# Complexes with Sulphur and Selenium Donor Ligands. Part 6.[1] Kinetics and Mechanism of the Reaction Between 1,2-Bis(diphenylphosphino)ethane and Tris(*OO'*-dimethyl phosphorodithioato)cobalt(III)

By **Elena Borghi, Valeria Di Castro,** and **Fabrizio Monacelli,*** Istituto di Chimica Generale, Università di Roma, 00185 Roma, Italy
**Anthony A. G. Tomlinson,*** Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del C.N.R., Via Montorio Romano 36, 00131 Roma, Italy

The kinetics and mechanism of the reaction between $[Co\{S_2P(OMe)_2\}_3]$ and $Ph_2P[CH_2]_2PPh_2$ (dppe) in $CH_2Cl_2$ have been investigated by spectrophotometric and conductance methods. The reaction proceeds in two steps. The first step is (i), deduced from the formation of ions during the reaction and on spectroscopic grounds. The

$$[Co\{S_2P(OMe)_2\}_3] + \text{dppe} \longrightarrow [Co\{S_2P(OMe)_2\}_2(\text{dppe})]^+ + [S_2P(OMe)_2]^- \qquad \text{(i)}$$

activation parameters are $\Delta H^\ddagger = 14.3 \pm 1.0$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -17 \pm 3$ cal K$^{-1}$ mol$^{-1}$. The low $\Delta S^\ddagger$ value and linear dependence of the rate on dppe concentration suggests rate-determining nucleophilic participation of the incoming ligand. A one-ended reversible dissociation of the dithioate ligand with the dppe competing for the resulting five-co-ordinate intermediate or direct nucleophilic attack of the phosphine on $[Co\{S_2P(OMe)_2\}_3]$ or on the dithioate phosphorus are mechanisms consistent with the data. The second step of the reaction is (ii).

$$[Co\{S_2P(OMe)_2\}_2(\text{dppe})]^+ + [S_2P(OMe)_2]^- \longrightarrow [Co\{S_2P(OMe)_2\}\{S_2PO(OMe)\}(\text{dppe})] + P(OMe)_2S(SMe) \qquad \text{(ii)}$$

Although a reliable estimate of the rate constants could not be obtained because of ion-producing side reactions after *ca.* 90% completion of reaction, it is probable that this step occurs *via* nucleophilic attack on the P–O–C carbon atom of the co-ordinated $[S_2P(OMe)_2]^-$.

THE continuing interest in dithiocarbamato- and phosphoro- and phosphino-dithioato-complexes of transition-metal ions[2] has not extended to kinetic studies. Although there has been much work on the adducts formed between nickel(II) complexes of these ligands and bases[3] and on their chemistry with Pt$^{II}$ and Ru$^{III}$,[4] so far as we are aware, the only kinetic investigation of such adducts is that of Sweigart and Heidtmann[5] concerned with the reaction of $[Ni\{S_2P(OEt)_2\}_2]$ and $[Ni\{S_2P(OEt)_2\}_2(PBu_3)]$ with bidentate nitrogen- and phosphorus-donor ligands. The final products of the reaction were not identified, although the closely related dimethyl analogue, $[Ni\{S_2P(OMe)_2\}_2]$, reacts with $Ph_2PC_2H_4PPh_2$ (dppe) and $Ph_2PC_2H_4AsPh_2$ (dadpe) (but not with the diarsino-analogue) to give neutral complexes, *e.g.* $[Ni\{S_2PO(OMe)\}(\text{dadpe})]$, in which, besides substitution by the phosphine ligand, demethylation of the remaining $[S_2P(OMe)_2]^-$ has occurred.[6] The crystal-

---

[1] Part 5, C. Bellitto, A. A. G. Tomlinson, C. Furlani, and G. De Munno, *Inorg. Chim. Acta*, 1978, **27**, 269.

[2] J. R. Wasson, G. M. Woltermann, and H. J. Stoklosa, *Topics Current Chem.*, 1973, **35**, 65; D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 233.

[3] For example, C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141; S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, 1970, **9**, 2545.

[4] M. C. Cornock and T. A. Stephenson, *J.C.S. Dalton*, 1977, 501 and refs. therein.

