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Sulfur Chelates
36. Structural Characterization of the *Trans* Isomers of the *O*-Ethylphenyldithiophosphonates of Pd(II) and Pt(II), $M[S_2P(OC_2H_5)C_6H_5]_2$. *Cis-Trans* Isomerization of the Planar Pd(II) Complex

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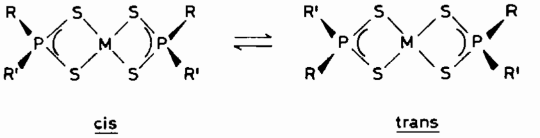
Ni(II), Pd(II) and Pt(II) complexes of O-ethyl-*phenyldithiophosphate,* $[S_2P(OEt)C_6H_5]^-$, *crystallize as* trans *products although the* MS_4 *coordination about the metal is square planar. Isomerization occurs in organic solvents to produce essentially (by NMR) equal amounts of* cis *and* trans *isomers. The rate of isomerization decreases Ni ≫ Pd > Pt. The isomerization of* trans-$Pd[S_2P(OEt)C_6H_5]_2$ *has been studied quantitatively in various solvents. In benzene* $E_a \cong 18$ *kcal/mole with* $\Delta H^{\ddagger} \cong 18$ *kcal/mole and* $\Delta S^{\ddagger} \cong -17$ *e.u. The rearrangement appears to be solvent assisted.* CS_2 *increases the isomerization rate by a factor of five. The X-ray crystal structures of the Pd(II) and Pt(II) complexes are described in detail. The M–S distances are approximately 2.34 Å in both complexes, although the space groups are different.*

Introduction

The *cis-trans* isomerization of planar palladium(II) and platinum(II) complexes of the type MX_2L_2 recently have received considerable attention [1–13, 20, 21]. In the platinum(II) complexes, isomerization usually is catalyzed by a small quantity of free ligand, L. One mechanism proposes the formation of a five-coordinate species, PtL_3X_2, which is fluxional, resulting in isomerization [10–12]. However, other data [8, 9, 13] are consistent with a consecutive displacement mechanism wherein an ionic intermediate, $[ML_3X]^+X^-$, is formed. Subsequent loss of L results in isomerization. Recently Romeo [1, 5] has proposed that isomerization can proceed through a three-coordinate intermediate in some sterically-hindered complexes.

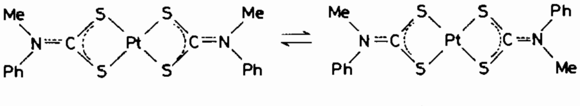
The more labile palladium(II), MX_2L_2 compounds were found to be isomerized catalytically by coordinating solvents as well as by a trace of the free ligand. Nelson [2–4] has suggested that they isomerize through a 5-coordinate transition state which then forms a neutral or ionic 4-coordinate intermediate depending on solvent, anion, ligand, steric considerations, basicity and catalytic effects. The intermediate goes through another 5-coordinate transition state to the isomerized product.

The observation that dithiophosphates of nickel triad elements undergo rather rapid structural rearrangements prompted us to investigate the kinetic lability of *cis-trans* isomers of some square-planar nickel(II), palladium(II) and platinum(II) complexes with an unsymmetrical dithiophosphate ligand, (I), containing four chemically equivalent M–S bonds.



(I)

A necessary requirement for the investigation of *cis-trans* isomerization is that the *cis* and/or *trans* isomers can be detected. In a series of unsymmetrical planar halo(N,N-disubstituted)dithiocarbamatophosphine metal(II) complexes of the nickel triad, Fackler *et al.* [14] have demonstrated that there is an observable magnetic non-equivalence between alkyl groups, "magnetic non-equivalence is induced by atoms six or more bond distances away from the resonating nucleus in these square-planar compounds". Directly related to the present work was the observation of two equally intense methyl resonances separated by 0.02 ppm for the unsymmetrical planar dithiocarbamate platinum complex, (II).



(II)

This result was interpreted to mean that both *cis* and *trans* isomers were present in solution. It was recognized, however, that magnetic equivalence of the R groups in the dithiocarbamate complexes could be produced, among other ways, by a 180° C┄N 'thioureide' bond rotation. For this reason, the unsymmetrical dithiophosphonate ligand, which is stereochemically rigid at the phosphorus atom, was synthesized.

