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NMR Studies of Inversion and Dithiophosphate Methyl Group Exchange in Dialkoxybis(*O*,*O'*-dimethyl dithiophosphato)titanium(IV) Complexes. Evidence for a Bond-Rupture Mechanism[1]

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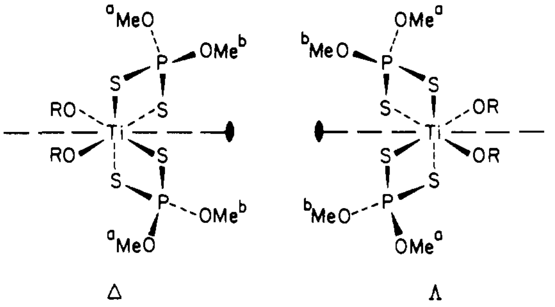
Dialkoxybis(*O*,*O'*-dimethyl dithiophosphato)titanium(IV) complexes, $Ti(Me_2dtp)_2(OR)_2$ ($Me_2dtp = S_2P(OMe)_2$; R = CH_2Ph, ^iPr, CMe_2Et), have been prepared and characterized by chemical analysis and IR and ^1H NMR spectroscopy. Rates and activation parameters for inversion and dithiophosphate methyl group exchange in these cis-octahedral complexes have been determined by ^1H NMR spectroscopy (total line-shape analysis). Inversion, probed by the diastereotopic groups in the alkoxide ligands, and exchange of dtp methyl groups occur at the same rate by a common, intramolecular mechanism; $R_k = k_{inv}/k_{ex} = 1.0 \pm 0.2$. Activation parameters for the two processes are nearly identical. Permutational analysis indicates that the R_k values are consistent with the A_6 NMR averaging set. The R_k values rule out intramolecular twist mechanisms and all of the common bond-rupture mechanisms except rupture of a Ti-S bond trans to an alkoxide ligand to give a trigonal-bipyramidal intermediate that has the dangling ligand in an axial position. In accord with a bond-rupture mechanism, the rates increase with increasing steric bulk of the OR group. Kinetic results for the $Ti(Me_2dtp)_2(OR)_2$ complexes are contrasted with results for the analogous β-diketonate complexes, $Ti(\beta\text{-dik})_2(OR)_2$, which rearrange via a twist mechanism. Also reported are related dichloro complexes, $Ti(R_2dtp)_2Cl_2$ (R = Me, Et, ^iPr), and $Ti(S_2PMe_2)_2(O^iPr)_2$.

Introduction

The mechanism of stereochemical rearrangements of metal chelate compounds has been an important problem in coordination chemistry since the days of Alfred Werner.[2] For intramolecular rearrangements of octahedral chelates, two classes of mechanisms have been considered: (1) metal-ligand bond rupture (chelate-ring opening) to give a five-coordinate intermediate[2] and (2) twisting mechanisms that effect rearrangement without rupture of any metal-ligand bonds.[3] Although much effort has been devoted to mechanistic studies of octahedral chelates,[4] in only a few cases has it proved possible to distinguish between bond-rupture and twisting mechanisms. The most thoroughly studied systems are cobalt(III) tris(β-diketonates),[5] which rearrange by a bond-rupture mechanism, and metal tris(α-substituted tropolonates)[6] and tris(N,N-disubstituted dithiocarbamates),[7] which undergo $\Delta \rightleftharpoons \Lambda$ inversion via the trigonal-twist mechanism.

A useful approach in mechanistic studies of metal chelate compounds is to compare the rates of two different processes.[5,8] For example, the relative rates of inversion and diketonate R group exchange in dialkoxybis(β-diketonato)titanium(IV) complexes, $Ti(dik)_2(OR)_2$ (OR = OCH_2Ph, OCH_2CHMe_2, $OCHMe_2$, $OCMe_2Ph$), and a dramatic decrease in these rates with increasing steric bulk of the alkoxide ligand strongly suggest that the $Ti(dik)_2(OR)_2$ complexes rearrange via a twist mechanism.[9] The closely related diolatobis(acetylacetonato)titanium(IV) complexes also rearrange by a twist mechanism.[10]

In this paper we report NMR studies of inversion and dithiophosphate (dtp) methyl group exchange in dialkoxybis(*O*,*O'*-dimethyl dithiophosphato)titanium(IV) complexes, $Ti(Me_2dtp)_2(OR)_2$ (OR = OCH_2Ph, $OCHMe_2$, $OCMe_2Et$). These complexes have a cis arrangement of alkoxide ligands (C_2 symmetry), and therefore they exist as chiral Δ and Λ enantiomers **1** that have



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inequivalent dtp methyl sites, a and b. The alkoxide ligands contain geminal H atoms or geminal methyl groups that serve as diastereotopic probes for measurement of the rates of $\Delta \rightleftharpoons \Lambda$ inversion (Figure 1). Comparison of the rates of inversion and dtp methyl group exchange indicates that the $Ti(Me_2dtp)_2(OR)_2$ complexes rearrange by a mechanism involving rupture of a Ti-S bond trans to an alkoxide ligand to give a trigonal-bipyramidal intermediate that has the dangling ligand in an axial position. By

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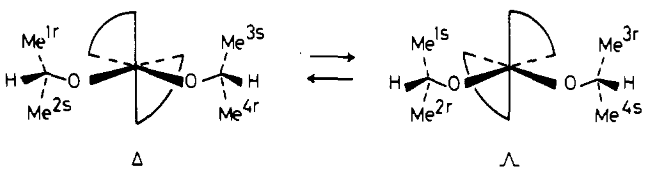
Inversion of $Ti[S_2P(OMe)_2]_2(O^iPr)_2$

Figure 1. Illustration of the inequivalence of the isopropoxide geminal methyl groups in $Ti(Me_2dtp)_2(O^iPr)_2$. The complex is viewed (approximately) along the C_2 axis. In the Δ enantiomer, methyl groups 1 and 4 are in r sites adjacent to a chelate ring, while methyl groups 2 and 3 are in s sites more distant from that chelate ring. In the Λ enantiomer, the site occupancies are reversed. Because inversion exchanges each methyl group from an r site to an s site, or vice versa, the rate of inversion is simply equal to the rate of exchange of the isopropyl methyl groups.

contrast to the behavior of the $Ti(dik)_2(OR)_2$ complexes, the rearrangement rates for the $Ti(Me_2dtp)_2(OR)_2$ complexes increase with increasing steric bulk of the alkoxide ligand, a result that further supports a bond-rupture mechanism.

Experimental Section

Reagents and General Techniques. Alcohols (methanol, ethanol, 2-propanol, *tert*-amyl alcohol) were dried by refluxing over calcium hydride and were freshly distilled; benzyl alcohol was dried over molecular sieves (Fisher). Titanium(IV) isopropoxide (Alfa) was freshly distilled (58–59 °C (0.5 Torr)) prior to use. Titanium(IV) benzyloxide and titanium(IV) *tert*-amyloxide were prepared by reaction of 4 mol of the appropriate alcohol with 1 mol of titanium(IV) isopropoxide in benzene. The reaction mixture was distilled at 72 °C to remove 2-propanol as the benzene–2-propanol azeotrope, and then the benzene was pumped off to give the desired titanium(IV) alkoxide.

O,O'-Dimethyl hydrogen dithiophosphate, $HS_2P(OMe)_2$, was prepared by reaction of 4 mol of methanol with 1 mol of phosphorus(V) sulfide (Alfa) in benzene; $HS_2P(OR)_2$ (R = Et, ^iPr) were synthesized by reaction of an excess of the appropriate alcohol with phosphorus(V) sulfide.[11] The dithiophosphoric acid derivatives were obtained as colorless liquids by distilling the reaction mixture under vacuum: $HS_2P(OMe)_2$, bp 44–45 °C (0.1 Torr), lit.[11] bp 62–63 °C (4.5 Torr); $HS_2P(OEt)_2$, bp 54–55 °C (0.6 Torr), lit.[11] bp 81–82 °C (5 Torr); $HS_2P(O^iPr)_2$, bp 51–52 °C (0.35 Torr), lit.[11] bp 71–72 °C (3 Torr). Dimethyldithiophosphinic acid, HS_2PMe_2, was obtained as a white powder by acidifying an aqueous solution of sodium dimethyldithiophosphinate[12] with 4 M H_2SO_4, followed by extracting the acidic solution with chloroform and then removing the chloroform in vacuo.

Solvents were dried by refluxing for at least 24 h over calcium hydride (dichloromethane) or sodium/benzophenone (benzene, hexane). Deuteriated solvents (Aldrich) were dried over molecular sieves. All syntheses and subsequent handling of the titanium complexes were carried out under anhydrous conditions in a dry nitrogen or argon atmosphere.

Dibenzoxybis(*O,O'*-dimethyl dithiophosphato)titanium(IV), $Ti(Me_2dtp)_2(OCH_2Ph)_2$. *O,O'*-Dimethyl hydrogen dithiophosphate (7.30 g, 46.2 mmol) was added to a solution of titanium(IV) benzyloxide (10.0 g, 21.0 mmol) in 40 mL of dichloromethane, and the mixture was stirred at room temperature for 2 h. The resulting yellow solution was pumped to dryness, yielding an off-white solid. The solid was dissolved in dichloromethane (20 mL), hexane (40 mL) was added slowly, and the solution was allowed to stand at 5 °C for 12 h, affording yellow crystals (5.30 g, 44% theoretical), mp 100–104 °C. A second crop (0.96 g, 8% theoretical) was obtained by pumping the filtrate to dryness and recrystallizing the residue from dichloromethane–hexane. Anal. Calcd for $Ti[S_2P(OCH_3)_2]_2(OCH_2C_6H_5)_2$: C, 37.50; H, 4.55; Ti, 8.31. Found: C, 37.26; H, 4.41; Ti, 7.32. IR (Nujol mull) (cm^{-1}): 1216 w, 1204 w, 1170 m, 1065 m, 1016 s (br), 917 w, 817 m, 791 s, 765 s, 706 w, 686 m, 671 m, 578 m, 535 m, 474 m, 434 w, 381 m, 365 m, 287 m, 258 w, 230 w, 208 m.

