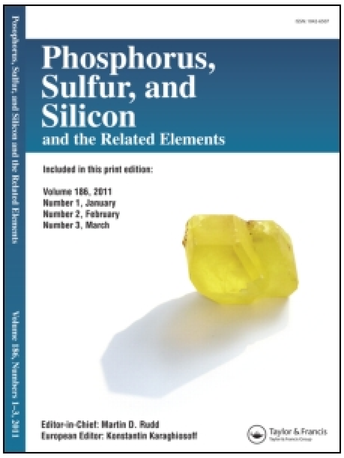

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LIGAND EXCHANGE REACTIONS OF ANTIMONY(III) *O,O*-DISUBSTITUTED PHOSPHORODITHIOATES WITH NICKEL SALTS

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Antimony(III) *tris*-(*O,O*-dialkyl phosphorodithioates) undergo ligand exchange reactions with nickel(II) chloride or nickel(II) octanoate in tetrahydrofuran solution to give nickel(II) *bis*-(*O,O*-dialkyl phosphorodithioates). The rates of the exchange reactions with nickel(II) chloride have been measured, and the rate constants can be correlated with polar substituent constants by use of the Taft–Hammett equation. The results suggest that the ligand exchange reactions occur by an initial S_N2 type of attack of chloride ion on the antimony atom of the antimony(III) *tris*-(*O,O*-dialkyl phosphorodithioates).

INTRODUCTION

In previous papers,[1-4] we have described model reactions of the type which antimony(III) *tris*-(*O,O*-di-*n*-propyl phosphorodithioate), the major active component of "Phil-Ad CA",[5-7] probably undergoes with components of crude petroleum prior to the eventual reductive pyrolysis which deposits metallic antimony on the zeolite catalyst used in the fluid catalyst cracking (FCC) process and brings about passivation of contaminant metals, such as nickel, vanadium and iron. The details of the passivation process have been published elsewhere.[5-7]

The contaminant metals in crude petroleum exist in three possible forms: (1) as salts dissolved in water suspended in the petroleum; (2) as metallic soaps of aliphatic, aromatic, or naphthenic acids; and (3) as organometallic complexes (e.g., complexes with porphyrins).[8] Of the contaminant metals, nickel appears to be the most troublesome in the FCC process. Although there is variation in values reported in the literature, nickel on the catalyst is about four times more reactive in promoting coking and formation of hydrogen than an equal concentration of vanadium or iron on the catalyst.[6,9] Therefore, in order to obtain some idea of what reactions nickel salts may undergo with the active components of "Phil-Ad CA" prior to the eventual reductive pyrolytic deposition of metallic nickel and antimony on the zeolite catalyst, we decided to carry out model reactions of nickel salts (chloride and octanoate) with a series of antimony(III) *tris*-(*O,O*-dialkyl phosphorodithioates) in tetrahydrofuran solution. The solvent was selected for reasons which will become apparent when the kinetics studies are described.

RESULTS AND DISCUSSION

A series of antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioates) was prepared as described previously.[1] When treated with nickel chloride (or nickel octanoate) in tetrahydrofuran solution, all of the antimony phosphorodithioates gave distinctive purple solutions after several hours at room temperature. Since nickel(II) *bis*-(*O*, *O*-dialkyl phosphorodithioates) are known to have a purple color, it was apparent that ligand exchange reactions had taken place

$$2[(RO)_2PS_2]_3Sb + 3NiCl_2 \overset{THF}{\rightleftharpoons} 3[(RO)_2PS_2]_2Ni + 2SbCl_3$$

Preparative scale reactions were carried out, and the nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates) were isolated and unambiguously identified by spectral and mixture melting point comparisons with authentic samples prepared by conventional methods.[10] [15] The results of the ligand exchange reactions are summarized in Table I.

