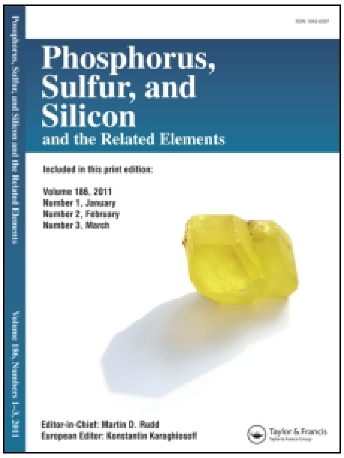

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LIGAND EXCHANGE REACTIONS OF ANTIMONY(III) *tris*-(*O,O*-DIALKYL PHOSPHORODITHIOATES) WITH NICKEL(II) *bis*-(*O,O*-DIALKYL PHOSPHORODITHIOATES)

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In a typical ligand exchange reaction, antimony(III) *tris*-(*O,O*)-di-*t*-butyl phosphorodithioate) undergoes reaction with nickel(II) *bis*-(*O,O*-diisobutyl phosphorodithioate) in tetrahydrofuran solution to give nickel(II) *bis*-(*O,O*-di-*t*-butyl phosphorodithioate) and antimony(III) *tris*-(*O,O*-diisobutyl phosphorodithioate). In general, the ligands having the more bulky alkoxy groups end up in the nickel complex in these exchange reactions. The driving force for the ligand exchange reaction consists of the relief of steric strain which results from the transfer of bulky alkoxy groups from the sterically hindered distorted octahedral antimony complex to the much less sterically hindered square planar nickel complex.

INTRODUCTION

In previous publications,[1–5] we have described model reactions of the types which antimony(III) *tris*-(*O,O*-di-*n*-propyl phosphorodithioate), the major active component of "Phil-Ad CA", probably undergoes with components of crude petroleum prior to the eventual reductive pyrolytic reactions which take place in the fluid catalytic cracking (FCC) process. The reductive pyrolytic reactions eventually lead to deposition of antimony metal on the zeolite catalyst. Contaminant metals in petroleum, such as nickel, vanadium and iron, originally present as salts dissolved in water suspended in the petroleum, or as metallic soaps of aliphatic, aromatic, or naphthenic acids, or as organometallic complexes (e.g. with porphyrins)[6] also undergo reductive pyrolysis to deposit the respective metals on the zeolite catalyst. In the absence of metallic antimony, these metals cause coking and formation of hydrogen. However, when metallic antimony is present, it forms alloys with the contaminant metals, and the alloys do not catalyze these undesirable reactions of the crude petroleum.[7–9] Thus, "Phil-Ad CA" functions as a passivation agent for the contaminant metals.

In our most recent paper,[5] we have carried out model reactions which demonstrate that antimony(III) *tris*-(*O,O*-dialkyl phosphorodithioates) undergo ligand exchange reactions with nickel(II) chloride or nickel(II) octanoate to form nickel(II) *bis*-(*O,O*-dialkyl phosphorodithioates). We have reported on the kinetics of the ligand exchange reactions with nickel(II) chloride in tetrahydrofuran, and we have suggested an S_N2 type of of mechanism for the reactions.

Since these ligand exchange reactions occur at a relatively slow rate at room temperature, it is clear that, for an appreciable period of time, antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioates) and nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates) coexist in solution. Therefore, the possibility exists that these two types of complexes might also undergo ligand exchange reactions, and we decided to investigate this possibility.