Diisopropoxybis(*O,O'*-dimethyl dithiophosphato)titanium(IV), $Ti(Me_2dtp)_2(O^iPr)_2$. Reaction of *O,O'*-dimethyl hydrogen dithiophosphate (3.34 g, 21.1 mmol) with titanium(IV) isopropoxide (3.00 g, 10.6 mmol) in dichloromethane (40 mL) for 4 h at room temperature gave a pale yellow solution. The solvent was pumped off, yielding the product as a very pale yellow solid (4.95 g, 98% theoretical), mp 47–49 °C. Anal. Calcd for $Ti[S_2P(OCH_3)_2]_2(OC_3H_7)_2$: C, 25.00; H, 5.46; Ti, 9.97. Found: C, 25.32; H, 5.65; Ti, 10.01. IR (Nujol mull) (cm^{-1}): 1320 w, 1175 m, 1161 m, 1125 m, 1111 m, 1049 sh, 1025 s, 976 sh, 859 m, 816 sh, 801 m, 729 w, 674 m, 615 w, 537 w, 463 w, 454 w, 437 w, 398 w, 376 w, 354 w, 325 w, 286 sh. Recrystallization of $Ti(Me_2dtp)_2(O^iPr)_2$ from hexane gives pale yellow crystals, but recrystallization is accompanied by slight decomposition. The solid compound decomposes slowly at room temperature under a nitrogen atmosphere.

Bis(*tert*-amyloxy)bis(*O,O'*-dimethyl dithiophosphato)titanium(IV), $Ti(Me_2dtp)_2(OCMe_2Et)_2$. This compound was prepared by reaction of *O,O'*-dimethyl hydrogen dithiophosphate (5.74 g, 36.3 mmol) with titanium(IV) *tert*-amyloxide (7.20 g, 18.2 mmol) in dichloromethane (30 mL) for 5 h at room temperature. The resulting yellow solution was pumped to dryness to give an orange oil, which was dissolved in 10 mL of hexane. Cooling the hexane solution to −15 °C for 48 h afforded a yellow crystalline material (7.07 g, 73% theoretical) with a wet appearance, mp 31–33 °C. Anal. Calcd for $Ti[S_2P(OCH_3)_2]_2(OC_5H_{11})_2$: C, 31.34; H, 6.39; Ti, 8.93. Found: C, 31.23; H, 6.13; Ti 9.03. IR (Nujol mull) (cm^{-1}): 1286 m, 1222 m, 1189 sh, 1167 s, 1137 m, 1023 s (br), 908 w, 796 s, 764 m, 728 w, 684 s, 621 w, 570 m, 533 m, 483 w, 442 w, 397 m, 380 m, 368 m, 322 m, 285 w.

Dichlorobis(*O,O'*-dimethyl dithiophosphato)titanium(IV), $Ti(Me_2dtp)_2Cl_2$. *O,O'*-Dimethyl hydrogen dithiophosphate (3.00 g, 19.0 mmol) was added dropwise to a solution of titanium(IV) chloride (1.73 g, 9.12 mmol) in 65 mL of benzene at room temperature. The resulting red solution was stirred for 5 h and then concentrated to a volume of about 20 mL. Slow addition of hexane (75 mL) yielded red crystals (3.01 g, 76% theoretical), mp 146–150 °C. Anal. Calcd for $Ti[S_2P(OCH_3)_2]_2Cl_2$: C, 11.09; H, 2.79; Ti, 11.06. Found: C, 11.12; H, 2.88; Ti, 10.95. IR (Nujol mull) (cm^{-1}): 1176 m, 1066 w, 1010 s, 815 s, 634 m, 515 w, 362 s (br), 320 m.

Dichlorobis(*O,O'*-diethyl dithiophosphato)titanium(IV), $Ti(Et_2dtp)_2Cl_2$. This compound was prepared by reaction of *O,O'*-diethyl hydrogen dithiophosphate (3.40 g, 18.3 mmol) with titanium(IV) chloride (1.73 g, 9.12 mmol) in benzene (50 mL) for 4 h at room temperature. The resulting red solution was pumped to dryness to give a red oil. The oil was dissolved in hexane (50 mL), and the solution was cooled to −15 °C for 4 h. The resulting orange-red crystalline material was dissolved in a minimum of dichloromethane, hexane (50 mL) was added, and the solution was cooled at −78 °C until some product precipitated. The mixture was then allowed to stand at −15 °C for 16 h. An orange-red microcrystalline product (2.49 g, 56% theoretical) was obtained, mp 66.5–68.5 °C. Anal. Calcd for $Ti[S_2P(OC_2H_5)_2]_2Cl_2$: C, 19.64; H, 4.12; Cl, 14.49; Ti, 9.79. Found: C, 19.86; H, 4.03; Cl, 14.68, Ti, 9.91. IR (Nujol mull) (cm^{-1}): 1290 w, 1163 m, 1107 m, 1050 sh, 1013 s, 970 s, 804 s, 724 w, 640 m, 536 m.

Dichlorobis(*O,O'*-diisopropyl dithiophosphato)titanium(IV), $Ti(^iPr_2dtp)_2Cl_2$. *O,O'*-Diisopropyl hydrogen dithiophosphate (3.91 g, 18.3 mmol) was added to a solution of titanium(IV) chloride (1.73 g, 9.12 mmol) in benzene (50 mL). The resulting red solution was stirred for 6 h at room temperature and then pumped to dryness to give a red residue, which was dissolved in a minimum of hot hexane. The solution was allowed to stand overnight at room temperature yielding red crystals (3.55 g, 71% theoretical), mp 90.5–92.5 °C. Anal. Calcd for $Ti[S_2P(OC_3H_7)_2]_2Cl_2$: C, 26.43; H, 5.18; Cl, 13.00; Ti, 8.78. Found: C, 26.37; H, 4.94; Cl, 12.77, Ti, 8.99. IR (Nujol mull) (cm^{-1}): 1180 m, 1141 m, 1103 w, 1022 s, 978 s, 893 m, 785 s, 734 m, 638 s, 540 m, 447 m, 378 s.

Diisopropoxybis(dimethyldithiophosphinato)titanium(IV), $Ti(S_2PMe_2)_2(O^iPr)_2$. Dimethyldithiophosphinic acid (1.33 g, 10.5 mmol) in 10 mL of dichloromethane was added dropwise to a solution of titanium(IV) isopropoxide (1.50 g, 5.28 mmol) in 40 mL of dichloromethane at room temperature. The solution was stirred for 3 h and then pumped to dryness. The resulting off-white residue was dissolved in dichloromethane (10 mL), hexane (30 mL) was added slowly, and the solution was cooled to −15 °C, yielding pale yellow crystals (0.88 g, 40% theoretical), mp 110–116 °C. Anal. Calcd for $Ti[S_2P(CH_3)_2]_2(OC_3H_7)_2$: C, 28.84; H, 6.29; Ti, 11.50. Found: C, 28.43; H, 6.13; Ti, 12.02. IR (Nujol mull) (cm^{-1}): 1321 m, 1292 w, 1280 m, 1163 m, 1128 s, 1109 s, 1010 s, 987 s, 972 s, 945 vs, 906 s, 848 s, 740 w, 727 s, 634 s, 611 s, 594 m, 574 w, 509 m, 462 m, 326 s, 304 m, 270 m, 258 m.

Physical Measurements. Infrared spectra were recorded in the 4000–400-cm^{-1} region with a Perkin-Elmer 337 grating spectrophotometer and in the 700–200-cm^{-1} region with an IBM FT/98 Fourier transform spectrometer. Proton chemical shifts were measured with a Varian XL-200 200-MHz or Bruker WM-300 300-MHz spectrometer. Variable-temperature ^1H NMR spectra of sealed, degassed solutions were obtained at 300 MHz with a Bruker WM-300 spectrometer. Probe temperatures were determined with use of a copper–constantan ther-

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Table I. Characteristic Infrared Frequencies (cm^{-1}) for Ti(Me$_2$dtp)$_2$(OR)$_2$, Ti(R$_2$dtp)$_2$Cl$_2$, and Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$ Complexes[a]

compd	ν_{as}(PS$_2$)[b]	ν_s(PS$_2$)[b]	ν(Ti–O)	ν(Ti–S), ν(Ti–Cl) region
Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$	686 m[c] 671 m	535 m	578 m	381 m, 365 m
Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$	674 s	537 w	615 w	376 w, 354 w, 325 w
Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$	684 s	533 m	570 m	380 m, 368 m, 322 m
Ti(Me$_2$dtp)$_2$Cl$_2$	634 m	515 w		326 s (br), 320 m
Ti(Et$_2$dtp)$_2$Cl$_2$	640 m	536 m		*d*
Ti(^{i}Pr$_2$dtp)$_2$Cl$_2$	638 m	540 m		378 s
Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$	634 s	509 m	611 s	325 s, 304 m

[a] As Nujol mulls between KBr plates (4000–400-cm^{-1} region) or polyethylene plates (700–200-cm^{-1} region). Additional frequencies are listed in the Experimental Section. [b] ν_{as} = asymmetric stretch; ν_s = symmetric stretch. [c] s = strong; m = medium; w = weak; br = broad. [d] This compound was not studied below 400 cm^{-1}.