When the ligand exchange reactions were carried out with antimony(III) *tris*-(*O*,*O*-diphenyl phosphorodithioate) or with antimony(III) *tris*-(*O*,*O*-di-*p*-tolyl phosphorodithioate), respectively, with Ni(II) salts in tetrahydrofuran at −20°C, yellow crystalline complexes of the nickel(II) *bis*-(*O*,*O*-diaryl phosphorodithioates) containing two molecules of tetrahydrofuran were obtained. The yellow crystals lost THF and became purple when allowed to stand in the air at room temperature. The formation of complexes of nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates) with two equivalents of a nitrogen base (such as pyridine, the isomeric picolines, and quinoline) has been reported,[16–19] but no isolable oxygen-coordinated complexes have been reported prior to the observation reported herein. The crystal structure of nickel(II) *bis*-(*O*,*O*-diethyl phosphorodithioate) has been determined,[20] and the nickel and four sulfur atoms lie in a square planar configuration. It can be assumed

TABLE I

Yields and melting points of nickel *bis*-(*O*,*O*-dialkyl phosphorodithioates) from the ligand exchange reactions

R	Yield[a] (%)	Yield[b] (%)	m.p. °C
methyl	44	51	129–130
ethyl	49	47	105
n-propyl	42	50	66–67
isopropyl	40	50	145 146
isobutyl	37	65	73–74
t-butyl	40	67	> 320 (at 110°C change color)
neopentyl	30	53	170–171
phenyl	25	---	130
p-tolyl	25	57	179–180
benzyl	--	23	137

[a] Yields from ligand exchange reactions of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioates) with nickel chloride.

[b] Yields from ligand exchange reactions of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioates) with nickel octanoate.

TABLE II

Specific rate constants for pseudo-first order reactions of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioates) with nickel chloride in tetrahydrofuran at temperature = 23.0 ± 0.5°C

R	k ($\times 10^{-2}$ min^{-1})	Correlation coefficient	Yield (equilibrium) (%)
methyl	1.144	0.986	82.7
ethyl	1.054	0.996	77.8
n-propyl	0.973	0.998	75.2
isobutyl	0.936	0.997	79.6
neopentyl	0.932	0.997	78.6
isopropyl	0.846	0.991	80.5
t-butyl	0.744	0.998	80.5

that the THF complexes reported herein have an octahedral configuration with the oxygen atoms of the tetrahydrofuran molecules in the apical positions.

In order to gain some insight into the mechanism of the ligand exchange reactions, we carried out a kinetics investigation of the reactions of the various antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioates) with a saturated solution of nickel chloride in tetrahydrofuran. The rate of appearance of each of the purple nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates) could be followed by visible spectroscopy, and, since undissolved nickel chloride was present throughout each run, the concentration of the nickel chloride in solution remained essentially constant. Thus, the rates were measured on the basis of a pseudo-first-order reaction, and the data are summarized in Table II. As shown in Figure 1, the rate data can be correlated by use of the Hammett–Taft equation.[21–23] The value of ρ^* was found to be $+0.649$ with a correlation coefficient of 0.976. A positive value of ρ^* means that increasing inductive electron donation by the alkyl group of the antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioate) causes a decrease in the rate of the ligand exchange reaction.

The rate data were also correlated by use of the Pavelich–Taft equation[24]

$$\log\frac{k}{k_0} = \sigma^*\rho^* + \partial E_s$$

(∂ = a reaction constant which measures the susceptibility of the reaction to a steric effect; ρ^* and σ^* have the same meaning as in the Hammett–Taft equation. The detailed mathematical treatment for the solution of the Pavelich–Taft equation using our data is available upon request.)

The value of ρ^* was found to be $+0.645$, and that of ∂ was essentially zero (-0.001). Thus, we can conclude that the rate of the ligand exchange reaction is dependent on the inductive effect of each alkyl group, but not on the steric effect.

The detailed mechanism of reaction of the ligand exchange reaction of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) with nickel chloride is unknown, but presumably, it takes place by an ionic process. Within this framework, there are two possible reaction pathways for the ligand exchange reaction: (a) an S_N2 type of reaction in which the chloride ion directly attacks the antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate), probably to form intermediate **1**, with subsequent departure of an *O*,*O*-dialkyl phosphorodithioate anion; (b) an S_N1 type of reaction in which the

