solution in contrast to the related polysulfides, e.g., $(RCp)_2TiS_5$.[11,22] The lability of these

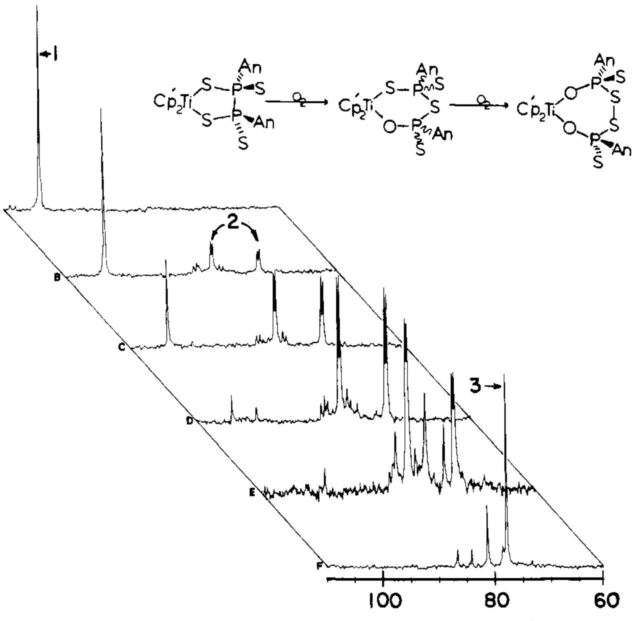


**Figure 2.** 40.5-MHz $^{31}P\{^1H\}$ NMR spectra of different stages in the reaction of $(MeCp)_2TiS_4(PAn)_2$ (**1**) with oxygen in THF. Spectra B–E were recorded at 24-h intervals while spectrum F was recorded 10 days after spectrum A. The monoxide $(MeCp)_2TiOS_4(PAn)_2$ (**2**) can best be seen in spectra B–E while the final product $(MeCp)_2TiO_2S_4(PAn)_2$ (**3**) is predominant in spectrum F. Also visible in the final spectrum are the two isomers of $(MeCp)_2TiO_2S_3(PAn)_2$ at 87 and 84 ppm.

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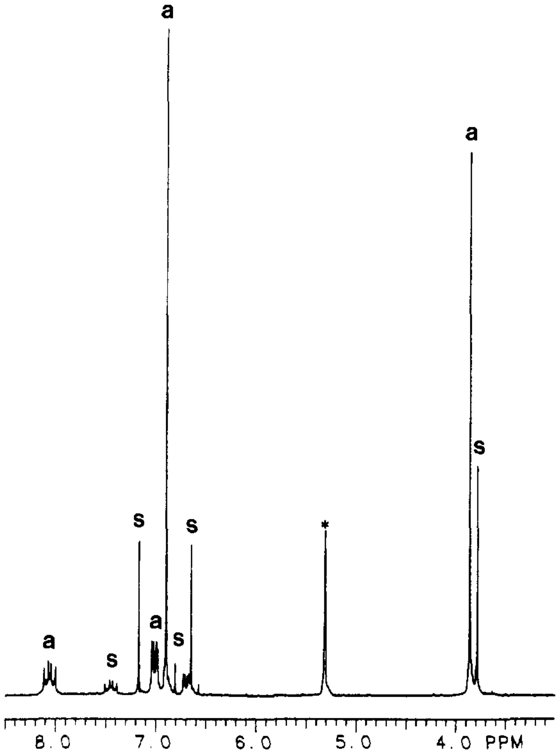

**Figure 3.** 200-MHz $^1$H NMR spectrum of $Cp_2TiO_2S_3(PAn)_2$ in $CD_2Cl_2$ (*). The labels a and s indicate those signals arising from the anti and syn isomers, respectively.

chelates involves the reversible release and capture of organophosphorus compounds of the type $RPS_2$, RPSO, and RPS. We term this type of reaction chelate fragmentation. These studies have provided evidence that long-lived intermediates of the formula $[RPSO]_n$ are formed in the atom-transfer reactions of $[PhPS]_3$ and $[AnPS_2]_2$.