Table II. Proton Chemical Shifts (ppm) and Coupling Constants (Hz) for Ti(Me$_2$dtp)$_2$(OR)$_2$, Ti(R$_2$dtp)$_2$Cl$_2$, and Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$ Complexes in Chloroform-d_1

compd	dithiophosphorus ligand	alkoxide ligand
Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$	3.69 dsat[a] (CH$_3$), $^3J_{HP}$ = 15.4, $^4J_{PP'}$ = 2.0–2.5[b]	5.32 s (CH$_2$) 7.32 m (C$_6$H$_5$)
Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$	3.79 dsat (CH$_3$), $^3J_{HP}$ = 15.2, $^4J_{PP'}$ = 2.3	1.33 d (CH$_3$), $^3J_{HH}$ = 6.2 5.14 sept (CH), $^3J_{HH}$ = 6.2
Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$	3.77 dsat (CH$_3$), $^3J_{HP}$ = 15.1, $^4J_{PP'}$ = 2.3	1.42 s (CH$_3$) 0.98 t (CH$_2$C*H*$_3$), $^3J_{HH}$ = 7.5 1.72 q (C*H*$_2$CH$_3$), $^3J_{HH}$ = 7.5
Ti(Me$_2$dtp)$_2$Cl$_2$	3.89 dsat (CH$_3$), $^3J_{HP}$ = 15.7, $^4J_{PP'}$ = 3.6	
Ti(Et$_2$dtp)$_2$Cl$_2$	1.39 t (CH$_3$), $^3J_{HH}$ = 7.1 4.23 dq (CH$_2$), $^3J_{HH}$ = 7.1 $^3J_{HP}$ = 10.1	
Ti(^{i}Pr$_2$dtp)$_2$Cl$_2$	1.37 d (CH$_3$), $^3J_{HH}$ = 6.2 4.87 dsept (CH), $^3J_{HH}$ = 6.2, $^3J_{HP}$ = 12.4	
Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$	2.07 d (CH$_3$), $^2J_{HP}$ = 13.3	1.31 d (CH$_3$), $^3J_{HH}$ = 6.2 5.21 m (CH)

[a] s = singlet; d = doublet; dsat = doublet with satellites due to virtual coupling; t = triplet; q = quartet; dq = doublet of quartets; sept = septet; dsept = doublet of septets; m = multiplet. [b] Estimated from position of shoulders at 56 °C. At room temperature, the satellite lines are obscured by line broadening.

mocouple immersed in toluene and are estimated to be accurate to ±0.5 °C.

Rate constants for exchange of dithiophosphate methyl groups, isopropoxide methyl groups, and *tert*-amyloxide methyl groups were determined by quantitative comparison of experimental spectra with theoretical spectra[13] iteratively calculated with use of a locally modified interactive version of Saunder's NMR line-shape program.[14] To determine an average value of the rate constant at each temperature, observed and calculated spectra were compared with respect to line widths at three-fourths ($w_{3/4}$), one-half ($w_{1/2}$), and one-fourth ($w_{1/4}$) maximum amplitude, the frequency separation ($\delta\nu$) between the resonances, and the ratio of the maximum amplitude to the amplitude at the central minimum. For exchange of the benzyloxide methylene protons, which are spin coupled to each other, theoretical spectra were calculated with the total line-shape program DNMR5,[15] and the two center lines of the AB pattern of experimental and theoretical spectra were compared with respect to the same line-shape parameters. Relaxation times, $T_2 = (\pi w_{1/2})^{-1}$, in the absence of exchange were determined by plotting log $w_{1/2}$ vs $1/T$ and then linearly interpolating between the slow- and fast-exchange regions. Similarly, chemical shifts ($\delta\nu_0$) in the coalescence region were obtained by extrapolating linear plots of $\delta\nu$ vs $1/T$ from the slow-exchange region into the coalescence region. Values of T_2 and $\delta\nu_0$ used in calculating theoretical line shapes are given in the footnotes to Table III.

Results and Discussion

Synthesis and Characterization of Complexes. Dialkoxybis(*O,O'*-dimethyl dithiophosphato)titanium(IV) complexes, Ti(Me$_2$dtp)$_2$(OR)$_2$ (R = CH$_2$Ph, ^{i}Pr, CMe$_2$Et), have been prepared by reaction of stoichiometric amounts of *O,O'*-dimethyl hydrogen dithiophosphate and the appropriate titanium(IV) alkoxide in dichloromethane at room temperature (eq 1). The corresponding

$$\mathrm{Ti(OR)_4 + 2HSP(S)(OMe)_2 \rightarrow Ti(Me_2dtp)_2(OR)_2 + 2ROH} \quad (1)$$

dimethyldithiophosphinato complex, Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$, was synthesized by a similar method. The dialkoxy complexes crystallized from hexane or from dichloromethane–hexane as relatively low-melting, yellow crystalline solids.

Analogous dichlorobis(*O,O'*-dialkyl dithiophosphato)titanium(IV) complexes, Ti(R$_2$dtp)$_2$Cl$_2$ (R = Me, Et, ^{i}Pr), were prepared by reaction of stoichiometric amounts of titanium(IV) chloride and the appropriate *O,O'*-dialkyl hydrogen dithiophosphate in benzene at room temperature (eq 2). The dichloro complexes crystallized from hexane, dichloromethane-hexane, or benzene–hexane as moisture-sensitive, red or orange-red crystalline solids.

$$\mathrm{TiCl_4 + 2HSP(S)(OR)_2 \rightarrow Ti(R_2dtp)_2Cl_2 + 2HCl} \quad (2)$$

All of the complexes are new except, possibly, Ti(Et$_2$dtp)$_2$Cl$_2$. Yadav et al.[16] have reported Ti(Et$_2$dtp)$_n$Cl$_{4-n}$ (n = 2–4) and some *O,O'*-alkylene dithiophosphate analogues. However, Yadav's compounds are yellowish red "semisolids" or highly viscous liquids that are immiscible with *n*-hexane and are unstable on standing. By contrast, our complexes are crystalline; Ti(Et$_2$dtp)$_2$Cl$_2$ and Ti(^{i}Pr$_2$dtp)$_2$Cl$_2$ are very soluble in hydrocarbon solvents, and all of our compounds appear to be stable (under anhydrous conditions) in the solid state and in solution, except solid Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$, which gradually changed color from pale yellow to orange when stored at room temperature under a nitrogen atmosphere. The sealed sample of Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$ in toluene-d_8 used for the variable-temperature NMR study was stored at 5 °C and did not show any significant decomposition during a period of several weeks.

The complexes have been characterized by chemical analysis, infrared spectra, and ^{1}H NMR spectra. They exhibit characteristic infrared bands (Table I) at 634–686 and 509–540 cm^{-1} due to ν_{as}(PS$_2$) and ν_s(PS$_2$) stretching modes,[17] respectively; the

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(13) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(14) Saunders, M., Department of Chemistry, Yale University, New Haven, CT.

(15) Quantum Chemistry Program Exchange, Indiana University.

(16) Yadav, J. S.; Mehrotra, R. K.; Srivastava, G. *Polyhedron* **1987**, *6*, 1687.

(17) Rudzinski, W.; Behnke, G. T.; Fernando, Q. *Inorg. Chem.* **1977**, *16*, 1206.

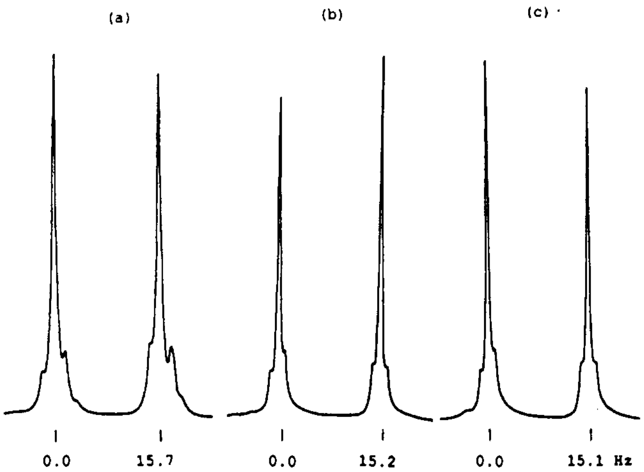

Figure 2. Dithiophosphate methyl proton resonances for $Ti(Me_2dtp)_2X_2$ at room temperature: (a) X = Cl; (b) X = O^iPr; (c) X = $OCMe_2Et$. The spectrometer frequency is 300 MHz.

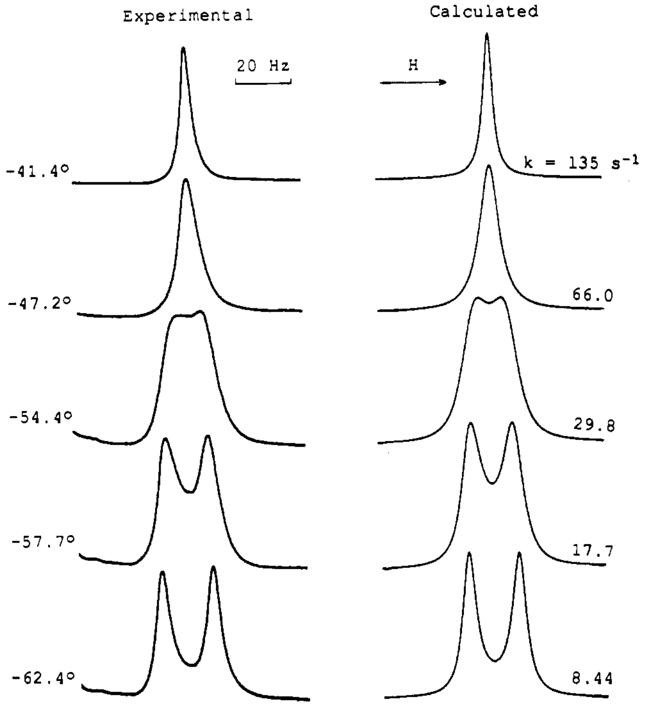

Figure 3. Observed and calculated ^1H NMR line shapes for the *tert*-amyloxide methyl resonances of $Ti(Me_2dtp)_2(OCMe_2Et)_2$, 0.059 M in toluene-$d_8$ at 300 MHz.

$\nu_{as}(PS_2)$ frequencies are about 40 cm^{-1} higher for the $Ti(Me_2dtp)_2(OR)_2$ complexes than for the $Ti(R_2dtp)_2Cl_2$ analogues, whereas the $\nu_s(PS_2)$ frequency is less sensitive to the nature of the monodentate ligand. For the $Ti(Me_2dtp)_2(OR)_2$ complexes, the ν(Ti–O) stretching mode[9b] is observed in the region 570–611 cm^{-1}.