[5] D. A. Sweigart and P. Heidtmann, *J.C.S. Dalton*, 1975, 1686.

[6] L. Gastaldi, P. Porta, and A. A. G. Tomlinson, *J.C.S. Dalton*, 1974, 1424.

structure determination of the complex $[Ni\{S_2PO(OMe)\}(dadpe)]$ also demonstrated that the P–C bond of the dadpe points in the same direction as the P=O bond of the demethylated phosphorodithioate. Similar behaviour is shown by $[Pt\{S_2P(OEt)_2\}_2]$, which gives the neutral species $[Pt\{S_2PO(OMe)\}(PR_3)_2]$ on reaction with unidentate phosphines,[7] and also by $[M(S_2COR)_3]$ (M = Pt or Pd) complexes which form $[M(S_2CO)(S_2COR)]$ on reaction with $[S_2COR]^-$ in chloroform or dichloromethane.[8]

We now describe a kinetic study of the reaction between $[Co\{S_2P(OMe)_2\}_3]$ and dppe in dichloromethane, which represents the first attempt to unravel the detailed mechanism of this interesting reaction. A preliminary communication of this work has been published.[9]

## EXPERIMENTAL

*Materials.*—1,2-Bis(diphenylphosphino)ethane, dppe, was a Strem product and was used as received. The complex $[Co\{S_2P(OMe)_2\}_2]$ was prepared by the usual method[10] involving reaction between $P(OMe)_2S(SH)$ (prepared *in situ* under nitrogen) and $CoCl_2$ and was recrystallised several times from methanol before use. Since this complex is light sensitive, decomposing to give cobalt(II) complexes,[11] freshly prepared samples were used and care was taken to avoid exposure of the solid and its solutions to light. Dichloromethane was a C. Erba RP reagent. It was dried over molecular sieves (4 Å) and distilled before use.

*OO'S*-Trimethyl phosphorodithioate, $P(OMe)_2S(SMe)$, was prepared following the procedure used to obtain *S*-methyl esters of dithiocarbazates.[12] Methyl iodide (14.2 g, 0.1 mol) was added slowly with vigorous stirring to a solution of $[NH_4][S_2P(OMe)_2]$ (17.5 g, 0.1 mol) in methanol–water (2 : 3) (50 cm$^3$) at 0 °C. The mixture was stirred until an organic layer appeared, ice-water was added (50 cm$^3$), and stirring continued for 10 min. The mixture was extracted with diethyl ether (*ca.* 80 cm$^3$), the extract dried overnight $(Mg[SO_4])$ and distilled to give a colourless oil (b.p. 105 °C at 15 mmHg).* The identity of the product was checked by n.m.r. measurements. The 90-MHz $^1H$ n.m.r. spectrum of a $CCl_4$ solution of the compound showed, as expected, two doublets at $\delta$ 2.27 ($SCH_3$) and 3.75 p.p.m. ($OCH_3$) from $SiMe_4$ [*J*(SMe–P) 15.8, *J*(OMe–P) 15.0 Hz] with integrals in the ratio 1 : 2. Quantitative measurements gave 9.08 hydrogens per mol, using the molecular weight of the expected trimethyl phosphorodithioate in the calculation.†

*Kinetics.—Spectrophotometry.* A solution of $[Co\{S_2P(OMe)_2\}_3]$ in $CH_2Cl_2$ (1.0 cm$^3$) of an approximately known concentration (*ca.* $1 \times 10^{-3}$ mol dm$^{-3}$) was placed in one compartment of a two-compartment quartz cell (total pathlength 0.874 cm). The other section was filled with an equal volume of a $CH_2Cl_2$ solution of dppe of known concentration. A 1-cm quartz cell filled with $CH_2Cl_2$ was used as the reference. A Varian Techtron 635 recording spectrophotometer, thermostatted by circulation of water at a constant temperature (±0.1 °C), was used. The spectrum of the cobalt(III) complex was recorded, and its concentration was calculated from the absorption at 735 nm ($\varepsilon$ 400 dm$^3$ mol$^{-1}$ cm$^{-1}$). After 15—20 min the reagent cell was shaken rapidly to mix the solutions and the absorbance at 593 nm was recorded (see below).