The conversion of **1** to **3** is an example of the coupling of sulfido ligands induced by oxidation. This is a novel pathway by which additional ligands can be added to the coordination sphere of a metal (or nonmetal, e.g., phosphorus) without ligand displacement. An important driving force for this process in the case of **1** → **3** is the relatively large S–S bond energy (~60 kcal/mol[23]). Related examples of the pattern of S–S coupling concomitant with substrate binding involve the oxidation of $(MeCp)_4Ti_4(S_2)_3S_2(\mu_4\text{-}O)$[24] and the addition of phenyltriazolinedione (PTD) to $(MeCp)_2V_2(S)_2(PTD)$[25] (eq 7 and 8).

$$(MeCp)_4Ti_4(S_2)_3S_2(\mu_4\text{-}O) + [O] \rightarrow (MeCp)_4Ti_4(S_2)_4(\mu\text{-}O)(\mu_4\text{-}O) \quad (7)$$

$$(MeCp)_2V_2(PTD)(S)_2 + PTD \rightarrow (MeCp)_2V_2(PTD)_2(S_2) \quad (8)$$

## Experimental Section

**Materials and Methods.** A detailed description of the materials and methods used in this work has been presented previously.[10] Lawesson's reagent, $An_2P_2S_4$, was prepared according to the literature method[26] although it is available commercially. Abbreviations for NMR data: s, singlet; dd, doublet of doublets; pt, pseudotriplet; m, multiplet.

**$(CH_3C_5H_4)_2TiO_2S_4(PAn)_2$ (3). From Oxygen.** This compound can be obtained in near-quantitative yields by exposure of red-brown solutions of $(MeCp)_2TiS_4(PAn)_2$ (**1**) to air followed by recrystallization of the orange-red product from $CH_2Cl_2$–MeOH. Anal. Calcd for $C_{26}H_{28}O_4S_4P_2Ti$: C, 48.59; H, 4.39; P, 9.64; Ti, 7.45. Found: C, 48.13; H, 4.41; P, 9.85; Ti, 7.11. FDMS (*m/e*): 642, $M^+$; 626, $(M - O)^+$; 610 $(M - 2O)^+$ (**1**). $^1$H NMR (360 MHz, $CDCl_3$): δ 8.13 (dd, 2 H, $J_{PH}$ = 8.8 Hz); 7.27 (pt, 1 H); 7.08 (pt, 1 H); 7/.2 (dd, 2 H, $J_{PH}$ = 1.9 Hz); 6.88 (pt, 1 H); 6.72 (pt, 1 H); 3.89 (s, 3 H); 2.03 (s, 3 H). $^{31}P\{^1H\}$ NMR (40.5 MHz, $C_6D_6$): δ 78.5 (s).

Table II. Positional Parameters for the Non-Hydrogen Atoms of $(CH_3C_5H_4)_2TiO_2S_4(PAn)_2$