Proton chemical shifts and coupling constants are listed in Table II. The dithiophosphate methyl proton resonances of $Ti(Me_2dtp)_2X_2$ (X = OCH_2Ph, O^iPr, $OCMe_2Et$, Cl) (cf. Figure 2) exhibit a "virtual coupling" pattern[18] owing to magnetic inequivalence of the two phosphorus nuclei. The hydrogen and phosphorus nuclei of the two dtp ligands constitute an $H_6PP'H_6'$ spin system[19] and give rise to a proton spectrum consisting of a strong doublet separated by $|^3J_{HP}|$ ($^7J_{HP'} = 0$) with each component of the doublet surrounded by a pair of weaker satellite lines that are separated by $|^4J_{PP'}|$. Values of $|^3J_{HP}|$ are in the range 15.1–15.7 Hz; $|^4J_{PP'}|$ is about 2.3 Hz for the dialkoxy complexes but substantially larger (3.6 Hz) for the dichloro complex.

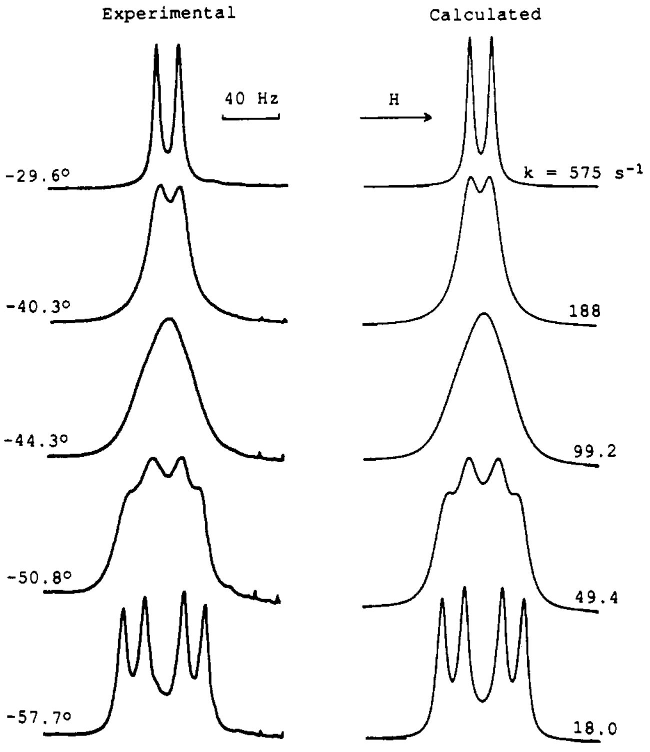

Figure 4. Observed and calculated ^1H NMR line shapes for the dithiophosphate methyl resonances of $Ti(Me_2dtp)_2(OCMe_2Et)_2$, 0.059 M in toluene-$d_8$ at 300 MHz.

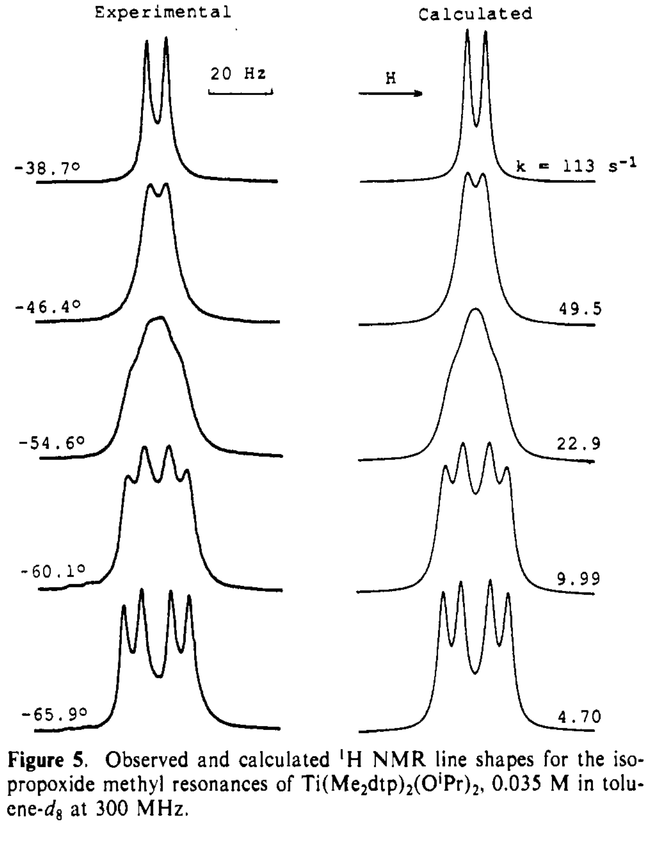

Figure 5. Observed and calculated ^1H NMR line shapes for the isopropoxide methyl resonances of $Ti(Me_2dtp)_2(O^iPr)_2$, 0.035 M in toluene-d_8 at 300 MHz.

The methylene protons of $Ti(Et_2dtp)_2Cl_2$ couple with both the methyl protons and the phosphorus nucleus ($^3J_{HH} = 7.1$ Hz; $^3J_{HP} = 10.1$ Hz). For $Ti(^iPr_2dtp)_2Cl_2$, the methine proton region consists of seven lines of relative intensity 6:16:26:28:26:16:6 separated by 6.2 Hz. This pattern is attributed to the central seven lines of two overlapping 1:6:15:20:15:6:1 binomial septets that are separated by twice 6.2 Hz. Thus, $^3J_{HH} = 6.2$ Hz and $^3J_{HP} = 12.4$

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[18] Akitt, J. W. *NMR and Chemistry*, 2nd ed.; Chapman and Hall: New York, 1983; pp 210–213.

[19] Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275 and references cited therein.

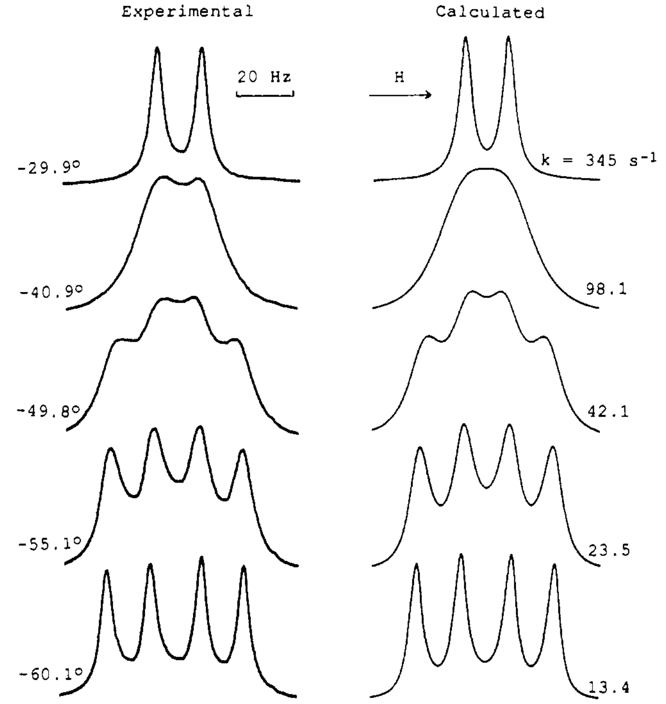

Figure 6. Observed and calculated ^{1}H NMR line shapes for the dithiophosphate methyl resonances of Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$, 0.035 M in toluene-d_8 at 300 MHz.

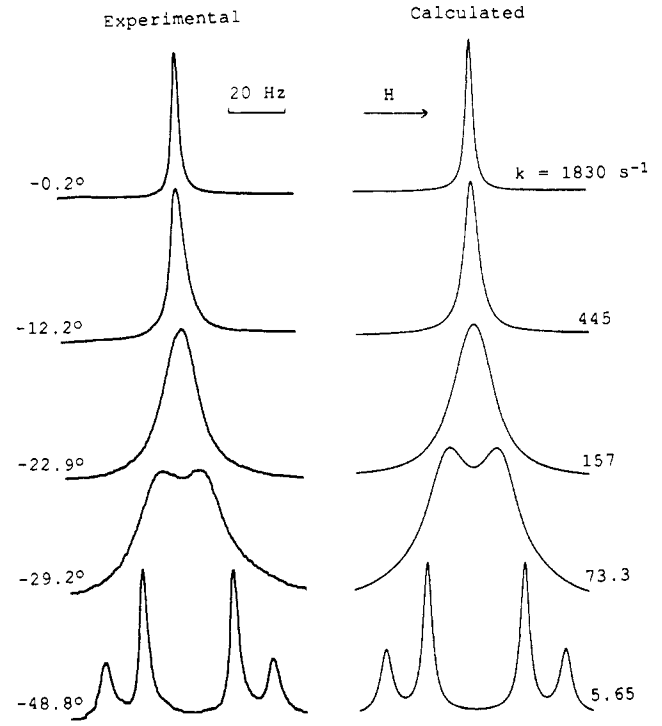

Figure 7. Observed and calculated ^{1}H NMR line shapes for the benzyloxide methylene resonances of Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$, 0.028 M in toluene-d_8 at 300 MHz.