RESULTS AND DISCUSSION

The following type of possible ligand exchange was investigated for several different antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioates) and nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates). In some cases exchange reactions were observed, and in other cases they were not. The results are summarized in Table I.

$$\underset{\mathbf{1}}{2[(RO)_2PS_2]_3Sb} + \underset{\mathbf{2}}{3[(R'O)_2PS_2]_2Ni} \rightleftharpoons \underset{\mathbf{3}}{2[(R'O)_2PS_2]_3Sb} + \underset{\mathbf{4}}{3[(RO)_2PS_2]_2Ni}$$

The most striking effect observable from the data of Table I (as evident in Exps. 1, 2, 4, 5, 6, and 8) is that a bulky alkoxy group preferentially ends up in the nickel complex rather than in the antimony complex; this, in fact, appears to be the main driving force for the ligand exchange reaction. When the unquestionably bulkier group is originally present in the nickel complex, no ligand exchange occurs (Exp. 3). Also, the presence of an exceptionally bulky alkoxy group in the antimony complex causes the rate of reaction to be slowed markedly (cf. Exps. 7 and 8).

The explanation for the experimental results can be deduced from the X-ray crystal and molecular structures of antimony(III) *tris*-(*O*,*O*-diethyl phosphorodithioate) and nickel(II) *bis*-(*O*,*O*-diethyl phosphorodithioate). We have found that

TABLE I

Ligand exchange reactions between antimony(III) *tris*-(*O*,*O*-di-R phosphorodithioates) and nickel(II) *bis*-(*O*,*O*-di-R′ phosphorodithioates) in tetrahydrofuran solution

					% Yield[a]			
Exp.	R	R′	Temp., °C	Time, h	**1**[b]	**2**[b]	**3**[b]	**4**[b]
1	*i*-Pr	*i*-Bu	60	24	—	—	—	62
2	*i*-Pr	Me	60	20	—	—	31	61
3	Me	*i*-Pr	60	20	rec.[c]	rec.[c]	0	0
4	*t*-Bu	*i*-Bu	5–10; 20[d]	5; 20	—	—	48	63
5	*t*-Bu	*n*-Pr	5–10; 25[d]	5; 20	—	—	—	76
6	*t*-Bu	*i*-Pr	5–10; 25[d]	5; 20	—	—	—	85
7	neopentyl	Et	25	20	rec.[c]	rec.[c]	0	0
8	neopentyl	Et	60	70	—	—	—	79

[a] A material balance could not be achieved owing to decomposition of **1** and **3** during reflux and to loss of products in the isolation.

[b] Numbers refer to the compounds in the equation of the main text.

[c] Starting material recovered.

[d] Antimony(III) *tris*-(*O*,*O*-di-*t*-butyl phosphorodithioate) decomposes rapidly, even at room temperature.

the coordination polyhedron of the Sb atom is a distorted capped octahedron with a stereochemically active lone pair in the capping position and approximately on a molecular pseudo triad axis which passes through the Sb atom.[4] Large alkyl groups are in close proximity to one another.

The crystal structure of nickel *bis*-(*O*,*O*-diethyl phosphorodithioate) was determined by McConnell and Kastalsky.[10] The molecule itself is centrosymmetric with nickel at the center of symmetry. The nickel and four sulfur atoms are in a square planar configuration, with nickel–sulfur bond lengths of 2.23 and 2.24 Å.

When the alkyl group in an antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioate) becomes bulky, the antimony complex is a decidedly sterically hindered molecule. On the other hand, nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates), with only four alkyl groups and a square planar configuration are not sterically hindered, even with large alkyl groups present in the alkoxy moieties. Therefore, when larger groups are present in the starting antimony complex rather than in the starting nickel complex, ligand exchange is favored because of the relief of steric strain.

The fact that the rate of ligand exchange is decreased markedly when a bulky alkoxy group is present suggests that the rate-determining step of the ligand exchange reaction is bimolecular. However, we do not have sufficient information available to state anything more meaningful about the mechanism at the present time.