Under pseudo-first-order conditions (*i.e.* with a sufficiently large excess of dppe) good linear plots of $\ln(A_\infty - A_t)$ against time were obtained over three or more half-lives ($A_\infty$ and $A_t$ are the absorbances at infinite time and at time *t*, respectively). The rate constants of the substitution reaction, obtained from the plots, are listed in Table 1 together with the reaction conditions. The estimated uncertainty in the pseudo-first-order rate constants was ±3%.

TABLE 1

Rate constants and reaction conditions for the substitution of a $[S_2P(OMe)_2]^-$ ligand of $[Co\{S_2P(OMe)_2\}_3]$ by dppe

| $\theta_c$ / °C | $10^3$ [Complex] / mol dm$^{-3}$ | $10^3$[dppe] / mol dm$^{-3}$ | $10^3k_1$ / min$^{-1}$ | $k_1'$ / dm$^3$ mol$^{-1}$ min$^{-1}$ |
|---|---|---|---|---|
| 17.3 | 1.13 | 11.1 | 9.9 | |
| | 0.71 | 11.2 | 9.8 | |
| | 0.83 | 18.7 | 17.4 | |
| | 0.80 | 22.4 | 19.8 | |
| | 0.86 | 31.3 | 24.9 | 0.815 (0.987) |
| 24.8 | 0.57 | 2.0 | 3.9 | |
| | 0.63 | 4.2 | 7.9 | |
| | 0.60 | 5.4 | 10.4 | |
| | 0.65 | 7.9 | 13.2 | |
| | 0.77 | 15.6 | 26.9 | |
| | 0.70 | 31.1 | 50.0 | |
| | 0.84 | 69.5 | 121.5 | 1.727 (0.998) |
| 35.4 | 0.51 | 3.7 | 12.5 | |
| | 0.62 | 9.4 | 34.0 | |
| | 0.62 | 15.1 | 50.1 | |
| | 0.60 | 18.7 | 68.7 | |
| | 0.67 | 30.3 | 114 | 3.751 (0.996) |

Values in parentheses are correlation coefficients.

*Conductance measurements.* Conductance measurements were carried out in a two-arm conductance cell (cell constant 0.31 cm$^{-1}$). The solutions containing $[Co\{S_2P(OMe)_2\}_3]$ and dppe were poured separately into the two arms and were allowed to equilibrate thermally in a thermostat. After a suitable period of time (see below) the solutions were mixed and the conductance measured with time using a Metrohm E 382 conductance bridge.

When $[Co\{S_2P(OMe)_2\}_2]$ reacts with dppe in $CH_2Cl_2$ solution the conductance increases smoothly, reaches a maximum, and then decreases, eventually reaching a very small, but finite, value. A plot of conductance against time for a typical run is shown in Figure 1. Blank experiments showed that, although the $CH_2Cl_2$ solution of $[Co\{S_2P(OMe)_2\}_3]$ was non-conducting, that of dppe had a conductance which tended to increase steadily, *i.e.* ions are formed. This may be ascribed to the formation of phosphonium chlorides by the reaction of the phosphine with $CH_2Cl_2$.[13] This reaction was not investigated further,

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

† Hydrogen-1 n.m.r. spectra were run on a Bruker HX 90 spectrometer. We thank Dr. A. M. Giuliani for recording and discussing the spectra.

[7] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254 and refs. therein.

[8] M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele, and T. A. Stephenson, *J.C.S. Dalton*, 1977, 496.

[9] V. Di Castro, L. Mattogno, C. Furlani, and A. A. G. Tomlinson, *Inorg. Chim. Acta*, 1978, **26**, L11.

[10] C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.

[11] L. L. Costanzo, I. Fragalà, S. Giuffrida, and G. Condorelli, 9th Meeting, Italian Association for Inorganic Chemistry, Padova, Italy, September 1976, paper B5.

[12] F. Tarli, personal communication.

[13] R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic Press, London, 1965, p. 131.

but allowance was made for the background conductance by simply subtracting it from that of the mixture.