Hz, in good agreement with a value of $^3J_{\mathrm{HP}}$ = 13.0 Hz reported for Th(^{i}Pr$_2$dtp)$_4$.[20]

Stereochemistry and Kinetics of Rearrangements. Variable-temperature ^{1}H NMR spectra of Ti(Me$_2$dtp)$_2$(OR)$_2$ (R = CH$_2$Ph, ^{i}Pr, CMe$_2$Et) have been studied in toluene-d_8; the less soluble Ti(Me$_2$dtp)$_2$Cl$_2$ was studied in dichloromethane-d_2. Typical experimental and calculated spectra at selected temperatures are presented in Figures 3–8. The low-temperature spectra show two

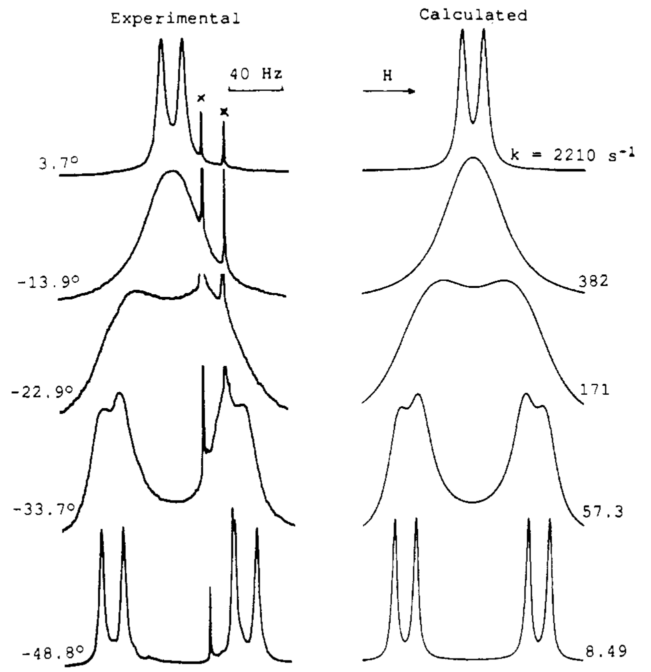

Figure 8. Observed and calculated ^{1}H NMR line shapes for the dithiophosphate methyl resonances of Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$, 0.028 M in toluene-d_8 at 300 MHz. The peaks marked with "x" are due to a trace impurity.

equally intense *tert*-amyloxide methyl resonances for Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$ (Figure 3), two equally intense isopropoxide methyl doublets for Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$ (Figure 5), and an AB pattern for the methylene protons of Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$ (Figure 7). These signals coalesce at higher temperatures to give a single time-averaged resonance for Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$ and Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$ and a single time-averaged doublet for Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$. All of the Ti(Me$_2$dtp)$_2$(OR)$_2$ complexes exhibit two equally intense dithiophosphate doublets at low temperatures (Figures 4, 6, and 8); these coalesce to a single time-averaged doublet in approximately the same temperature region in which the alkoxide resonances coalesce. Spectra of Ti(Me$_2$dtp)$_2$Cl$_2$ (not shown) also exhibit coalescence of two dtp methyl doublets to give a single doublet at higher temperatures.

The low-temperature spectra indicate that the Ti(Me$_2$dtp)$_2$X$_2$ complexes exist in solution as the cis geometrical isomer. The two dtp methyl doublets arise from inequivalent methyl groups (a and b in **1**), and the alkoxide resonances result from diastereotopic[21] geminal hydrogen atoms or geminal methyl groups, which occupy inequivalent r and s sites in the chiral cis isomer (see Figure 1).

The observed coalescence of the dithiophosphate and alkoxide resonances (Figures 3–8) is due to simultaneous exchange of dtp methyl groups and inversion of configuration; first-order rate constants for inversion, k_{inv}, and exchange, k_{ex}, are presented in Table III along with values of $R_k = k_{\mathrm{inv}}/k_{\mathrm{ex}}$. Arrhenius and Eyring activation parameters were obtained from the least-squares straight lines of log k vs $1/T$ and log $(k/T$ vs $1/T$ plots, respectively. The Eyring plots are shown in Figures 9 and 10. The activation parameters are listed in Table IV along with coalescence temperatures, T_c, values of ΔG^*, rate constants at a common temperature in the coalescence region (−35 °C), and extrapolated rate constants at 25 °C.

For the Ti(Me$_2$dtp)$_2$(OR)$_2$ complexes, inversion and dtp methyl group exchange occur at the same rate (Tables III and IV), and the two processes have nearly identical activation parameters; ΔH^* is about 11–13 kcal/mol, and ΔS^* is near zero to slightly positive. Average values of $R_k \pm 1\sigma$ (Table III) are 1.04 ± 0.10 for Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$, 0.89 ± 0.07 for Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$, and 1.00 ± 0.07 for Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$. The rate constants

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[20] Pinkerton, A. A.; Storey, A. E.; Zellweger, J.-M. *J. Chem. Soc., Dalton Trans.* **1981**, 1475.

[21] Mislow, K.; Rabin, M. *Top. Stereochem.* **1967**, *1*, 1.

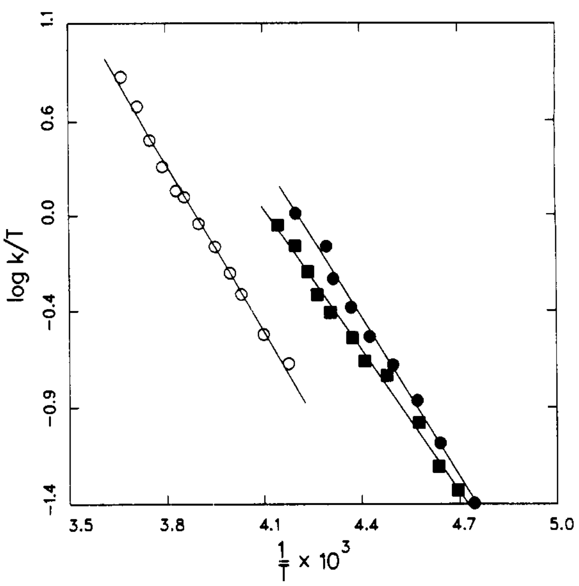

Figure 9. Eyring plots for inversion of configuration in Ti(Me$_2$dtp)$_2$(OR)$_2$: OR = OCH$_2$Ph (○); O^{i}Pr (■); OCMe$_2$Et (●).

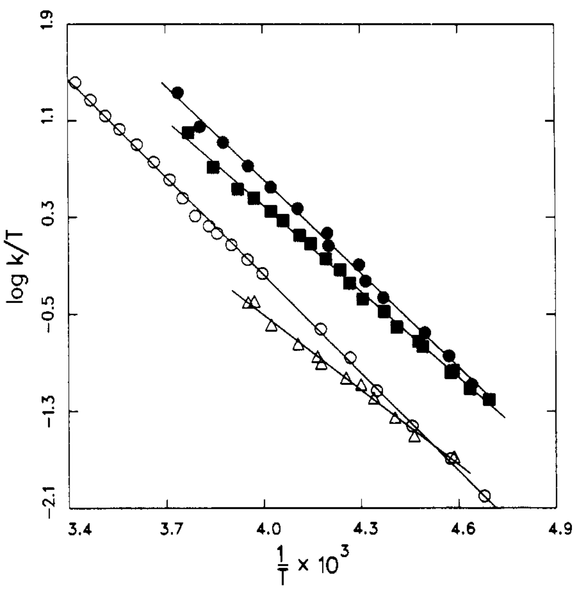

Figure 10. Eyring plots for exchange of dithiophosphate methyl groups in Ti(Me$_2$dtp)$_2$X$_2$: X = OCH$_2$Ph (○); O^{i}Pr (■); OCMe$_2$Et (●); Cl (△).

increase (by a factor of about 7; cf. Table IV) with increasing steric bulk, as the alkoxide ligand varies from a primary to a secondary to a tertiary alkoxide. Ti(Me$_2$dtp)$_2$Cl$_2$ rearranges somewhat more slowly than the Ti(Me$_2$dtp)$_2$(OR)$_2$ complexes and exhibits a lower $\Delta H^\ddagger$ and a negative $\Delta S^\ddagger$ (Table IV); however, comparison of results for the dichloro and dialkoxy complexes is complicated by the fact that solubility considerations required use of two different solvents.

Proton NMR spectra of the complexes in the presence of free alcohol or free *O,O'*-dimethyl hydrogen dithiophosphate indicate that intermolecular ligand exchange is slow on the NMR time scale at temperatures where inversion and dtp methyl group exchange are fast. For example, a mixture of Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$ and HOCMe$_2$Et in CDCl$_3$ at room temperature gives separate, sharp *tert*-amyl proton resonances for the complex and the free alcohol. In the presence of HS$_2$P(OMe)$_2$, the dtp proton resonances of Ti(Me$_2$dtp)$_2$X$_2$ (X = OCH$_2$Ph, OCMe$_2$Et, Cl) in CDCl$_3$ at room temperature remain sharp and separated from the resonances of the free acid.

Table III. Rate Constants for Inversion and Dithiophosphate Methyl Group Exchange in Ti(Me$_2$dtp)$_2$X$_2$ (X = OCH$_2$Ph, O^{i}Pr, OCMe$_2$Et, Cl)

Ti(Me$_2$dtp)$_2$(OCH$_2$Ph)$_2$[a]				Ti(Me$_2$dtp)$_2$(O^{i}Pr)$_2$[b]			
temp, °C	k_{inv}, s^{-1}	k_{ex}, s^{-1}	R_k[c]	temp, °C	k_{inv}, s^{-1}	k_{ex}, s^{-1}	R_k
18.9		7610		-7.9		2660	
15.0		5360		-13.1		1350	
11.3		3910		-18.1		868	
7.8		3000		-21.3		726	
3.7		2210		-24.6		556	
-0.2	1830	1560	1.17	-26.9		464	
-3.8	1280	1100	1.16	-29.9		345	
-6.6	852	766	1.11	-31.9	270	292	0.92
-9.3	605	540	1.12	-34.9	207	216	0.96
-12.2	445	441	1.01	-37.1	149	174	0.86
-13.9	410	382	1.07	-38.7	113	134	0.84
-16.8	292	303	0.96	-40.9	90.4	98.1	0.92
-20.0	218	226	0.96	-44.4	65.9	76.1	0.87
-22.9	157	171	0.92	-46.4	49.5	56.3	0.88
-25.1	120			-49.8	41.0	42.1	0.97
-29.2	73.3			-50.5		38.1	
-33.7	50.8	57.3	0.89	-54.6	22.9	22.9	1.00
-38.8		32.5		-55.1		23.5	
-43.2		17.0		-57.4	13.4	16.5	0.81
-48.8		8.49		-60.1	9.99	13.4	0.75
-54.6		4.42					
-59.4		2.13					