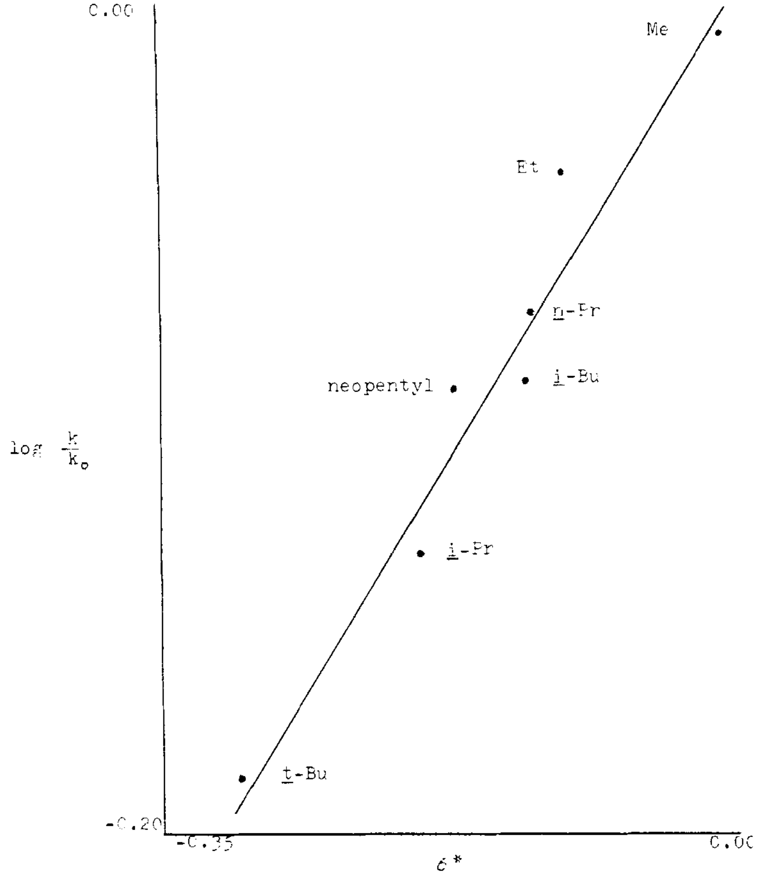

FIGURE 1 Hammett–Taft plot for ligand exchange reactions of antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioates) with nickel chloride.

dissociation of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) occurs to form intermediate **2** with subsequent addition of the chloride ion to **2**. The possible equations are shown below:

S_N2 type of reaction

$$[(RO)_2PS_2]_3Sb + \overset{\ominus}{Cl} \rightleftharpoons [(RO)_2PS_2]_3\overset{\ominus}{Sb}\text{-}Cl \quad \underset{\sim}{1}$$

$$\underset{\sim}{1} \xrightleftharpoons{-(RO)_2\overset{\ominus}{PS_2}} [(RO)_2PS_2]_2Sb\text{-}Cl \xrightleftharpoons[\text{same procedure}]{\text{repetition of the}}$$

$$\begin{array}{l} 3(RO)_2\overset{\ominus}{PS_2} + SbCl_3 \\ Ni^{+2}\ \Big\updownarrow \\ [(RO)_2PS_2]_2Ni \end{array}$$

S_N1 type of reaction

$$[(RO)_2PS_2]_3Sb \xrightleftharpoons{\text{dissociation}} \underset{\underset{\sim}{2}}{\overset{\oplus}{[(RO)_2PS_2]_2Sb}} + \overset{\ominus}{(RO)_2PS_2}$$

$$\underset{\sim}{2} + \overset{\ominus}{Cl} \rightleftharpoons [(RO)_2PS_2]_2Sb\text{-}Cl \xrightleftharpoons[\text{same procedure}]{\text{repetition of the}}$$

$$\begin{tikzcd}3\overset{\ominus}{(RO)_2PS_2} + SbCl_3 \arrow[d, shift left, "Ni^{+2}"] \\ {[(RO)_2PS_2]_2Ni} \arrow[u, shift left]\end{tikzcd}$$

Of course, it is understood that each antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioate) has a slightly distorted capped octahedral configuration with the lone pair of electrons in the capping position.[4] However, it would be unduly involved to depict this configuration repeatedly in the above equations for the possible broadly conceived mechanisms, and for which the fine details are not yet known.

If the assumption is made that the first step in the ligand exchange reaction is rate-limiting, it follows that increased electron donation by the alkyl groups would lead to acceleration of reaction in the S_N1 type of mechanism but to a decrease in rate in the S_N2 type of reaction. Since a positive value of ρ^* is indicative of the latter situation, it is probable that the mechanism of ligand exchange is of the S_N2 type.