EXPERIMENTAL

Starting Materials. The preparations of the various antimony(III) *tris*-(*O*,*O*-dialkyl phosphorodithioates) and nickel(II) *bis*-(*O*,*O*-dialkyl phosphorodithioates) used in these studies have been described in our previous papers.[1-5] Melting points and spectral data reported for the products of the ligand exchange reactions are identical with the corresponding data in our most recent previous publication.[5]

Ligand exchange reaction of antimony tris-(O,O-diisopropyl phosphorodithioate) with nickel bis-(O,O-diisobutyl phosphorodithioate). A solution of 2.71 g (5.0×10^{-3} mole) of nickel *bis*-(*O*,*O*-diisobutyl phosphorodithioate) and 3.68 g (4.83×10^{-3} mole) of antimony *tris*-(*O*,*O*-diisopropyl phosphorodithioate) in 80 ml of tetrahydrofuran was refluxed overnight under an argon atmosphere. Some orange-yellow precipitate (an inorganic salt, m.p. > 280°C) was removed by filtration, and the purple filtrate was concentrated to dryness. The solid, purple residue was then purified by column chromatography (frosil as absorbent, ether as eluent) and the appropriate fraction recrystallized from hexane; 1.50 g (62%) of nickel *bis*-(*O*,*O*-diisopropyl phosphorodithioate) was obtained (purple crystals); m.p. 145–146°C; NMR ($CDCl_3$) δ = 5.3–4.8 (1H, m), 1.40 (6 H, d). No starting material were recovered from this reaction mixture; the yield is not quantitative due to the decomposition of antimony *tris*-(*O*,*O*-diisopropyl phosphorodithioate) during reflux.

Ligand exchange reaction of antimony tris-(O,O-diisopropyl phosphorodithioate) with nickel bis-(O,O-dimethyl phosphorodithioate). A solution of 1.52 g (4.09×10^{-3} mole) of nickel *bis*-(*O*,*O*-dimethyl phosphorodithioate) and 2.07 g (2.72×10^{-3} mole) of antimony *tris*-(*O*,*O*-diisopropyl phosphorodithioate) in 50 ml of tetrahydrofuran was stirred at 60°C for 20 hours under an argon atmosphere. Some red precipitate (an inorganic salt, m.p. > 300°C) was removed by filtration, and the purple filtrate was concentrated to dryness. The solid, purple residue was recrystallized from ether–pentane (1 : 1) to give two kinds of crystals; i.e., purple crystals and pale yellow crystals. Each of these was purified by a series of recrystallizations from ether–pentane (1 : 1). The purple solid (1.2 g, 61% yield) was identified as nickel *bis*-(*O*,*O*-diisopropyl phosphorodithioate), m.p. 145–146°C; NMR ($CDCl_3$) δ = 5.3–4.8 (1 H, m), 1.40 (6 H, d). The pale yellow solid (0.5 g, 31% yield) was identified as antimony *tris*-(*O*,*O*-dimethyl phosphorodithioate), m.p. 86–97°C; NMR ($CDCl_3$) δ = 3.86 (d J_{P-H} = 16 Hz). No starting materials were recovered from this reaction mixture.

Ligand exchange reaction of antimony tris-(O,O-di-tert-butyl phosphorodithioate) with nickel bis-(O,O-diisobutyl phosphorodithioate). A solution of 0.83 g (9.82 × 10^{-4} mole) of antimony *tris*-(*O,O*-di-*tert*-butyl phosphorodithioate) and 0.80 g (1.47 × 10^{-3} mole) of nickel *bis*-(*O,O*-diisobutyl phosphorodithioate) in 100 ml of tetrahydrofuran was stirred at 5–10°C for 5 hours under an argon atmosphere. The temperature of the reaction mixture was then raised to 20°C, with another 20 hours of stirring. The resulting purple solution was concentrated to dryness by blowing argon through the solution. The solid, purple residue was then dissolved in ether–pentane (1 : 1); a white precipitate (m.p. > 300°C) which did not dissolve in the solvent was removed by filtration. After the filtrate had been cooled to −20°C, 0.5 g (62.7% yield) of nickel *bis*-(*O,O*-di-*tert*-butyl phosphorodithioate) was obtained (purple crystals); m.p. > 320°C (color changed at 110°C); NMR ($CDCl_3$) δ = 1.69 (s). The filtrate obtained after collection of the purple solid was concentrated somewhat further and then cooled to −20°C; 0.4 g (48% yield) of antimony *tris*-(*O,O*-diisobutyl phosphorodithioate) was obtained (pale yellow crystals); m.p. 124–125°C; NMR ($CDCl_3$) δ = 4.05–3.80 (2 H, 2 sets of doublets), 1.90 (1 H, m), 0.95 (6 H, d). No starting materials were recovered from this reaction mixture.