| atom type[b] | fractional coordinates x/a | y/b | z/c |
|---|---|---|---|
| Ti | 0.26131 (3) | 0.03825 (3) | 0.27192 (2) |
| $S_{a1}$ | −0.10337 (7) | −0.16533 (7) | 0.37839 (4) |
| $S_{a2}$ | −0.11773 (6) | 0.11036 (6) | 0.31887 (4) |
| $S_{b1}$ | 0.19278 (9) | 0.42823 (6) | 0.18853 (4) |
| $S_{b2}$ | −0.08636 (6) | 0.21961 (6) | 0.22153 (4) |
| $P_a$ | −0.10401 (5) | −0.07907 (5) | 0.27579 (3) |
| $P_b$ | 0.15777 (6) | 0.32192 (5) | 0.27768 (3) |
| $O_a$ | 0.0364 (1) | −0.0540 (1) | 0.2442 (1) |
| $O_b$ | 0.2432 (2) | 0.2179 (1 | 0.2997 (1) |
| $C_{pa1}$ | 0.4043 (2) | −0.0961 (2) | 0.3605 (1) |
| $C_{pa2}$ | 0.2834 (2) | −0.0878 (2) | 0.3905 (1) |
| $C_{pa3}$ | 0.3100 (2) | 0.0456 (2) | 0.4264 (1) |
| $C_{pa4}$ | 0.4506 (2) | 0.1218 (2) | 0.4195 (1) |
| $C_{pa5}$ | 0.5080 (2) | 0.0361 (2) | 0.3783 (1) |
| $C_{pam}$ | 0.4328 (4) | −0.2213 (3) | 0.3315 (2) |
| $C_{pb1}$ | 0.1811 (3) | −0.0869 (2) | 0.1199 (1) |
| $C_{pb2}$ | 0.3426 (3) | −0.0650 (3) | 0.1664 (2) |
| $C_{pb3}$ | 0.4210 (3) | 0.0728 (3) | 0.1858 (2) |
| $C_{pb4}$ | 0.3084 (3) | 0.1359 (2) | 0.1506 (1) |
| $C_{pb5}$ | 0.1614 (3) | 0.0395 (2) | 0.1125 (1) |
| $C_{pbm}$ | 0.0545 (5) | −0.2198 (3) | 0.0838 (2) |
| $C_{a1}$ | −0.2764 (2) | −0.1622 (2) | 0.1755 (1) |
| $C_{a2}$ | −0.3783 (2) | −0.2837 (2) | 0.1744 (1) |
| $C_{a3}$ | −0.5119 (2) | −0.3508 (2) | 0.0985 (2) |
| $C_{a4}$ | −0.5454 (2) | −0.2943 (2) | 0.0223 (1) |
| $C_{a5}$ | −0.4460 (3) | −0.1709 (3) | 0.0225 (1) |
| $C_{a6}$ | −0.3118 (3) | −0.1065 (2) | 0.0976 (1) |
| $O_{a1}$ | −0.6725 (2) | −0.3491 (2) | −0.0556 (1) |
| $C_{a7}$ | −0.7815 (3) | −0.4732 (3) | −0.0600 (2) |
| $C_{b1}$ | 0.1938 (2) | 0.4180 (2) | 0.3852 (1) |
| $C_{b2}$ | 0.2789 (3) | 0.3864 (2) | 0.4645 (2) |
| $C_{b3}$ | 0.3055 (3) | 0.4564 (3) | 0.5486 (2) |
| $C_{b4}$ | 0.2441 (2) | 0.5604 (2) | 0.5536 (1) |
| $C_{b5}$ | 0.1582 (3) | 0.5939 (2) | 0.4749 (2) |
| $C_{b6}$ | 0.1337 (3) | 0.5244 (2) | 0.3919 (2) |
| $O_{b1}$ | 0.2616 (2) | 0.6334 (2) | 0.6328 (1) |
| $C_{b7}$ | 0.3226 (3) | 0.5843 (3) | 0.7133 (2) |

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [a] Atoms are labeled in agreement with Figure 1.

**From Organic Sulfoxides.** In a typical reaction $Me_2SO$ (2.9 μL, 0.04 mmol) was added to a red-brown $CD_2Cl_2$ (0.5 mL) solution of $(MeCp)_2TiS_4(PAn)_2$ (11.5 mg, 0.02 mmol), effecting an immediate color change to orange. The $^1$H NMR spectrum of this mixture showed resonances attributable only to excess $Me_2SO$ (δ 2.50), $(CH_3)_2S$ (δ 2.05), and those identical with those of authentic samples of **3**.

**$(CH_3C_5H_4)_2TiOS_4(PAn)_2$ (2). From Oxygen.** A THF (30 mL) solution of **1** (305 mg, 0.5 mmol) was treated with dry $O_2$ (5.6 mL, 0.5 mmol of O) for 48 h. The reaction mixture was evaporated to dryness and the orange-red residue extracted with toluene (50 mL). Concentration of these extracts to ca. 10 mL and cooling to 0 °C afforded 200 mg (65%) of orange, air-sensitive, crystalline **2** isolated by Schlenk filtration. Anal. Calcd for $C_{26}H_{28}O_3S_4P_2Ti$: C, 49.84; H, 4.51; P, 9.88; Ti, 7.63. Found: C, 50.32; H, 4.73; P, 9.70; Ti, 7.42. FDMS (*m/e*): 626, $M^+$; 610, $(M - O)^+$ (**1**). $^1$H NMR (200 MHz, $CD_2Cl_2$): δ 8.5–6.0 (m, 32 H); isomer A, δ 3.97 (s, 3 H), 3.85 (s, 3 H), 2.19 (s, 3 H), 2.03 (s, 3 H; isomer **B**, δ 3.81 (s, 3 H), 3.79 (s, 3 H), 1.98 (s, 3 H), 1.92 (s, 3 H). $^{31}P\{^1H\}$ NMR (40.5 MHz, $C_6D_6$): isomer A, δ 84.0, 75.6 (dd ×2, $J_{PP}$ = 14.0 Hz); isomer **B**, δ 87.0, 82.4 (dd ×2, $J_{PP}$ = 24.2 Hz).