There is evidence available that the first step of the attack of a strong nucleophile on antimony *tris*-(*O*,*O*-dialkyl phosphorodithioates) is rate-determining. This evidence consists of the report by McEwen, Woo and Kalbacher[2] that a 33% yield of sodium, *O*,*O*-dialkyl phosphorodithioate is obtained by reaction of an antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) with one equivalent of pyrrolylsodium in tetrahydrofuran, 67% of the starting antimony complex being recovered unchanged. The yield of sodium, *O*,*O*-dialkyl phosphorodithioate is 67%, with 33% recovery of the starting antimony complex when two equivalents of pyrrolylsodium are employed. Finally, a 100% yield of sodium *O*,*O*-dialkyl phosphorodithioate is obtained when three equivalents of pyrrolylsodium are employed. Since chloride ion is also a strong nucleophile with respect to antimony, this strengthens the supposition that the first step of the ligand exchange reaction is rate-limiting.

EXPERIMENTAL

Antimony(III) tris-(O,O-dialkyl phosphorodithioates). With the exception of the differences reported below, the antimony complexes were prepared and purified as described previously.[1] In some of the preparations of previously reported compounds, the yields were 10–20% higher than given in the previous paper, mainly because the antimony trichloride was purified by sublimation before use as a reagent.

Antimony(III) tris-(O,O-diisopropyl phosphorodithioate). The m.p. was 79–80° in agreement with Malone and Tompkins,[25] rather than 71–72° as reported in our previous paper.[1]

Antimony(III) tris-(O,O-diisobutyl phosphorodithioate). M.p. 124–125° (lit.[25] m.p. 123–124°). The value of 92–93° reported previously[1] might represent an allotropic form; NMR ($CDCl_3$) 0.95 (d, 36, $J = 6.5$), 1.90 (m, 6), 3.91 (d of d, 12, $J_{H-H} = 6.5$, $J_{P-H} = 2.5$).

Sodium O,O-Di-t-butyl phosphorodithioate. *t*-Butyl alcohol (3.36 g, 0.04 mole) was added dropwise to a suspension of 2.2 g (0.01 mole) of "phosphorus pentasulfide" in 100 ml of tetrahydrofuran under an argon atmosphere. The mixture was stirred at room temperature until evolution of hydrogen sulfide ceased (3 h). To this solution was added 1.0 g (0.02 mole) of sodium hydride, and the mixture was stirred for 10 m. A precipitate which formed upon addition of hexane to the solution was collected by filtration; 3.25 g (62%); m.p. 250°C (dec.); NMR ($CDCl_3$) δ 1.64 (s).

Antimony(III) tris-(O,O-Di-t-butyl phosphorodithioate). A solution of 1.52 g (6.6×10^{-3} mole) of antimony trichloride (purified by sublimation) in 100 ml of anhydrous ether was added to 5.28 g (0.02 mole) of sodium *O,O*-di-*t*-butyl phosphorodithioate under an argon atmosphere. The cloudy reaction mixture was stirred at 0°C for 5 h, then filtered. The filtrate was washed with 100 ml of ice-cold water, and the ether layer was dried over anhydrous magnesium sulfate. The ether solution was concentrated to half its volume by passing argon through the solution. Pentane (20 ml) was added, and, after having been cooled to −20°C for 2 days, antimony *tris-O,O*-di-*t*-butyl phosphorodithioate crystallized (1.5 g, 26%); m.p. 95°C (dec.); NMR ($CDCl_3$) δ 1.55 (s). The compound decomposes at room temperature within 1 h. Anal. Calcd. for $C_{24}H_{54}O_6P_3S_6Sb$: C, 34.09; H, 6.39; P, 11.00. Found: C, 34.06; H, 6.62; P, 10.70.

Antimony(III) tris-(O,O-dineopentyl phosphorodithioate). Neopentyl alcohol (3.53 g, 0.04 mole) dissolved in 100 ml of anhydrous tetrahydrofuran was added in a dropwise manner to 2.24 g (0.001 mole) of "phosphorus pentasulfide" under an argon atmosphere. The reaction mixture was stirred at room temperature until evolution of hydrogen sulfide ceased. To the homogeneous solution was added 1.52 g (0.006 mole) of freshly sublimed antimony trichloride. A white precipitate which had formed during 30 m of stirring was collected and washed with ether; 3.0 g (48%) of antimony *tris-(O,O*-dineopentyl phosphorodithioate) was obtained, m.p. 280°C (dec.); NMR ($CDCl_3$) δ 1.00 (54 H, s), 3.86 (12 H, d). Anal. Calcd. for $C_{30}H_{66}O_6P_3S_6Sb$: C, 38.79; H, 7.11; P, 10.00. Found: C, 38.65; H, 6.99; P, 9.84.