Experimental

Chemicals were used as purchased unless specified. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Syntheses

Sodium O-ethylphenyldithiophosphonate, $Na(S_2P(OC_2H_5)C_6H_5)$

In a three-necked, 250 ml round bottom flask fitted with a reflux condenser and drying tube, 10.0 g (0.178 mol) of freshly prepared NaSH [15] was dissolved in 85 ml absolute ethanol (commercially available NaSH – Alfa Products – works as well). To this solution was rapidly added 9.2 ml (12.52 g, 0.057 mol) of phenylphosphonothioic dichloride ($PhP(S)Cl_2$), commercially available from Aldrich Chemical Company. A white compound formed upon this addition. The resulting mixture was refluxed for 30 minutes, cooled and filtered. The white precipitate was NaSH. Evaporation of the excess alcohol from the filtrate gave a yellow oil which was recrystallized with dichloromethane and pentane, giving 8.12 g (60% yield) of fine, white powder.

Bis(O-ethylphenyldithiophosphonato)nickel(II), $Ni(S_2P(OC_2H_5)C_6H_5)_2$

To 0.238 g (0.001 mol) $NiCl_2 \cdot 6H_2O$ in 20 ml water was added 0.48 g (0.002 mol) $NaS_2P(OC_2H_5)C_6H_5$ dissolved in 20 ml water. The purple compound was filtered and washed with three 20 ml portions of water and vacuum dried. The compound was purified by passing a methylene chloride solution through a 50 cm alumina column. Slow evaporation of a methylene chloride-pentane solution gave large purple crystals: yield 0.43 g (90%) (m.p. 179–182 °C); reported m.p. 180 °C [16]; 180–182 °C [17, 28].

Bis(O-ethylphenyldithiophosphonato)palladium(II), $Pd(S_2P(OC_2H_5)C_6H_5)_2$

The compound was prepared by adding 0.96 g (0.004 mol) of $NaS_2P(OC_2H_5)C_6H_5$ in 20 ml water to 0.652 g (0.002 mol) K_2PdCl_4 in 40 ml water. As the ligand was added, a brown sticky glob formed. The compound was recovered from the water solution by extraction with methylene chloride. Purification was accomplished by concentrating the methylene chloride solution and filtering through an alumina column as above. Red-brown crystals were formed by slow evaporation of the methylene chloride-pentane solution, yield 1.0 g (95%) (m.p. 191–195 °C). The molecular weight determined by freezing point depression in benzene was within 10% of the molecular weight of the monomer. *Anal.* Calcd. for $C_{16}H_{20}S_4P_2O_2Pd$: C, 35.52; H, 3.70; S, 23.72. Found: C, 35.57; H, 3.77; S, 23.57%.

Bis(O-ethylphenyldithiophosphonato)platinum(II), $Pt(S_2P(OC_2H_5)C_6H_5)_2$

This compound was prepared in a manner similar to that used above for the palladium derivative. To 0.83 g (0.002 mol) K_2PtCl_4 in 40 ml water was added 1.02 g (0.0042 mol) $NaS_2P(OC_2H_5)C_6H_5$ in 20 ml water. As the ligand was added, the solution became milk white. Over a period of two hours, a fine yellow compound formed. The yellow compound was extracted from the water with methylene chloride. A concentrate of this solution was passed through an alumina column as above. Black or dark brown sulfide compounds remained at the top of the column (this also was the case with the palladium compound). Fast evaporation of a methylene chloride-pentane solution gave a fine yellow powder. Yield 1.07 g (85%); (m.p. 158–189 °C)*. *Anal.* Calcd. for $C_{16}H_{20}S_4P_2O_2Pt$: C, 30.51; H, 3.18; S, 20.38. Found: C, 30.71; H, 3.12; S, 20.39%. Yellow crystal were formed by slow* evaporation of the methylene chloride-pentane solution placed in a freezer at approximately –20 °C. Decomposition took place with slow evaporation at room temperature.

Nuclear Magnetic Resonance Spectra

Proton NMR spectra were recorded on the Varian A60-A and HA-100 spectrometers, both equipped with V-6040 variable temperature controller. The controller was calibrated with methanol. The ^{31}P spectra were recorded on a Varian XL-100 spectrometer in the Fourier transform mode.