Ti(Me$_2$dtp)$_2$(OCMe$_2$Et)$_2$[d]				Ti(Me$_2$dtp)$_2$Cl$_2$[e]	
temp, °C	k_{inv}, s^{-1}	k_{ex}, s^{-1}	R_k	temp, °C	k_{ex}, s^{-1}
-5.7		5720		-20.1	101
-10.4		2950		-21.3	102
-15.2		2140		-24.6	64.4
-20.2		1340		-29.6	43.8
-24.6		879		-33.1	33.9
-29.6		575		-33.8	29.9
-34.9		352		-38.1	22.2
-35.1	307	277	1.11	-40.6	19.4
-40.3	201	188	1.07	-42.7	14.8
-41.4	135	138	0.98	-46.1	10.1
-44.3	94.7	99.2	0.95	-49.1	6.20
-47.2	66.0			-55.1	4.55
-50.8	46.3	49.4	0.94		
-54.4	29.8	31.4	0.95		
-57.7	17.7	18.0	0.98		
-62.4	8.44				

[a] 0.028 M in toluene-d_8; for the benzyloxide CH$_2$ resonances, variation in T_2 from low temperature (-33.7 °C) to high temperature (-0.2 °C) is 0.132-0.144 s and variation in $\delta\nu_0$ is 39.01-27.95 Hz; for the dtp CH$_3$ resonances, T_2 (-59.4 to 18.9 °C) = 0.197-0.314 s, $\delta\nu_0$ = 96.98-90.21 Hz. [b] 0.035 M in toluene-d_8; isopropoxide CH$_3$, T_2 = 0.140-0.272 s, $\delta\nu_0$ = 14.89-9.57 Hz; dtp CH$_3$, T_2 = 0.265-0.513 s, $\delta\nu_0$ = 33.40-30.07 Hz. [c] $R_k = k_{inv}/k_{ex}$. [d] 0.059 M in toluene-d_8; *tert*-amyloxide CH$_3$, T_2 = 0.099-0.183 s, $\delta\nu_0$ = 18.84-12.58 Hz; dtp CH$_3$, T_2 = 0.175-0.429 s, $\delta\nu_0$ = 42.25-38.58 Hz. [e] 0.014 M in CD$_2$Cl$_2$; dtp CH$_3$, T_2 = 0.287-0.412 s, $\delta\nu_0$ = 12.84-11.61 Hz.

The ^{1}H NMR spectrum of the dithiophosphinate complex, Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$, exhibits time-averaged dithiophosphinate methyl and isopropoxy methyl resonances at -70 to -80 °C. Thus, the coalescence temperature is considerably lower, and the rearrangement rate considerably faster, than for the analogous dithiophosphate complexes.

Permutational Mechanisms. A permutational analysis for complexes of the type *cis*-M(AA)$_2$X$_2$, where AA is a symmetrical bidentate ligand and X is a monodentate ligand, has been reported by Bickley and Serpone.[22] The allowed permutations and permutation inversions are listed in Table V, grouped into NMR averaging sets (A$_i$). Operations that effect the same net site interchanges belong to the same averaging set. For Ti(Me$_2$dtp)$_2$(OR)$_2$ complexes that contain diastereotopic nuclei in the alkoxide ligands, the allowed site interchanges involve (1) exchange of dtp methyl groups between the inequivalent a and b sites in one dtp ligand (interchange (ab)) or both dtp ligands (interchange 2(ab)) and (2) exchange of diastereotopic nuclei between the inequivalent r and s sites in the alkoxide ligands. The

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(22) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1976**, *15*, 948.

Table IV. Kinetic Data for Inversion and Dithiophosphate Methyl Group Exchange for $Ti(Me_2dtp)_2X_2$ Complexes[a]

X	process	T_c,[b] °C	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
OCH_2Ph	inversion	−27	13.9 ± 0.7	14.4 ± 0.6	13.4 ± 0.7	6 ± 3
	exchange	−21	12.8 ± 0.2	13.4 ± 0.2	12.3 ± 0.2	1 ± 1
O^iPr	inversion	−50	11.7 ± 0.7	13.0 ± 0.7	11.2 ± 0.7	0 ± 3
	exchange	−42	11.3 ± 0.3	12.6 ± 0.2	10.8 ± 0.3	−2 ± 1
$OCMe_2Et$	inversion	−53	13.0 ± 0.9	14.4 ± 0.9	12.6 ± 0.9	6 ± 4
	exchange	−44	12.3 ± 0.4	13.7 ± 0.4	11.8 ± 0.4	3 ± 2
Cl[c]	exchange	−36	9.9 ± 0.5	10.6 ± 0.5	9.4 ± 0.5	−12 ± 2

X	process	$\Delta G^{\ddagger}$(−35 °C), s^{-1} kcal/mol	k(−35 °C), s^{-1}	$\Delta G^{\ddagger}$(25 °C), kcal/mol	k(25 °C), s^{-1}
OCH_2Ph	inversion	12.1 ± 0.1	40 ± 8	11.8 ± 0.1	(1.4 ± 0.3) × 10^4
	exchange	12.0 ± 0.1	46 ± 8	11.9 ± 0.1	(1.1 ± 0.2) × 10^4
O^iPr	inversion	11.4 ± 0.1	186 ± 42	11.4 ± 0.2	(2.8 ± 1.0) × 10^4
	exchange	11.3 ± 0.1	202 ± 33	11.5 ± 0.1	(2.5 ± 0.4) × 10^4
$OCMe_2Et$	inversion	11.1 ± 0.1	315 ± 79	10.7 ± 0.3	(8.3 ± 4.1) × 10^4
	exchange	11.1 ± 0.1	302 ± 66	11.0 ± 0.1	(5.7 ± 1.1) × 10^4
Cl[c]	exchange	12.2 ± 0.1	30 ± 6	12.9 ± 0.1	(2.0 ± 0.5) × 10^3

[a] In toluene-d_8 unless indicated otherwise. All errors are random errors estimated at the 95% confidence level. [b] Coalescence temperature. [c] In CD_2Cl_2.

Table V. Permutational Analysis for Rearrangements of a *cis*-$M(AA)_2X_2$ Complex

operation	configurational change	net site interchanges	averaging set	$R_k = k_{inv}/k_{ex}$
E (56)	none	none	A_1	
(12) (12)(56) (34) (34)(56)	none	(ab)	A_2	0
(12)(34) (12)(34)(56)	none	2(ab)	A_3	0
E* (56)*	$\Delta \rightleftharpoons \Lambda$	2(rs)	A_4	∞
(12)* (12)(56)* (34)* (34)(56)*	$\Delta \rightleftharpoons \Lambda$	2(rs), (ab)	A_5	2.0
(12)(34)* (12)(34)(56)*	$\Delta \rightleftharpoons \Lambda$	2(rs), 2(ab)	A_6	1.0

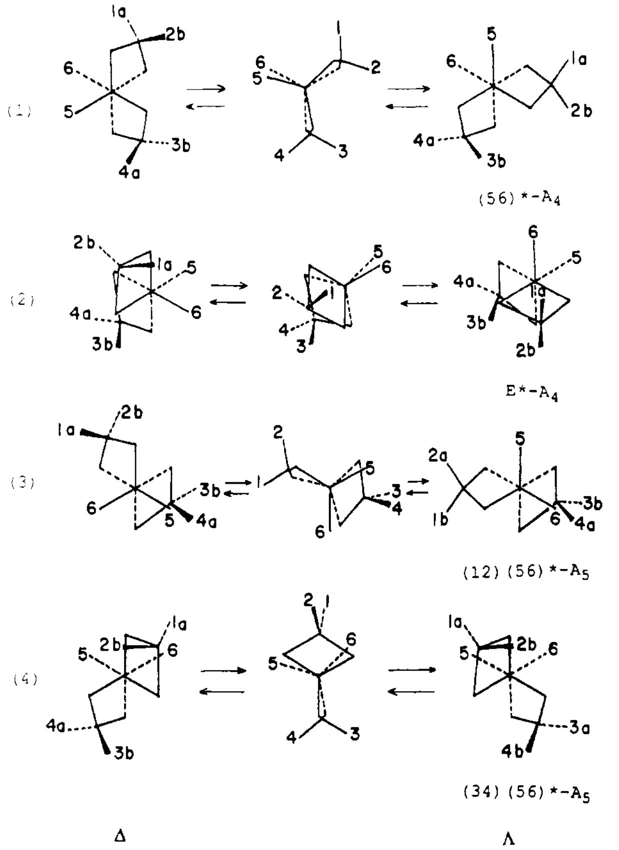

Figure 11. Rearrangements of a $Ti(Me_2dtp)_2(OR)_2$ complex via twisting about the four C_3 axes of the octahedral coordination polyhedron. Numbers label the dtp methyl groups (1–4) and the alkoxide ligands (5 and 6), and letters designate the inequivalent methyl group environments (a and b). The permutation inversion and averaging set for each mechanism are given under the product.

latter exchange results from $\Delta \rightleftharpoons \Lambda$ inversion and occurs simultaneously in both alkoxide ligands (interchange 2(rs)). Also included in Table V are predicted values of R_k for each of the averaging sets. Since experimental values of R_k are 1.0, the permutational mechanism is uniquely defined by the A_6 averaging set.

Physical Mechanisms. The essentially identical values of the rate constants and activation parameters for inversion and dtp methyl group exchange indicate that these two processes occur by a common physical mechanism. This mechanism must be intramolecular because intermolecular ligand exchange between the complexes and free alcohol or free *O,O'*-dimethyl hydrogen dithiophosphate is slow compared with the rates of inversion and dtp methyl group exchange. Thus, mechanisms involving dissociation of alkoxide or dtp ligands may be ruled out. We consider the following intramolecular mechanisms: (1) twist mechanisms and (2) bond rupture (chelate-ring opening) to give five-coordinate trigonal-bipyramidal or square-pyramidal intermediates.

Twist mechanisms involve a 120° rotation of an octahedral face about the C_3 axis[23] that passes through the center of that face. Because a regular octahedron has four C_3 axes, the twist can be carried out in four ways (Figure 11). Each twist proceeds via a trigonal-prismatic transition state. Two of the twists (1 and 2) effect inversion but no dtp methyl group exchange (averaging set A_4, $R_k = \infty$), while the other two (3 and 4) give inversion and methyl group exchange in only one dtp ligand at a time (averaging set A_5, $R_k = 2.0$). For a mixture of twists about the various C_3 axes, $R_k > 2.0$. Averaging sets and values of R_k for the twist mechanisms are summarized in Table VI. They do not agree with experiment (averaging set A_6, $R_k = 1.0$), and therefore twist mechanisms may be ruled out.