Although the background conductance was not negligible, it was demonstrated that the amount of dppe involved in this side reaction was always very small. Ligand concentrations could then be taken as constant. 1,2-Bis(diphenylphosphino)ethane (254.1 mg) was dissolved in $CH_2Cl_2$ (10.0 $cm^3$) giving a concentration of $6.38 \times 10^{-2}$ mol $dm^{-3}$ and the solution was kept at 35 °C for 24 h. It was then evaporated to dryness and the residue weighed (255.6 mg). A portion of this residue (96.1 mg) was shaken with water (10 $cm^3$) and the conductance of the solution measured ($\kappa$ $1.7 \times 10^{-4}$ S). The conductance of a saturated solution of untreated dppe was also measured ($\kappa$ $1.2 \times 10^{-5}$ S). It was found that the conductance due to the ions formed *via* the side reaction was *ca.* $1.6 \times 10^{-4}$ S, which corresponds to a concentration of 1 : 1 electrolyte impurities of *ca.* $8 \times 10^{-4}$ mol $dm^{-3}$, *i.e.* only 0.1% of the starting dppe concentration.

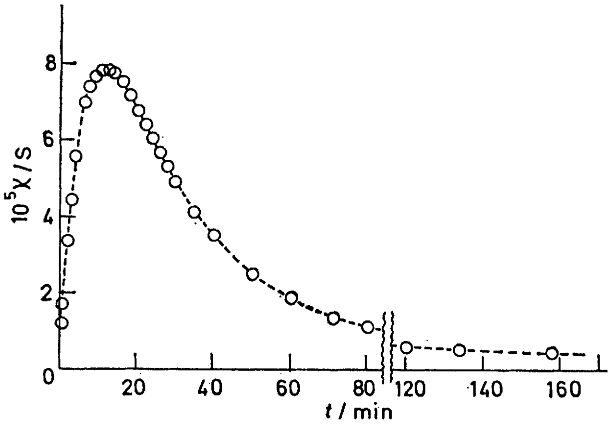


FIGURE 1 Corrected plot of conductance against time for the reaction between $[Co\{S_2P(OMe)_2\}_3]$ and dppe in $CH_2Cl_2$. $[Co\{S_2P(OMe)_2\}_3] = 6.05 \times 10^{-3}$ mol $dm^{-3}$, [dppe] $= 3.2 \times 10^{-2}$ mol $dm^{-3}$, 35.3 °C

*Catalytic effects of unknown nature.* Occasionally, some of the spectrophotometric experiments led to rate constants five to ten times higher than those expected. In correspondence with this, the conductance experiments showed a large contraction of the time required to reach the maximum.

There was no evidence for a change in the stoicheiometry of the two steps (see below), the only apparent effect being an acceleration of the first step. Recrystallisation of $[Co\{S_2P(OMe)_2\}_3]$ from $CHCl_3$, or repeated washing with methanol followed by thorough drying of the crystals *in vacuo*, was sufficient to remove this 'catalytic' effect.

Since it is known that the starting $[Co\{S_2P(OMe)_2\}_3]$ complex is light sensitive,[11] the light-induced formation of trace amounts of a catalyst was first considered. This was soon eliminated, since direct prolonged exposure (20 min) of a $CH_2Cl_2$ solution of $[Co\{S_2P(OMe)_2\}_3]$ to sunlight did not produce the expected acceleration effect on reaction (2) (see below). All the impurities which might reasonably be expected to be present in the complex and/or in the reaction solution {such as $Co^{2+}$ and $[S_2P(OMe)_2]^-$} were tested, without success. In addition, ageing of the solid complex in the dark also resulted in no systematic kinetic effect.

## RESULTS AND DISCUSSION

The overall stoicheiometry of the reaction is as in (1).

$$[Co\{S_2P(OMe)_2\}_3] + dppe \longrightarrow [Co\{S_2P(OMe)_2\}\{S_2PO(OMe)\}(dppe)] + P(OMe)_2S(SMe) \quad (1)$$

Comparison of the absorption of the related solution with the absorption coefficient of the (isolated) final cobalt(III) product (for which the above formulation has been confirmed[9,14]) indicates that reaction (1) goes virtually to completion. The presence of *OO'S*-trimethyl phosphorodithioate was demonstrated by gas-chromatographic analysis of the product solution. A solution of an authentic sample of the ester was used for comparison.* The formulation of the cobalt(III) complex formed is consistent with elemental analyses, with the fact that it is not ionic, and is strongly suggested by the formation of the *S*-methyl phosphorodithioate ester. Full details of the characterisation and the crystal structure of the dadpe analogue will be reported elsewhere.[14] The crystal-structure analysis confirms that one of the remaining $[S_2P(OMe)_2]^-$ ligands is demethylated.