Rate and equilibrium constant data for the *cis-trans* isomerization (I) of the palladium(II) complex were obtained in carbon disulfide, methylene chloride, chloroform, carbon tetrachloride, bromobenzene, and benzene. Samples for the kinetic runs were prepared by dissolving (in the dark) finely ground crystals, in NMR tubes, and immediately recording their spectra covering the spectrometer probe with a black cloth, since preliminary work showed that the samples photoisomerize. Zero time was considered to be the time at which the solvent was added. Mole fractions, χ, of the *cis* and *trans* isomers were determined from peak heights of the methyl resonances.

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*The large melting point range suggests a mixture of isomers may be present. The NMR spectrum of a multicrystal sample shows the presence of two ethyl triplets. Single crystals obtained upon slow evaporation at –20 °C proved to be *trans* isomer.

TABLE I. Isomerization Rates of 0.052 *M Trans* $Pd[S_2P(OEt)C_6H_5]_2$.

Solvent	°C	Loss^a of *Trans* Species × 10^4 sec^{-1}	Rate^b × 10^3 sec^{-1}
Bromobenzene	37°	1.0	0.21
CS_2		6.2	2.8
CS_2 (0.086 *M*)		5.5	2.4
$CDCl_3$		1.5	0.46
CCl_4		1.2	0.27
Benzene	10°	0.26	0.062
	20°	0.57	0.15
	30°	0.58	0.11
	37°	1.6	0.34
	40°	1.2	0.28
	50°	11.7	7.5
	Ea ~ 18 kcal/mole $\Delta H^{\ddagger}$ ~ 18 kcal/mole $\Delta S^{\ddagger}$ ~ −17 e.u.		

^{a}Slope of linear plot of ln X_{trans} *versus* time. ^{b}Calculated assuming K = 1.0 for *trans* ⇌ *cis* from plot of ln $(X_{trans} - 0.5)$ *versus* time.

The rate of isomerization was evaluated assuming simple equilibrium kinetics, $trans \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cis$. Since $K_{eq} = 1.0$, plots of $\ln(\chi_{trans} - 0.5)$ versus time, where χ_{trans} = mole fraction of *trans* complex, produced a slope equal to $(k_f + k_r) = 2k_f$. The rate of disappearance of the *trans* isomer also was found to be approximated reasonably well by simple 1st order kinetics (Table I).

The kinetic parameters ΔH^* and ΔS^* were determined from a linear plot of ln (k/T) *vs.* 1/T (the slope is $-\Delta H^*/R$ and the intercept is ln (k/H) + $\Delta S^*/R$, with the constants having their usual meaning [18]). The activation energy, E_a, was determined by plotting ln k *vs.* 1/T. All data were analyzed by linear least-squares methods. Samples were also run in dry benzene under a nitrogen atmosphere to eliminate the possibility of water and oxygen acting as catalysts.

X-ray Data for the Palladium(II) and Platinum(II) Complexes

$Pd[S_2P(OC_2H_5)C_6H_5]_2$

A crystal of approximate dimension 0.26 × 0.15 × 0.14 mm was mounted on a glass fiber with the long dimension parallel to C_6H_5. Preliminary examination on the Pyntex $P2_1$ autodiffractometer indicated that the crystal belonged to the monoclinic system. The systematic absences in the subsequent data set uniquely defined the space group as $P2_1/c$. (The proper systematic absences were obtained by transforming h into $-l$ and l into h from the original data set.) Cell constants were obtained from least-squares refinement of the setting angles of 15 computer-centered reflections in the range $20° < 2\theta < 25°$ which were a = 8.870(2) Å, b = 10.736(6) Å, c = 12.170(5) Å, β = 104.51° and V = 1121.9 Å^3. For Z = 2, the calculated density, 1.54 g/cm^3, is in good agreement with the value 1.60 g/cm^3 determined by flotation in mixture of bromoform and pentane.

Intensity data were collected using MoK_α radiation which had been monochromatized with a graphite crystal. The θ–2θ scan technique was used with scan rates which varied between 2.02 and 29.30°/min. to obtain comparable counting statistics for all data. Backgrounds were measured at each end of the scan for a total time equal to one-half the scan time. The scan range was from 1.0° below the $K\alpha_1$ peak to 1.0° above the $K_{\alpha 2}$ peak. The intensities of four standard reflections, recollected every 50 reflections, underwent no significant change during data collection. A total of 2.351 reflections were collected in the range $0° \leq 2\theta \leq 50$ of which 1,385 had $I > 3\sigma(I)$. Data reduction was carried out using SYNCOR [19].