Ligand exchange reactions of antimony(III) (O,O-dialkyl phosphorodithioates) with nickel(II) chloride. A solution of 0.01 mole of each antimony(III) *tris-(O,O*-dialkyl phosphorodithioate) and 1.30 g (0.01 mole) of nickel(II) chloride in 100 ml of anhydrous tetrahydrofuran was refluxed for 10 h under an argon atmosphere. The resulting mixture was filtered and the purple filtrate concentrated to dryness. The purple solid which remained was worked up as indicated for each of the individual products. When the compounds were known, identities were established by mixture m.p. tests and comparisons of NMR spectra.

Nickel(II) bis-(O,O-dimethyl phosphorodithioate). The purple residue was chromatographed on silica gel, with benzene as the eluent. The product was crystallized from ether; yield, 43%, m.p. 129–130°C (reported,[10,11] m.p. 129–130°); NMR ($CDCl_3$) δ 3.93 (d, $J_{P-H} = 15$).

Nickel(II) bis-(O,O-diethyl phosphorodithioate). The purple residue was crystallized from Skelly F solvent; 49% yield; m.p. 105°C (reported,[10–12] m.p. 105°); NMR ($CDCl_3$) δ 4.5–4.0 (2 H, 2 sets of quartets), 1.43 (3 H, t).

Nickel(II) bis-(O,O-di-n-propyl phosphorodithioate). The purple residue was chromatographed on silica gel, with hexane as the eluent. The product was crystallized from hexane; yield, 42%; m.p. 66–67°C (reported,[13] m.p. 66–67°); NMR ($CDCl_3$) δ 4.41–4.03 (2 H, 2 sets of triplets), 2.00–1.42 (2 H, m), 1.00 (3 H, t).

Nickel(II) bis-(O,O-diisopropyl phosphorodithioate). The purple residue was crystallized from ether; yield, 40%; m.p. 145-146°C (reported,[13] m.p. 145–146°); NMR ($CDCl_3$) δ 5.3–4.8 (1 H, m), 1.40 (6 H, d).

Nickel(II) bis-(O,O-diisobutyl phosphorodithioate). The purple residue was chromatographed on silica gel, with hexane as the eluent. The product was crystallized from hexane; yield, 37%; m.p. 73–74°C (reported,[14] m.p. 73–74°); NMR ($CDCl_3$) δ 4.20–3.92 (2 H, 2 sets of doublets), 2.32–1.70 (1 H, m), 1.00 (6 H, d).

Nickel(II) bis-(O,O-di-p-tolyl phosphorodithioate). The purple residue was chromatographed on silica gel, with benzene as the eluent. The product was crystallized from benzene; yield, 25%; m.p. 179–180°C (reported,[14] m.p. 179–180°); NMR ($CDCl_3$) δ 7.21 (4 H, s), 2.38 (3 H, s).

Nickel(II) bis-(O,O-di-p-tolyl phosphorodithioate) · 2THF complex. A solution of 10.5 g (0.01 mole) of purple nickel(II) *bis*-(*O*,*O*-di-*p*-tolyl phosphorodithioate), m.p. 179–180°C, in 50 ml of tetrahydrofuran was cooled to $-20°C$ overnight. A yellow crystalline product which had formed was collected; 8.2 g (73%); NMR ($CDCl_3$) δ 7.21 (8 H, s), 3.74 (4 H, m), 2.38 (6 H, s), 1.83 (4 H, m). The yellow crystals lost THF and became purple when dried in the air at room temperature or during a m.p. determination.

Nickel(II) bis-(O,O-diphenyl phosphorodithioate). The purple residue (a liquid instead of a solid on this occasion) was chromatographed on silica gel, with benzene as the eluent. A purple, crystalline solid was obtained, m.p. 130°C (reported,[14] m.p. 130°); NMR ($CDCl_3$) δ 7.39 (s).