*First Step of the Reaction.*—When $[Co\{S_2P(OMe)_2\}_3]$ reacts with dppe in $CH_2Cl_2$ there are marked spectral changes in the 500—800 nm region (see Figure 2). However, in the presence of a large excess of dppe, when pseudo-first-order conditions should hold, plots of $\ln(A_\infty - A_t)$ against time are generally not linear. This, together with the absence of an isosbestic point in a case where the initial and final spectra do intersect, suggests that the overall reaction is a multi-step process. Fortunately, a careful examination of the spectra shows that within a narrow range, 590 ± 20 nm, the absorption reaches a nearly constant value, whilst outside this range it is still changing appreciably. Inside this range, and under pseudo-first-order conditions, first-order plots were linear, the best linearity being achieved at 593 nm. Departure from this wavelength resulted in a progressive curvature in plots of $\ln(A_\infty - A_t)$ against time at longer times. This behaviour may be explained by assuming that only the first step of the reaction affects the spectrum at 593 nm. This wavelength is then useful for following this step. The pseudo-first-order rate constants are listed in Table 1. As shown in Figure 3, they are linearly dependent on dppe concentration.

The second-order constants were obtained by least-squares analysis of the lines in Figure 3 and are reported in the last column of Table 1. The corresponding activation parameters were $\Delta H^\ddagger = 14.3 \pm 1.0$ kcal $mol^{-1}$ and $\Delta S^\ddagger = -17 \pm 3$ cal $K^{-1}$ $mol^{-1}$.

*Stoicheiometry.* We assume the overall stoicheiometry of the first step to be as in (2). The evidence for this is:

---

* The g.c. experiments were carried out on a Carlo Erba GI instrument (column 1.80 m × 4 mm i.d.; Apiezon 1 × 100 on 100—120-mesh glass spheres; injector temperature 150 °C, column temperature 70 °C; flame-ionisation detection).

[14] V. Di Castro, P. Porta, L. Gastaldi, and A. A. G. Tomlinson, in preparation.

(*i*) the reaction occurs with the formation of ions (see Figure 1), (*ii*) the spectrum of the cobalt(III) complex

$$[Co\{S_2P(OMe)_2\}_3] + dppe \longrightarrow [Co\{S_2P(OMe)_2\}_2(dppe)]^+ + [S_2P(OMe)_2]^- \quad (2)$$

formed *via* reaction (2) is very close to that of the final product,[13] as expected for a similar chromophore in both cases.

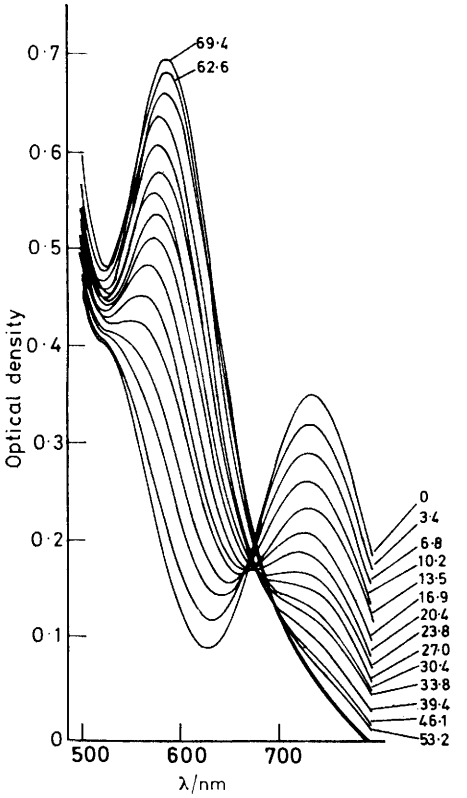


FIGURE 2 Variation in the electronic spectrum of $[Co\{S_2P(OMe)_2\}_3]$ + dppe in $CH_2Cl_2$ with time. $[Co\{S_2P(OMe)_2\}_3] = 6.05 \times 10^{-3}$ mol dm$^{-3}$, [dppe] $= 3.2 \times 10^{-2}$ mol dm$^{-3}$, 35.3 °C. The numbers refer to $t$/min