This structure was solved using heavy atom techniques. Full-matrix, least-squares was used to refine all non-hydrogen atomic positions. Isotropic treatment converged to an $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.104. All non-hydrogen atoms were then treated anisotropically and a weighting scheme was employed. The R values converged to R = 0.043 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0.047; w was defined as $1/\sigma(F)^2$. In the final cycle of refinement, the largest shift was less than 0.3σ.

A summary of crystal data and intensity collection is found in Table II. Table III contains a listing of the atomic coordinates and thermal parameters.

$Pt[S_2P(OC_2H_5)C_6H_5]_2$

A crystal of approximate dimensions 0.15 × 0.15 × 0.22 mm was mounted on a glass fiber with the long dimension parallel to phi. Preliminary examina-

TABLE II. Summary of Crystal Data and Intensity Collection.

Compound	$Pd(S_2P(OC_2H_5)(C_6H_5))_2$	$Pt(S_2P(OC_2H_5)(C_6H_5))_2$
Formula	$PdS_4P_2O_2C_{16}H_{20}$	$PtS_4P_2O_2C_{16}H_{20}$
Formula wt.	540.5 amu	629.2 amu
a	8.870(2) Å	8.065(3) Å
b	10.736(6) Å	8.209(1) Å
c	12.170(5) Å	9.561(3) Å
α	90.0°	78.42(2)°
β	104.51(3)°	105.45(3)°
γ	90°	116.16(2)°
V	1121.9(8) Å^3	545.1(8) Å^3
Z	2	1
Density	1.59 g/cm^3 (calcd.) 1.60 g/cm^3 (exptl.)	1.92 g/cm^3 (calcd.) 1.87 g/cm^3 (exptl.)
Space group	$P2_1/c$	$P\bar{1}$
Crystal dimensions	0.26 × 0.15 × 0.14 mm	0.15 × 0.10 × 0.22 mm
Crystal shape	Monoclinic	
Radiation	MoK$_{\alpha 1}$ (0.71069)	MoK$_{\alpha 1}$ (0.71069)
Temp.	22.0(10)°	22.0(10)°
μ	13.2 cm^{-1}	72.9 cm^{-1}
Scan speed	2.02° to 29.3°/min in 2θ	2.02° to 29.3°/min in 2θ
Scan range	1° below K$_\alpha$ to 1° above K$_{\alpha 2}$	1° below K to 1° above K$_{\alpha 2}$
Background counting	0.5 scan time	0.5 scan time
2θ limits	0–50°	0–50°
Final no. of variables	115	115
Unique data used ($I > 3\sigma I$)	1385	1789

tion on the diffractometer indicated the crystal system to be triclinic. Refinement showed the crystal to be centrosymmetric, and also defined the space group to be $P1$. Accurate cell constants were obtained from a least-squares refinement of the setting angles of 15 computer-centered reflections in the range 20° $< 2\theta <$ 25° which were a = 8.065(3) Å, b = 8.209(1) Å, c = 9.561(3) Å, α = 78.42(2)°, β = 105.45(3)°, γ = 116.16(2)°, and V = 545.1(8) Å^3. For Z = 1, the calculated density (1.92 g/cm^3) is in good agreement with the value 1.87 g/cm^3 determined by flotation in a mixture of bromoform and pentane.

The intensity data and structure refinement are similar to that described above. A total of 1,900 reflections were collected out to 50° in 2θ, of which 1,789 had $I > 3\sigma(I)$. Isotropic treatment of non-hydrogen atoms converged to R = 0.122. The atoms' positions were then treated anisotropically and a weighting scheme was employed. After two cycles of the least-squares, the R values converged to R = 0.051 and R_w = 0.048.

A summary of crystal data and intensity collection is found in Table II. Table IV contains a listing of the atomic coordinates and thermal parameters.

Results

Pd[S₂P(OEt)Ph]₂

The molecular structure of $Pd[S_2P(OC_2H_5)C_6H_5]_2$ is that of the *trans* isomer, with two such molecules per unit cell. A view of the molecular structure is shown in Fig. 1. Some important bond distances and angles are given in Table V. No unusual bond distances and angles were observed. The coordination geometry about the palladium atom is rectangular (D_{2h}) as demonstrated by a least-squares plane of the Pd, S1, S2 and P atoms and the bond lengths and angles associated with these atoms. The shortest intermolecular distance is 3.7 Å.