**By Conproportionation of 1 and 3.** Solvent (2:1 THF/$C_6D_6$ (v/v), 4 mL) was added to an NMR tube contining both $(MeCp)_2TiS_4(PAn)_2$ (30 mg, 0.05 mmol) and **3** (33 mg, 0.05 mmol); the $^{31}P\{^1H\}$ NMR spectrum of this solution showed resonances coincident with those of authentic samples of **2** along with weaker ones attributable to both **1** and **3**. After the solution was allowed to stand 20 h, the color changed to an orange-red

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and the $^{31}$P{$^1$H} NMR spectrum consisted only of resonances attributable to **2**.

**$(CH_3C_5H_4)_2TiS_5(PAn)_2$.** $(AnPS_2)_2$ (20 mg, 0.05 mmol) was added to a stirred solution of $(MeCp)_2TiS_3(PAn)$ (60 mg, 0.1 mmol) in THF (10 mL) and the resulting solution stirred 24 h. Toluene (10 mL) was added, and the solution was concentrated to 5 mL and cooled to 0 °C. Schlenk filtration gave air-sensitive, purple crystalline $(MeCp)_2TiS_5(PAn)_2{\cdot}0.5C_7H_8$ in 80% yield (55 mg). Anal. Calcd for $C_{26}H_{28}O_2S_5P_2Ti{\cdot}0.5C_7H_8$: C, 51.30; H, 4.93; P, 8.98; Ti, 6.94. Found: C, 51.43; H, 4.95; P, 8.90; Ti, 6.73. FDMS (*m/e*): 644, M$^+$; 440, $(MeCp)_2TiS_3PAn^+$. $^1$P{$^1$H} NMR (40.5 MHz $C_6D_6$): $\delta$ 84.7 (s, 1 P); 80.8 (s, 1.2 P); 33.9 (s, 1.8 P, $(MeCp)_2TiS_3(PAn)$); 14.8 (s, 1.4 P, $(AnPS_2)_2$).

**$(C_5H_5)_2TiO_2S_3(PAn)_2$.** A mixture of $Cp_2TiS_4(PAn)_2$ (**2b**) (582 mg, 1.0 mmol) and acetamide (128 mg, 1.0 mmol) in THF (20 mL) was heated to reflux for 1 h. The cooled reaction mixture was evaporated to dryness and the residue extracted with diethyl ether (50 mL), from which a 97% yield (140 mg) of thioacetamide (pure by $^1$H NMR) was recovered. The ether-insoluble orange residue was extracted with $CH_2Cl_2$ (40 mL) and filtered. Orange crystalline **6** was isolated from this filtrate by addition of methanol (10 mL), concentration to 10 mL, and cooling to −30 °C; yield 48% (280 mg). Anal. Calcd for $C_{24}H_{24}TiO_4S_3P_2$: C, 49.49; H, 4.15; P, 10.63; S, 16.51; Ti, 8.22. Found: C, 48.85; H, 4.16; P, 10.83; S, 15.45; Ti, 8.43. $^1$H NMR ($CD_2Cl_2$): isomer A, $\delta$ 8.06 (q, 4 H), 7.00 (q, 4 H), 6.89 (s, 10 H), 3.87 (s, 6 H); isomer B, $\delta$ 7.45 (q, 4 H), 7.17 (s, 5 H), 6.68 (q, 4 H), 6.65 (s, 5 H), 3.79 (s, 6 H). The A:B ratio is 2.3:1 (see Figure 2). $^{31}$P{$^1$H} NMR: $\delta$ 86.8 (s, isomer B), 83.8 (s, isomer A). FDMS (*m/e*): 626, M$^+$.

**From 4 and $Ph_2CO$.** Compound **4** (24 mg, 0.035 mmol) and $Ph_2CO$ (14 mg, 0.077 mmol) were dissolved in ca. 4 mL of dry THF in a 12-mm NMR tube. The $^{31}$P NMR spectrum of the solution showed that compound **3** was the predominant phosphorus species after 3 h at room temperature. After 8 h, the two isomers of $(MeCp)_2TiO_2S_3(PAn)_2$ (87 and 84 ppm) are fully formed. This reaction was conducted on a larger scale on a Schlenk line and worked up by chromatography on silica gel. Elution with ether/hexane gave an intense blue band containing $Ph_2CS$, which was crystallized from hexane at −78 °C and identified by its visible spectrum.