Rearrangements involving rupture of one Ti–S bond to give a five-coordinate intermediate are illustrated in Figures 12–14 and averaging sets and R_k values for those mechanisms are included in Table VI. The Ti–S bond that breaks may be trans to an alkoxide oxygen atom or trans to a dtp sulfur atom. The intermediate may have trigonal-bipyramidal geometry with the dangling ligand in an axial position (TBP-axial; cf. Figure 12),

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(23) We use the term C_3 axis loosely to refer to the 3-fold axis of the reference regular octahedral coordination polyhedron. The $Ti(Me_2dtp)_2(OR)_2$ complexes, of course, do not have a real C_3 axis.

Table VI. Summary of Averaging Sets and R_k Values for Physical Rearrangement Mechanisms for a *cis*-$Ti(Me_2dtp)_2(OR)_2$ Complex

mechanism	averaging set	$R_k = k_{inv}/k_{ex}$
twist (1 and 2)[a]	A_4	∞
twise (3 and 4)	A_5	2.0
twist (mixture of 1–4)	$A_4 + A_5$	>2.0
TBP-axial (cleavage trans to O)	A_6	1.0
TBP-axial (cleavage trans to S)	A_5	2.0
TBP-axial (mixture of cleavage trans to O and trans to S)	$A_5 + A_6$	1.0–2.0
TBP-equatorial	A_2	0
SP-axial (exclusive cleavage trans to S or trans to O)	$A_1 + A_5$	2.0
SP-axial (random cleavage)	$(A_1 + A_5) + (A_2 + A_4)$[b]	2.0
SP-axial (mixture of cleavage trans to S and trans to O)	$(A_1 + A_5) + (A_2 + A_4)$[c]	2.0

[a] Numbers in parentheses refer to the twist mechanisms in Figure 11. [b] Equally weighted linear combination. [c] Nonequally weighted linear combination.

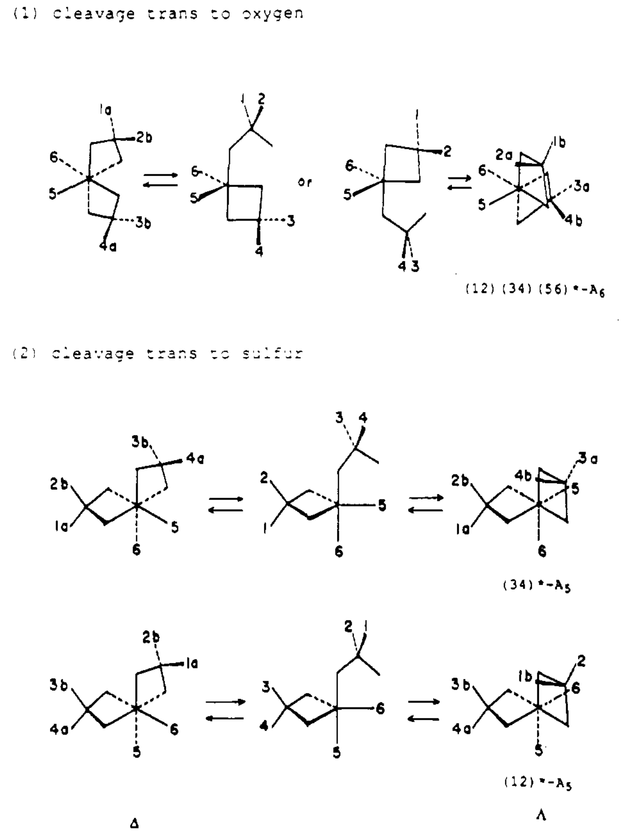


Figure 12. Rearrangements of a $Ti(Me_2dtp)_2(OR)_2$ complex via Ti–S bond rupture to give a TBP-axial intermediate. The numbers and letters have the same significance as in Figure 11.

trigonal-bipyramidal geometry with the dangling ligand in an equatorial position (TBP-equatorial; cf. Figure 13), or square-pyramidal geometry with the dangling ligand in an axial position (SP-axial; cf. Figure 14); SP intermediates with the dangling ligand in a basal position are not considered because SP-basal and TBP-axial intermediates may be shown to be kinetically equivalent.[5a]

Rupture of a Ti–S bond trans to an alkoxide oxygen atom to give a TBP-axial intermediate (Figure 12) results in simultaneous inversion and exchange of methyl groups in both dtp ligands. This mechanism is in accord with experiment because it predicts equal rates for inversion and methyl group exchange (A_6 averaging set; R_k = 1.0).

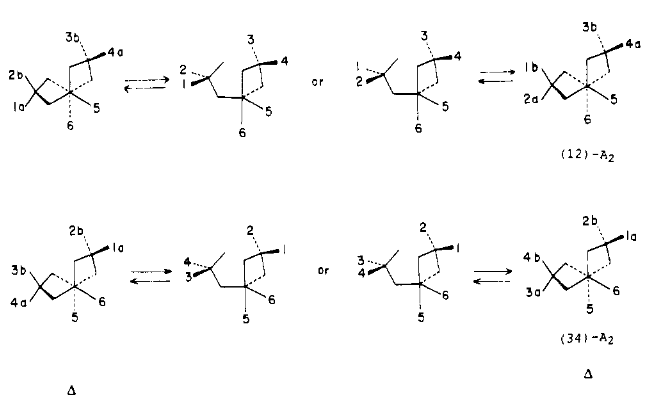


Figure 13. Rearrangements of a $Ti(Me_2dtp)_2(OR)_2$ complex via Ti–S bond rupture to give a TBP-equatorial intermediate. The numbers and letters have the same significance as in Figure 11.

Cleavage of a Ti–S bond trans to a dtp sulfur atom to give a TBP-axial intermediate (Figure 12) predicts simultaneous inversion and methyl group exchange in only one dtp ligand at a time (averaging set A_5, R_k = 2.0), not in agreement with experiment.

Similarly, rearrangement via a TBP-equatorial intermediate (Figure 13) can be ruled out because that mechanism effects methyl group exchange in one dtp ligand at a time but gives no inversion of configuration (averaging set A_2, R_k = 0).

Rearrangement via a SP-axial intermediate is depicted in Figure 14. Formation of the intermediate by rupture of a Ti-S bond trans to a dtp sulfur atom involves migration of an alkoxide ligand to the vacant coordination site, whereas formation of the intermediate via cleavage of a Ti–S bond trans to an alkoxide oxygen atom entails migration of a dtp sulfur atom to the vacant coordination site. If the intermediate forms exclusively by alkoxide migration, then microscopic reversibility requires that the intermediate decays to products exclusively by alkoxide migration, i.e., exclusive attack of the dangling ligand at one of the two symmetry-equivalent basal sites that are occupied by an alkoxide ligand. On the other hand, if the intermediate forms exclusively by migration of a dtp sulfur atom, then microscopic reversibility requires that products form by exclusive migration of a dtp sulfur atom, i.e., exclusive attack of the dangling ligand at one of the two symmetry-equivalent basal sites occupied by a dtp sulfur atom. Figure 14 shows that exclusive Ti–S bond rupture trans to sulfur or exclusive cleavage trans to oxygen gives an equally weighted linear combination of averaging sets A_1 and A_5, which results in an R_k value of 2.0.

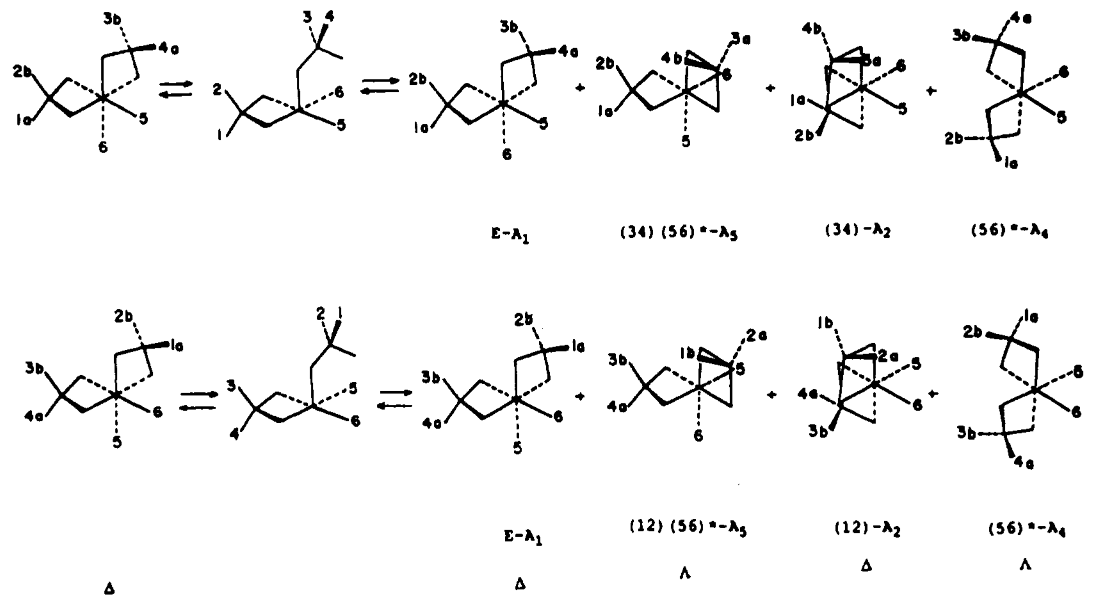
If Ti–S bond rupture trans to sulfur and trans to oxygen occur with equal probability, then one gets random migration of the alkoxide ligands and dtp sulfur atoms and subsequent random attack of the dangling ligand at any one of the four basal sites of the SP-axial intermediate. This results in an equally weighted linear combustion of the A_1, A_2, A_4, and A_5 averaging sets, which also gives an R_k value of 2.0. Therefore, for any combination of Ti–S bond ruptures trans to sulfur and trans to oxygen, the predicted value of R_k is 2.0, again not in accord with experiment.