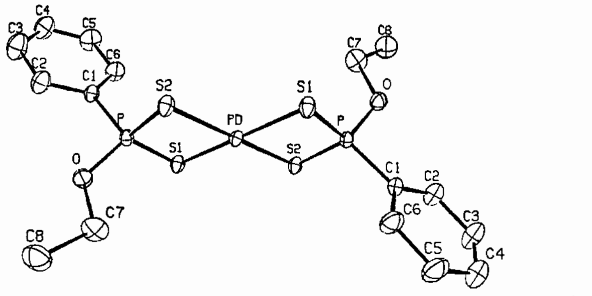

Fig. 1. A perspective view of the $Pd(S_2P(OEt)\phi)_2$ molecule with the labeling scheme. The atoms are represented by 30% probability thermal ellipsoids. The same labeling scheme was used for the platinum(II) compound.

The ^{1}H NMR spectrum of the methyl region of $Pd[S_2P(OC_2H_5)C_6H_5]_2$ consists of two triplets, separated by 2.5 Hz in benzene. This result (see Fig. 2) is consistent with the presence of both *cis* and *trans* isomers. The methylene region (not shown) has an unresolved multiplet formed from two overlapping quartets of doublets. The ^{1}H NMR spectrum in the

TABLE III. Atomic Coordinates and Thermal Parameters for Pd(S$_2$P(OC$_2$H$_5$)C$_6$H$_5$)$_2$.

	Atomic Coordinates		
Atom	x	y	z
Pd	0.00000	0.50000	0.50000
S1	0.11644	0.40844	0.63281
S2	−0.01610	0.67747	0.61428
P	0.08513	0.57372	0.71251
O	−0.01308	0.56733	0.84008
C1	0.26103	0.63973	0.73088
C2	0.26162	0.72204	0.81663
C3	0.40233	0.77690	0.82586
C4	0.53869	0.74740	0.75026
C5	0.54027	0.66567	0.66242
C6	0.40163	0.60939	0.65052
C7	−0.17005	0.51600	0.86676
C8	−0.24941	0.56096	0.98324

	Thermal Parameters					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.013049	0.009428	0.007950	0.000369	−0.004262	−0.000530
S1	0.021647	0.009627	0.010117	0.002780	−0.008142	−0.001082
S2	0.017934	0.009883	0.010077	0.002867	−0.006942	−0.001769
P	0.012160	0.010433	0.007215	0.000523	−0.003816	−0.000588
O	0.016906	0.015920	0.010070	−0.000916	−0.003333	−0.000252
C1	0.015652	0.011081	0.008440	0.001270	−0.005370	−0.001362
C2	0.021160	0.016666	0.015726	0.000708	−0.007320	−0.003962
C3	0.020618	0.022692	0.020742	−0.000199	−0.009448	−0.007091
C4	0.023415	0.019798	0.020153	−0.001021	−0.011536	−0.003340
C5	0.014652	0.026966	0.019490	−0.003638	−0.004337	−0.001553
C6	0.014838	0.021722	0.014700	−0.002662	−0.001773	−0.002579
C7	0.014145	0.025516	0.015981	0.004724	−0.001723	0.001074
C8	0.022522	0.029838	0.014823	0.000816	0.001221	−0.001145

TABLE IV. Atomic Coordinates and Thermal Parameters of Pt(S$_2$P(OEt)ϕ)$_2$.

Atom	Atomic Coordinates		
	x	y	z
Pt	0.000000	0.000000	0.000000
S1	0.288968	0.101630	0.163982
S2	0.003406	−0.286590	0.079439
P1	0.212924	−0.163113	0.242807
C1	0.140999	−0.212549	0.414560
C2	−0.033670	−0.225325	0.415538
C3	−0.094049	−0.255606	0.546597
C4	0.024865	−0.278288	0.675215
C5	0.195184	−0.268473	0.675783
C6	0.256952	−0.236768	0.543300
O1	0.378882	−0.227383	0.285075
C7	0.485406	−0.212500	0.173985
C8	0.476726	−0.394614	0.170870

(Continued overleaf)