Ligand exchange reaction of antimony tris-(O,O-di-tert-butyl phosphorodithioate) with nickel bis-(O,O-di-n-propyl phosphorodithioate). A solution of 0.43 g (8.85 × 10^{-4} mole) of nickel *bis*-(*O,O*-di-*n*-propyl phosphorodithioate) and 0.5 g (5.0 × 10^{-4} mole) of antimony *tris*-(*O,O*-di-*tert*-butyl phosphorodithioate) in 50 ml of tetrahydrofuran was stirred at 0–5°C for 5 hours under an argon atmosphere. The temperature of the reaction mixture was then raised to 20°C, with another 20 hours of stirring. The resulting purple solution was concentrated to dryness by blowing argon through the solution. The solid, purple residue was washed with pentane and then recrystallized from pentane : ether (1 : 1); 0.36 g (76% yield) of nickel *bis*-(*O,O*-di-*tert*-butyl phosphorodithioate) was obtained (purple crystals); m.p. > 320°C (color changed at 110°C); NMR ($CDCl_3$) δ = 1.69 (s). No starting materials were recovered from this reaction mixture.

Ligand exchange reaction of antimony tris-(O,O-di-tert-butyl phosphorodithioate) with nickel bis-(O,O-diisopropyl phosphorodithioate). A solution of 0.43 g (8.85 × 10^{-4} mole) of nickel *bis*-(*O,O*-diisopropyl phosphorodithioate) and 0.5 g (5.9 × 10^{-4} mole) of antimony *tris*-(*O,O*-di-*tert*-butyl phosphorodithioate) in 50 ml of tetrahydrofuran was stirred at 5–10°C for 5 hours under an argon atmosphere. The temperature of the reaction mixture was then raised to 20°C, with another 20 hours of stirring. The resulting purple solution was concentrated to dryness by blowing argon through the solution. The solid, purple residue was then recrystallized from ether; 0.4 g (85% yield) of nickel *bis*-(*O,O*-di-*tert*-butyl phosphorodithioate) was obtained (purple crystals); m.p. > 320°C (color changed at 110°C); NMR ($CDCl_3$) δ = 1.69 (s). No starting materials were recovered from this reaction mixture.

Ligand exchange reaction of antimony tris-(O,O-dineopentyl phosphorodithioate) with nickel bis-(O,O-diethyl phosphorodithioate). A solution of 0.5 g (5.38 × 10^{-4} mole) of antimony *tris*-(*O,O*-di*neo*pentyl phosphorodithioate) and 0.35 g (8.08 × 10^{-4} mole) of nickel *bis*-(*O,O*-diethyl phosphorodithioate) in 250 ml of tetrahydrofuran was refluxed for 72 hours under an argon atmosphere. Some red precipitate (an inorganic salt, m.p. > 300°C) was removed by filtration, and the purple filtrate was concentrated to dryness. The solid, purple residue was recrystallized from ether–pentane (1 : 1); 0.38 g (79% yield) of nickel *bis*-(*O,O*-di*neo*pentyl phosphorodithioate) was obtained (purple crystals); m.p. 170–171°C; NMR ($CDCl_3$) δ = 3.92 (2H, d), 1.00 (9 H, s). No starting materials were recovered. Note: when this reaction was attempted at room temperature for 20 hours, no reaction occurred.

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