*Mechanism.* Substitution reactions on cobalt(III) substrates are known to be essentially dissociative processes.[15-17] Their rates are normally independent of the concentration of entering nucleophile and, with the possible exception of those cases where solvation effects are important, the activation entropy is positive or close to zero.[15]

The present results do not fit this picture. The rates are linearly dependent on dppe concentration and the very low $\Delta S^\ddagger$ falls in the range typical of associative substitutions, *e.g.* those on square-planar[16] and tetrahedral[17] complexes. Nevertheless, the kinetic data are consistent with the mechanism shown in (3), where the first step is, in fact, dissociative (only labile ligands shown). Under steady-state conditions,[18] the overall reaction follows pseudo-first-order kinetics with $k_1 = k'k'''[\text{dppe}]/(k'' + k'''[\text{dppe}])$. If $k'' \gg k'''[\text{dppe}]$, $k_1$ reduces to the form $k_1 = k'k'''[\text{dppe}]/k''$ and is therefore linearly dependent on the dppe concentration, as observed. Moreover, although the entropy change for formation of the five-co-ordinate intermediate should be positive (or near to zero), the substitution step, being associative, may well predominate, yielding an overall negative activation entropy. Thus, the observed low value of $\Delta S^\ddagger$ then refers essentially to an associative process. [*N.B.* The formula corresponding to a five-co-ordinate intermediate in (3) is not to be taken as a structure.]

In addition to this possibility, two alternative mechanisms may be proposed, each of which fits the main kinetic features of reaction (2). The first involves attack on the cobalt(III) centre by the dppe, with release of a $[S_2P(OMe)_2]^-$ anion. This mechanism seems unlikely since associative nucleophilic substitutions on Co$^{III}$ are rare.[19] Tetrahedral phosphorus is also known to undergo substitutions by nucleophilic attack, with the formation of trigonal-bipyramidal intermediates.[20] Most of the activation entropies for an extensive series of tetrahedral phosphorus compounds are close to $-20$ cal K$^{-1}$ mol$^{-1}$,[13] *i.e.* the value observed experimentally for reaction (2). Thus, attack of dppe on the phosphorus of a co-ordinated $[S_2P(OMe)_2]^-$ ligand, with consequent distortion of the S–P–S angle * and weaken-

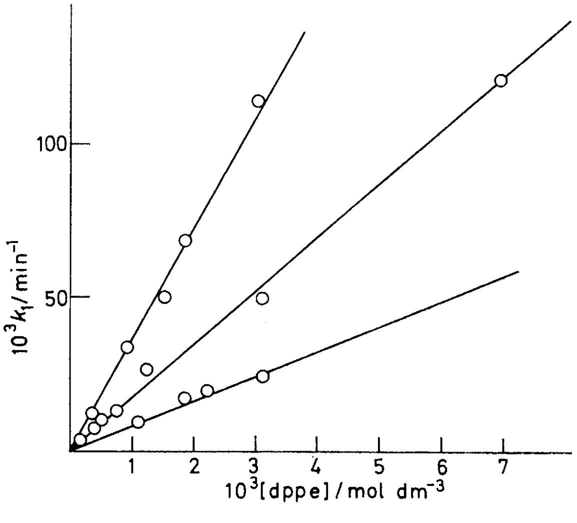


FIGURE 3 Pseudo-first-order rate constants for the reaction between $[Co\{S_2P(OMe)_2\}_3]$ and dppe in $CH_2Cl_2$ as a function of [dppe]

---

[15] J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.

[16] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965.

[17] M. L. Tobe, 'Inorganic Reaction Mechanisms,' Nelson, London, 1972, p. 39.