Of all of the plausible physical mechanisms, the only one that gives an R_k value in agreement with experiment is a mechanism involving rupture of a Ti–S bond trans to an alkoxide ligand to give a trigonal-bipyramidal intermediate that has the dangling ligand in an axial position. Cleavage of a Ti–S bond trans to an alkoxide ligand may be facilitated by a trans influence of the alkoxide ligand owing to strong bonding between the π-donor alkoxide ligand and the oxophilic d^0 titanium(IV) atom.

Further support for a bond-rupture mechanism comes from the observed increase in rearrangement rate with increasing steric bulk of the alkoxide ligand (Table IV). Bond-rupture processes should be accelerated as the alkoxide ligand becomes more bulky since steric strain is relieved on going to an intermediate of reduced coordination number. On the other hand, the rate of a twisting process should decrease with increasing steric bulk of the alkoxide ligand because trigonal-prismatic transition states are more crowded than the octahedral ground state.

It is interesting to compare results of the present study with our previous results for analogous dialkoxybis(β-diketonato)titanium(IV) complexes[9] (Table VII). Rearrangement rates are

(1) cleavage trans to sulfur



(2) cleavage trans to oxygen

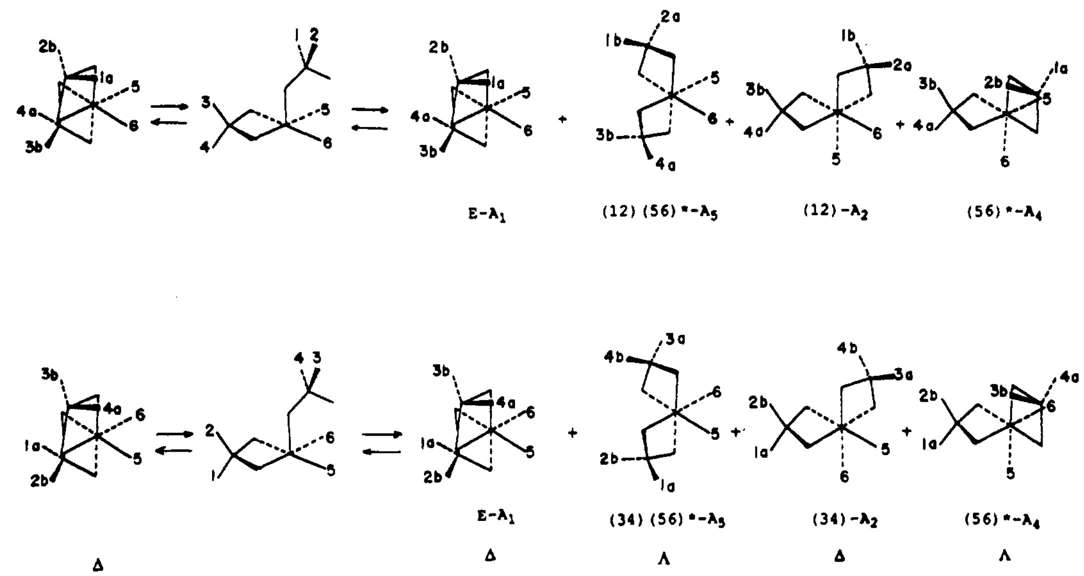


Figure 14. Rearrangements of a Ti(Me_2dtp)$_2$(OR)$_2$ complex via Ti–S bond rupture to give a SP-axial intermediate. The numbers and letters have the same significance as in Figure 11.

Table VII. Comparison of Kinetic Results for Ti(Me_2dtp)$_2$(OR)$_2$ and Ti(β-diketonate)$_2$(OR)$_2$

	Ti(Me_2dtp)$_2$(OR)$_2$	Ti(β-dik)$_2$(OR)$_2$
k(25 °C), s^{-1}	10^4–10^5	10^{-2}–10^2
$\Delta H^‡$, kcal/mol	11–13	12–17
$\Delta S^‡$, eu	−2 to +6	−14 to −6
mechanism	bond rupture	twist (mixture
(based on R_k)	(TBP-axial)	of C_3 axes)
variation in k[a]	increase (7×)	decrease (50–1000×)

[a] Variation as steric bulk increases from a primary to a tertiary alkoxide.

about 10^4 times slower for the β-diketonates; $\Delta H^‡$ is somewhat higher, and $\Delta S^‡$ is negative. The rate constant ratios for inversion and exchange in the β-diketonate complexes point to a twist mechanism, which is confirmed by a dramatic decrease in rate as the steric bulk of the alkoxide ligand increases.

The following factors may contribute to the change in mechanism: (1) the oxophilic titanium atom should form stronger bonds to β-diketonate oxygen atoms than to dtp sulfur atoms, thus suppressing a bond-rupture mechanism in the β-diketonate complexes; (2) dtp ligands are somewhat more versatile than β-diketonates. Dithiophosphate ligands often adopt a monodentate[24] or unsymmetrical bidentate[24a,e,f,25] attachment to metal atoms, suggesting that rupture of a bond to a dtp ligand may be a rather facile process.

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Contrasting Behaviors of Phosphorus and Arsenic in a Polycyclic Framework Favoring Pnictogen Square Pyramidality

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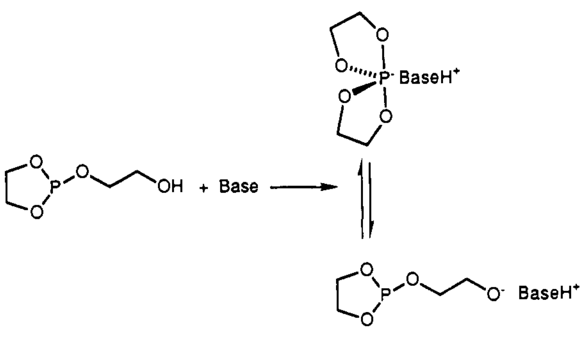
The preparations of the novel polycyclic compounds $Z\overline{Pn(OCH_2)_2CHCHCH_2O}(CH_2OH)$ and $Z\overline{Pn(OCH_2)_2\underline{C(CH_2)_x}CCH_2O}$-$(CH_2OH)$ (Z = $W(CO)_5$, $Mn(CO)_4Br$, $Fe(CO)_4$, $CpFe(CO)_2^+$, $CpCoI_2$, $Ni(CO)_3$, Pn = P, x = 1–4; Z = lone pair, Pn = As, x = 2, 3) and also $Z\overline{P(OCH_2)_2CHCH_2CH_2O}$ (Z = $W(CO)_5$, $CpFe(CO)_2^+$, $Ni(CO)_3$) are reported. The phosphorus compounds possessing a pendant alcohol group displayed no tendency to coordinate the alcoholic oxygen from 223 to 350 K, even under deprotonation conditions. This was also true where Z = lone pair, O, S, Se, and Ph_3C^+. Also reported are the preparations of $\overline{As(OCH_2)_2CHCHCH_2O}(CH_2OH)$ and $\overline{As(OCH_2)_2\underline{C(CH_2)_x}CCH_2O}(CH_2OH)$ (x = 2, 3). The first and second (x = 2) of these compounds are fluxional on the ^1H and ^{13}C NMR time scales, presumably owing to the larger size of the pnictogen. A mechanism for the fluxionality, which involves a square-pyramidal transition state, is discussed. The molecular structures of $CpCoI_2L$ (L = $P(OCH_2)_3CMe$ and $\overline{P(OCH_2)_2\underline{C(CH_2)_3}CCH_2O}(CH_2OH)$) determined by X-ray means are presented. The former was found to exhibit a monocline space group $P2_1/n$ with a = 9.474 (2) Å, b = 8.346 (3) Å, c = 19.416 (5) Å, Z = 4, and β = 102.81 (2)°. The latter compound was found to exhibit a monoclinic space group $P2_1/c$ with a = 7.758 (3) Å, b = 19.327 (4) Å, c = 11.958 (2) Å, Z = 4, and β = 97.28 (2)°. The Co–P distances in these complexes are 2.140 (1) and 2.140 (3) Å, respectively.

Introduction

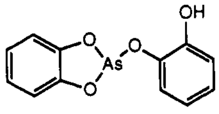
The small energy increase in the square-pyramidal (SP) geometry relative to the trigonal-bipyramidal (TBP) geometry represents an excited state in pentacoordinate pnictogen compounds undergoing Berry pseudorotation.[1] Even in reactions of species such as phosphoranyl radicals and phosphoranide anions containing one and two electrons, respectively, in the fifth ligand site, SP intermediates are believed to be present[2] as a result of Berry pseudorotation.[3] Recently a number of SP phosphorus, arsenic, and antimony compounds, stabilized by steric and electronic factors introduced by the ligands, have been prepared and structured by others.[4]

The deprotonation of phosphites containing pendant alcohol groups has been reported to yield stable phosphoranide anions that exist in equilibrium with the phosphite species as shown in reaction 1.[5,6] Although in the one instance in which such a phosphoranide anion has been structurally characterized[7] the phosphorus experiences a TBP coordination geometry, the energy barrier between the TBP and the SP geometries is probably small.[8]



(1)

The equilibrium between tricoordinate and pentacoordinate forms of hydrospiroarsoranes can be observed in the ^1H NMR spectrum of aromatic **1**.[9] In compounds containing saturated five-membered rings, however, only the tricoordinate form is detectable.[9] Reaction of the equilibrium mixture with base yields the arsoranide anion in reaction 2.



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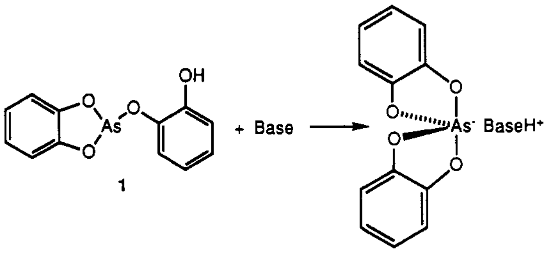

(2)

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