Nickel(II) bis-(O,O-diphenyl phosphorodithioate) · 2THF complex. A solution of 9.61 g (0.01 mole) of the purple solid of m.p. 130° in 50 ml of tetrahydrofuran was cooled to $-20°C$ overnight. A yellow, crystalline solid which had formed was collected by filtration; yield, 8.50 g (83%); NMR ($CDCl_3$) δ 7.39 (10 H, s), 3.74 (4 H, m), 1.83 (4 H, m). The yellow crystals lost THF when dried in the air at room temperature or during a m.p. determination.

Ligand exchange reaction of antimony(III) tris-(O,O-di-t-butyl phosphorodithioate) with nickel chloride. A solution of 0.78 g (9.30×10^{-4} mole) of antimony *tris*-(*O*,*O*-di-*t*-butyl phosphorodithioate) and 0.21 g (1.6×10^{-3} mole) of nickel chloride in 100 ml of tetrahydrofuran was stirred at 24–25°C for 3 h under an argon atmosphere. A purple solution resulted, and it was concentrated to dryness. One hundred ml of ether was added to dissolve the purple precipitate, and the ether solution was then washed with 100 ml of water. The ether layer was dried over sodium sulfate and then concentrated to half of its original volume. Ten ml of pentane was added to the ether solution, and it was cooled to $-20°C$; 0.38 g (40% yield) of nickel *bis*-(*O*,*O*-di-*t*-butyl phosphorodithioate) was obtained (purple crystals); m.p. > 320° (at 110°C change of color); NMR ($CDCl_3$) $\delta = 1.69$ (s) ppm. Anal. Calcd. for $C_{16}H_{36}O_4P_2S_4Ni$: C, 35.50; H, 6.60; P, 11.40; S, 23.70. Found: C, 35.50; H, 6.68; P, 11.38; S, 23.87.

Ligand exchange reaction of antimony(III) tris-(O,O-di-neopentyl phosphorodithioate) with nickel chloride. A solution of 2.78 g (3×10^{-3} mole) of antimony *tris*-(*O*,*O*-di-neopentyl phosphorodithioate) and 0.6 g (4.63×10^{-3} mole) of nickel chloride in 100 ml of tetrahydrofuran was stirred at room temperature for 24 h under an argon atmosphere. A purple solution resulted, and it was evaporated to dryness. One hundred ml of ether was added to dissolve the purple precipitate, and some undissolved white-yellow solid was removed by filtration. The purple solution was washed twice with 100 ml of water and dried over magnesium sulfate. The purple solution was then concentrated to one third of its original volume and 10 ml of pentane was added. When cooled to $-20°C$, 0.8 g (30% yield) of nickel *bis*-(*O*,*O*-di-neopentyl phosphorodithioate) was obtained (purple crystals); m.p. 170–171°C; NMR ($CDCl_3$) $\delta = 3.92$ (2 H, d), 1.00 (9 H, s) ppm. Its structure was confirmed by its NMR spectrum and a mixed melting point test with an authentic sample. Anal. Calcd. for $C_{20}H_{44}O_4P_2S_4Ni$: C, 40.26; H, 7.44; P, 10.39. Found: C, 40.43; H, 7.82; P, 10.57.

Ligand exchange reactions of antimony(III) tris-(O,O-disubstituted phosphorodithioates) with nickel(II) octanoate. These reactions were carried out in essentially the same manner as the ligand exchange reactions with nickel(II) chloride. The results are summarized in Table I. A typical reaction, and one not carried out with nickel chloride, is described below.

Antimony(III) tris-(O,O-dibenzyl phosphorodithioate). A solution of 1.40 g (1.34×10^{-3} mole) of antimony(III) *tris*-(*O*,*O*-dibenzyl phosphorodithioate) and 0.69 g (0.002 mole) of nickel octanoate in 50 ml of tetrahydrofuran was stirred at room temperature for 1 h under an argon atmosphere. The resulting purple solution was concentrated to dryness, and the solid purple residue was crystallized from benzene–hexane (1 : 1). There was obtained 0.30 g (23%) of the title compound, m,p. 136–137°C (reported,[15] m.p. 137°); NMR ($CDCl_3$) δ 5.3 (2 H, d), 7.38 (5 H, s).

Preparation of authentic samples of nickel(II) bis-(O,O-disubstituted phosphorodithioates). Literature procedures were employed.[10–14] A typical example is given below.