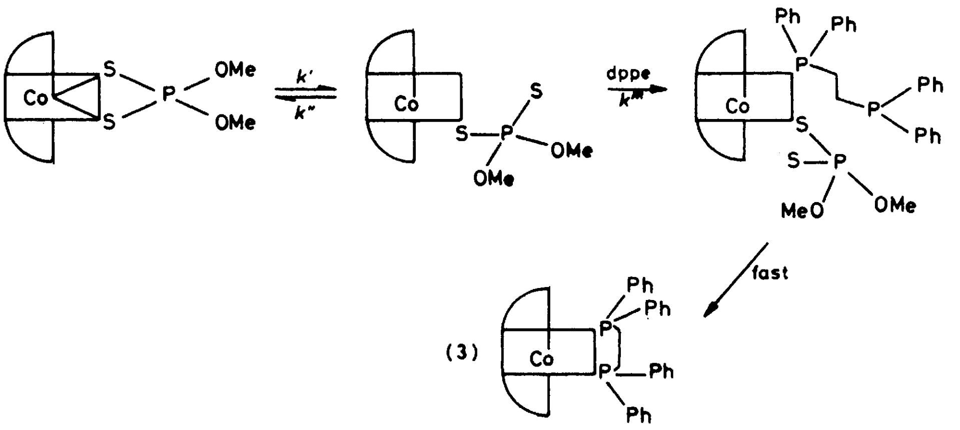
* This angle will tend to 90° if one sulphur atom occupies an axial position, or to 120° if both lie in the equatorial plane, for the limiting case of a regular trigonal bipyramid.

[18] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 195.

[19] Ref. 15, p. 90.

[20] L. Almasi, 'The Sulphur–Phosphorus Bond,' in 'Sulphur in Organic and Inorganic Chemistry,' vol. 1, ed. A. Senning, Marcel Dekker, New York, 1972.

ing of the Co–S bond, is also conceivable. Since there was no evidence for the formation of any compound containing a P–P bond, the phosphine–phosphorodithioate interaction should be relatively weak and completely reversible. A clear-cut choice between these mechanisms cannot be made, as yet.



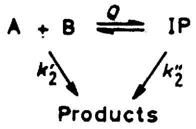
(3)

*Second Step of the Reaction.*—Given the known overall reaction (1) and that suggested above for (2), the second step must involve demethylation of a co-ordinated $[S_2P(OMe)_2]^-$ ligand by a free $[S_2P(OMe)_2]^-$ ion, *i.e.* as in (4). In agreement with this, the conductance of the

$$[Co\{S_2P(OMe)_2\}_2(dppe)]^+ + [S_2P(OMe)_2]^- \longrightarrow [Co\{S_2P(OMe)_2\}\{S_2PO(OMe)\}(dppe)] + P(OMe)_2S(SMe) \quad (4)$$

reaction solution showed a maximum when the production of ions *via* reaction (2) proceeds at the same rate as their consumption *via* reaction (3). It then decreases, eventually reaching a very low, and nearly constant, value (Figure 1).

Now, it is likely that $[Co\{S_2P(OMe)_2\}_2(dppe)]^+$ and $[S_2P(OMe)_2]^-$ are partially associated in $CH_2Cl_2$, to give an ion pair. The simple reaction mechanism in (5) may



(5)

then be formulated, where A is $[Co\{S_2P(OMe)_2\}_2(dppe)]^+$, B is $[S_2P(OMe)_2]^-$, and IP represents the corresponding ion pair. Since A is produced *via* reaction (2) at the rate $k_1'[Co\{S_2P(OMe)_2\}_3][dppe]$ ($k_1' = k_1/[dppe]$) and [A] must always be equal to [B], it can readily be shown that (6) is applicable. The conductance, $\kappa$, of the

$$(d[A]/dt)(1 + 2Q[A]) = k_1'[dppe][Co\{S_2P(OMe)_2\}_3] - (k_2' + k_2''Q)[A]^2 \quad (6)$$

solution should be proportional to the concentration of *free* A, according to equation (7) where $c$ is the cell

$$[A] = 10^3 c\kappa/\Lambda \quad (7)$$

constant (in $cm^{-1}$) and $\Lambda$ the sum of the molar conductances of the ions A and B. Equation (6) then becomes (8) where $a = 1\,000\ c/\Lambda$.