TABLE IV. *(continued)*

	Thermal Parameters					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0.025674	0.017294	0.007120	0.010972	0.005039	0.000920
S1	0.028258	0.020948	0.012792	0.010934	0.002846	−0.000668
S2	0.038081	0.019460	0.009799	0.014270	0.002499	−0.000637
P1	0.028563	0.023217	0.008998	0.015211	0.003916	−0.000040
C1	0.027902	0.024168	0.009736	0.013743	0.005127	−0.000054
C2	0.047736	0.081847	0.013836	0.042595	0.009060	0.001551
C3	0.052663	0.094847	0.015555	0.040159	0.013159	−0.001627
C4	0.048529	0.031011	0.014889	0.012851	0.011133	−0.004352
C5	0.040841	0.043672	0.012541	0.010724	0.005530	−0.000095
C6	0.036611	0.045322	0.011219	0.020157	0.005044	0.005261
O1	0.035902	0.036058	0.013396	0.024679	0.006012	0.001176
C7	0.042433	0.038345	0.022361	0.025135	0.016806	0.002778
C8	0.042541	0.028324	0.035218	0.012714	0.019780	−0.007252

TABLE V. Some Bond Lengths (Å) and Angles (deg.) for $Pd(S_2P(OEt)C_6H_5)_2$ and $Pt(S_2P(OEt)C_6H_5)_2$.

		Metal	
		Pd	Pt
Lengths	M–S1	2.341(2)	2.341(3)
	M–S2	2.342(2)	2.333(3)
	S1–P	2.008(3)	2.022(3)
	S2–P	2.003(3)	2.020(3)
	P–O	1.580(5)	1.575(9)
	P–C1	1.773(7)	1.812(10)
	O–C7	1.456(9)	1.499(17)
Angles	M–S1–P	86.04(17)	85.69(16)
	S1–M–S2	84.46(16)	83.53(13)
	M–S2–P	86.12(19)	85.94(16)
	S1–P–S2	103.39(20)	100.78(19)
	S1–P–C1	113.17(32)	113.08(39)
	S2–P–O	113.08(27)	114.81(33)
	S2–P–C1	113.08(32)	114.02(39)

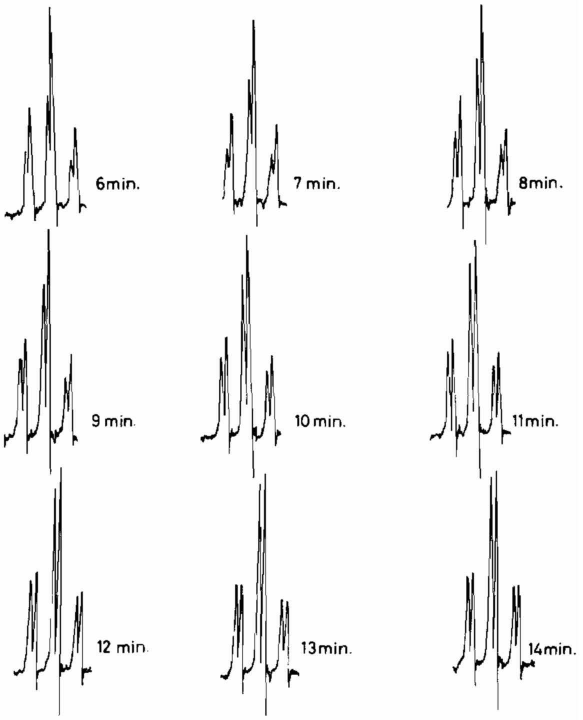

Fig. 2. The changes in the methyl region of the NMR spectrum of $Pd(S_2P(OC_2H_5)C_6H_5)_2$ in CS_2 at room temperature with approach to equilibrium. Equilibrium is achieved in about an hour in benzene and about 10 minutes in CS_2.

methyl and methylene regions of the sodium salt of the ligand is a triplet and a doublet of quartets (phosphorous and proton coupling to the methylene protons), respectively. The proton decoupled ^{31}P spectrum of the metal complex gives two singlets.

The ^1H NMR of the methyl region of an equilibrated sample of $Pd[S_2P(OEtPh]_2$ in all solvents investigated is two equally intense triplets, establishing that the equilibrium constant associated with *cis-trans* isomerism (I) is unity to a few percent. The spectra are independent of temperature from 140° to −50 °C ($\Delta H_{ct} \sim 0$ and $\Delta S_{ct} \sim 0$).