**X-ray Crystallography.** Orange rectangular crystals of $(MeCp)_2TiO_2S_4(PAn)_2$ (**3**) were obtained by slow diffusion of methanol into concentrated dichloromethane solutions. The data collection and structural analysis was performed by Dr. C. S. Day (Crystalytics Co., P.O. Box 82286, Lincoln, NE) employing direct methods. A crystal of dimensions 0.80 × 0.75 × 0.35 mm was mounted on a thin glass fiber and was assigned the space group $P\bar{1}$ with parameters $a = 9.458$ (3) Å, $b = 10.611$ (3) Å, $c = 15.975$ (5) Å, $\alpha = 94.96$ (2)°, $\beta = 109.34$ (2)°, $\gamma = 105.38$ (2)°, $V = 11431.6$ (7) Å$^3$, and $\rho_{calcd} = 1.49$ g cm$^{-3}$ for $Z = 2$. The data were collected on a Nicolet autodiffractomer using an $\omega$-scanning technique over the range $3.0 < 2\theta < 63.7°$ at ambient temperatures with monochromatized Mo K$\alpha$ ($\lambda = 0.71069$ Å) radiation. Of the 9805 unique intensities processed, 7288 were observed at the $3.00\sigma(I)$ level of confidence and only these reflections were used during the refinement. The data were isotropically corrected for a 5% decline in the average intensity of 6 standards monitored every 300 reflections. The intensity data were corrected empirically for absorption effects with use of $\psi$ scans for 8 reflections having $2\theta$ between 7 and 41° and were then reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

The 37 non-hydrogen atoms were located and thermal parameters determined by SHELXTL, with the hydrogen atom positional parameters fixed. Successful convergence led to conventional residuals of $R = 0.037$ and $R_w = 0.048$, with all non-hydrogen atoms refined anisotropically and all hydrogen atoms refined isotropically. Atomic coordinates are presented in Table II.

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**Registry No.** **1**, 90432-13-6; *trans*-**2**, 100815-57-4; *cis*-**2**, 100896-65-9; **3**, 100815-58-5; **4**, 100815-59-6; *trans*-**6**, 100815-60-9; *cis*-**6**, 100896-67-1; *trans*-$(MeCp)_2TiO_2S_3(PAn)_2$, 100815-61-0; *cis*-$(MeCp)_2TiO_2S_3(PAn)_2$, 100896-66-0; $(AnPS_2)_2$, 19172-47-5; *trans*-$Cp_2TiS_4P_2An_2$, 90412-98-9; acetamide, 60-35-5.

**Supplementary Material Available:** Details of the X-ray data collection and structure solution and tables of bond lengths, bond angles, thermal parameters, complete hydrogen atom parameters, and structure factors (50 pages). Ordering information is given on any current masthead page.

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# Thermodynamic Studies on Equilibria between the Branched Hexaamine *N*,*N*,*N*′,*N*′-Tetrakis(3-aminopropyl)ethylenediamine (TAPEN) and Hydrogen, Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Ions

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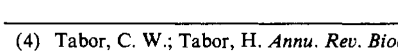
The branched hexaamine *N*,*N*,*N*′,*N*′-tetrakis(3-aminopropyl)ethylenediamine (TAPEN) has been synthesized and characterized. Potentiometric and spectrophotometric studies on the equilibria between TAPEN and hydrogen, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions have been carried out. The equilibrium constants between TAPEN and the above-mentioned ions have been determined by potentiometry at 25 °C in 0.5 mol dm$^{-3}$ $KNO_3$ as ionic medium. The presence of many hindered six-membered chelate rings in the 1:1 metal complex has been invoked to explain the low stability of these complexes and the great tendency of TAPEN to form protonated complexes. With the exception of the $[Mn(TAPEN)]^{2+}$ complex, where all six nitrogen donor atoms are involved in the coordination, in all the 1:1 complexes TAPEN acts as a pentadentate ligand. In the case of Ni(II) the presence of a minor, square-planar, low-spin species has been detected.

## Introduction

Polyamines, both cylcic and noncyclic, are the ligands studied most with respect to their basicity and coordination capability toward metal ions.[2-4] Continuing our systematic studies on the thermodynamics of metal complex formation with polyamines as ligands, we have studied the branched polyamine *N*,*N*,*N*′,*N*′-tetrakis(3-aminopropyl)ethylenediamine (abbreviated as TAPEN)



n=2 ; m=2 PENTEN
n=2 ; m=3 TAPEN
n=3 ; m=2 PTETRAEN

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