Preparation of nickel(II) bis-(O,O-di-n-propyl phosphorodithioate). Absolute 1-propanol (40 ml) was added to 10 g (0.045 mole) of "phosphorus pentasulfide" under an argon atmosphere. The mixture was stirred overnight at room temperature, and a homogeneous solution resulted. Nickel(II) chloride (5.8 g, 0.045 mole) was added, and the mixture (now purple) was stirred for 2 h at room temperature. Evaporation of the excess 1-propanol gave a purple solid which was treated with 100 ml of hexane and filtered through a thick frosil pad. The purple filtrate was cooled to $-20°C$, and there was obtained 10.3 g (47%) of purple nickel(II) *bis*-(*O*,*O*-di-*n*-propyl phosphorodithioate), m.p. 66–67°C.

TABLE III

ξ (molar extinction coefficient) values of nickel *bis*-(*O*,*O*-dialkyl phosphorodithioates) in tetrahydrofuran

R	λ_{max} (nm)	ξ (from slope)	Correlation coefficient
methyl	525	71.92	0.999
ethyl	525	72.71	0.999
n-propyl	523	74.90	0.999
isopropyl	523	74.32	0.998
isobutyl	525	75.39	0.999
t-butyl	520	78.39	0.999
neopentyl	524	73.2	0.999

Kinetics studies of ligand exchange reactions of antimony(III) tris-(O,O-dialkyl phosphorodithioates) with nickel(II) chloride.

a. Determination of ε (molar extinction coefficient of nickel bis-(O,O-dialkyl phosphorodithioates). Each pure nickel *bis*-(*O*,*O*-dialkyl phosphorodithioate) was dissolved in tetrahydrofuran to make a series of samples having different concentrations. The concentrations of the samples ranged approximately from 1.0×10^{-2} M to 1.0×10^{-3} M. The ε of each nickel *bis*-(*O*,*O*-dialkyl phosphorodithioate) was calculated from the slope of a plot of absorbance vs. concentration and by use of the Lambert–Beer law. Usually, five different concentrations were used to determine the slope (ε) of each plot of absorbance vs. concentration; the correlation coefficient of ε for all the nickel *bis*-(*O*,*O*-dialkyl phosphorodithioates) ranged from 0.998–0.999. The data are summarized in Table III.

b. Determination of k (rate constant) of the ligand exchange reaction of each antimony tris-(O,O-dialkyl phosphorodithioate) with nickel chloride. An excess* of nickel chloride was treated with tetrahydrofuran to make a saturated solution at a temperature of 23.0 ± 0.5°C, and then the antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) was added to this mixture. The initial concentration of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) ranged from 5.9068×10^{-3} M to 7.8081×10^{-3} M. A purple color developed [indication of formation of the nickel *bis*-(*O*,*O*-dialkyl phosphorodithioate)] after the addition of the antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate). The concentration of nickel *bis*-(*O*,*O*-dialkyl phosphorodithioate) could then be calculated by use of the Lambert–Beer law.

Aliquots of the reaction mixture were taken at certain time intervals, filtered, and the absorbance of the filtrate at λ_{max} was measured until the final equilibrium reading was reached.

The concentration of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) during the reaction can be calculated by use of the following equation:

$$2[(RO)_2PS_2]_3Sb + 3NiCl_2 \rightleftharpoons 3[(RO)_2PS_2]_2Ni + 2SbCl_3$$

$$C_{Sb} = C_{Sb}^{0} - \tfrac{2}{3}C_{Ni}$$

where C_{Sb} = molar concentration of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate) at any point during the reaction.

C_{Sb}^{0} = initial molar concentration of antimony *tris*-(*O*,*O*-dialkyl phosphorodithioate), a known value.

C_{Ni} = concentration of nickel *bis*-(*O*,*O*-dialkyl phosphorodithioate) at any point during the reaction.

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*An excess means that there was always some undissolved nickel chloride in equilibrium with the dissolved salt.

For the pseudo-first order reaction:

$$\frac{-dC_{Sb}}{dt} = k'[NiCl_2]^{*}C_{Sb}$$
$$= kC_{Sb}$$

The values of the specific rate constants and the equilibrium yields are given in Table II.

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*$[NiCl_2]$ = constant (since an excess amount of nickel chloride was always present in contact with the saturated tetrahydrofuran solution.