A triplet appears in the NMR spectrum immediately upon dissolving the sample, with the second triplet appearing 2.5 Hz downfield as time progresses. The shift varies from 2.5 Hz down to 2.0 Hz in methylene chloride. Equilibrium is reached in about 1 hour in benzene and in about 12 minutes in methylene chloride. The results can be obtained many times in the same NMR tube by regrowing crystals by slow evaporation of the solvent from the tube. Data used for a typical kinetic run is shown in Fig. 2. Table I lists the first order rate constants at 37 °C in various solvents, and rate constants in benzene at various temperatures. The rates are concentration independent in CS_2 and in benzene where a fourfold concentration range was used. The kinetic parameters [18] in benzene also are given in Table I. The solubility of $Pd[S_2P(OC_2H_5)Ph]_2$ is good in benzene, bromobenzene, chloroform, methylene chloride and CS_2; fair in nitrobenzene and CCl_4; poor in acetone, acetonitrile, nitromethane and pentane.

$Pt[S_2P(OC_2H_5)C_6H_5]_2$

The molecular structure of $Pt[S_2P(OC_2H_5)C_6H_5]_2$ is that of the trans isomer with one molecule per unit cell. The molecular structure is the same as for the palladium complex (Fig. 1) with the same labeling except for the metal atom. Atomic coordinates are listed in Table IV. Important bond distances and angles are included in Table V. The shortest intermolecular distance is 3.7 Å.

Upon dissolving single crystals in benzene, the ^1H NMR spectrum of the methyl region is a single triplet. After 24 hours, there are two triplets of equal intensity. The shift is 1.7 Hz in benzene. No detailed kinetic investigation has been performed on this rearrangement.

$Ni[S_2P(OC_2H_5)C_6H_5]$

The ^1H NMR spectrum of the methyl region of this complex shows a single triplet down to –60 °C in various solvents. The X-ray structure of the complex, as the *trans* isomer, has been reported [28].

Discussion

The rearrangement of square planar complexes has been the subject of considerable study in recent years [1–13, 20, 21]. However, the isomerization of MS_4 complexes has received little study except [22] in the presence of phosphine bases where recent work [22] with ^{77}Se NMR has demonstrated the associative, intramolecular nature of the phosphine catalyzed process. The uncatalyzed rearrangement has not been studied previously with sulfur ligands. The observation that the $M[S_2P(OEt)C_6H_5]_2$ complexes of Ni(II), Pd(II) and Pt(II) all crystallize in a *trans* geometry has produced an opportunity to investigate the uncatalyzed rearrangement of planar MS_4 complexes of these ions.

The structures of the Pd(II) and Pt(II) complexes of $M[S_2P(OEt)C_6H_5]_2$ are normal and comparable with other structures of 1,1-dithiolates. They will not be discussed further.

NMR data obtained on dissolution of the *trans*-$M[S_2P(OEt)C_6H_5]_2$ complexes in organic solvents has established that the rate of *trans* → *cis* isomerization follows the normal order [25] Ni(II) ≫ Pd(II) > Pt(II). The rate for the Ni(II) complex is sufficiently fast that isomers were not observed to –40 °C. While it remains possible that the proton signals are degenerate, it appears more reasonable to assume that the activation energy for *trans*→*cis* equilibration is less than 10 kcal/mole with rearrangement remaining rapid on the NMR time scale even at –40 °C.

The equilibrium concentration of *trans* and *cis* isomers with Pd(II) and Pt(II) appears to be identical. The asymmetry of the ligands appear to have a negligible influence on the equilibrium constant. Molecular weight measurements on the Pd(II) complex also rule out strong association which is sometimes observed with dithiophosphinato complexes [23, 24]. Since the four M–S bond energies are identical by symmetry, the rate of *trans* → *cis* isomerization can be assumed to be identical with the rate for *cis* → *trans* conversion. Statistically the thermodynamic entropy difference between the *trans* and *cis* species also is zero.

The rates of isomerization of the Pd(II) complex in various solvents and the solubility properties of the complex suggest solvent assistance in the rearrangement. Ionic species are not likely to be formed, but solvent assisted M–S dissociation appears to control the rate. The activation parameters obtained in benzene also support this view with $\Delta S^{\ddagger}$ rather large and negative [25]. While a twist mechanism [29] also can lead to the isomerization observed, the kinetic parameters and the solvent dependencies do not support the occurrence of this symmetry forbidden mechanism [26], at least for the thermal (as opposed to photolytic) [27] process.

The ten-fold increase in isomerization rate observed in CS_2 compared with benzene suggests that CS_2 is not an inert solvent for Pd(II) dithiolate species. The electrophilicity of the CS_2 carbon atom apparently allows interaction with the metal and the ligand sulfur atoms.

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