At the conductance maximum, $d\kappa/dt = 0$ and, given that under pseudo-first-order conditions $[Co\{S_2P(OMe)_2\}_3]_{max.} = [Co\{S_2P(OMe)_2\}_3]_0 \exp(-k_1'[dppe]t_{max.})$, after straightforward rearrangements we obtain (9)

$$a(d\kappa/dt)(1 + 2Qa\kappa) = k_1'[dppe][Co\{S_2P(OMe)_2\}_3] - (k_2' + k_2''Q)a^2\kappa^2 \quad (8)$$

$$\ln[dppe][Co\{S_2P(OMe)_2\}_3]_0 - k_1'[dppe]t_{max.} = \ln(k_2a^2/k') + 2\ln \kappa_{max.} \quad (9)$$

where $k_2 = k_2' + k_2''Q$. The left-hand side of equation (9) should thus be linearly dependent on $\ln \kappa_{max.}$, with a gradient of two. Table 2 lists values of $t_{max.}$ and $\kappa_{max.}$

TABLE 2

Maximum conductances for some reactant solutions at 35.3 °C

| $10^3[Co\{S_2P(OMe)_2\}_3]_0$ / mol dm$^{-3}$ | $10^2$[dppe] / mol dm$^{-3}$ | $t_{max.}$ / min | $10^5\kappa_{max.}$ / S |
|---|---|---|---|
| 0.40 | 3.16 | 11.6 | 7.90 |
| 0.51 | 3.16 | 12.7 | 9.27 |
| 0.53 | 3.16 | 11.5 | 11.7 |
| 1.08 | 3.16 | 10.7 | 14.0 |
| 1.08 | 3.16 | 11.3 | 13.9 |
| 2.04 | 3.16 | 10.2 | 22.3 |
| 2.30 | 3.16 | 9.8 | 22.8 |
| 4.13 | 3.16 | 9.5 | 34.7 |
| 4.16 | 3.16 | 8.4 | 35.6 |
| 4.19 | 3.23 | 9.0 | 32.0 |
| 0.64 | 6.39 | 7.5 | 10.0 |
| 1.15 | 6.33 | 7.0 | 16.9 |
| 2.22 | 6.02 | 6.7 | 23.1 |
| 4.08 | 6.35 | 6.0 | 36.6 |

$k_1' = 3.75$ dm$^3$ mol$^{-1}$ min$^{-1}$.

for a series of reactant solutions at 35.3 °C. Figure 4 shows a plot of equation (9), which is, indeed, linear and has the expected gradient (1.90).

At this stage attempts were made to evaluate the rate constant $k_2$. When the first step has virtually gone to completion the total concentration of $[Co\{S_2P(OMe)_2\}_2(dppe)]^+$ decreases according to the rate equation (10). Since $d[A]_t = d[A](1 + 2Q[A])$, equation (11) follows which on integration gives (12). Recalling equation (7), we obtain (13). Since the variation in the logarithmic term in equation (13) is small with respect to $\kappa^{-1}$, a plot of $\kappa^{-1}$ against $t$ should approach a straight line, of gradient $k_2a$.

$$d[A]_t/dt = -k_2[A]^2 \qquad (10)$$

$$d[A]/[A]^2 + 2Qd[A]/[A] = -k_2dt \qquad (11)$$

$$-[A]^{-1} + 2Q \ln [A] = -k_2t + \text{constant} \qquad (12)$$

$$\kappa^{-1} - 2Qa \ln \kappa = +k_2at + \text{constant} \qquad (13)$$

It is difficult to evaluate $a$ since the molar conductances of the ions A and B in $CH_2Cl_2$ are not known. However, even if these parameters were known, it would still be impossible to determine $k_2$ because the plot is not as expected, *i.e.* the limiting conductance did not go to zero at $t_\infty$ (after applying the corrections mentioned in the Experimental section). Presumably, other ion-producing side reactions interfere towards the end of the second stage (*i.e.* at >90% completion of reaction), which is precisely the crucial stage for evaluating $k_2$. The only way of obtaining a reliable estimate for $a$ would be to isolate reaction (4), thus avoiding interference from reaction (2), and also measure the conductances of ions A and B in $CH_2Cl_2$. Despite all attempts (precipitation with $[AsPh_4]^+$, chromatography), the intermediate complex $[Co\{S_2P(OMe)_2\}_2(dppe)]^+$ could not be separated.

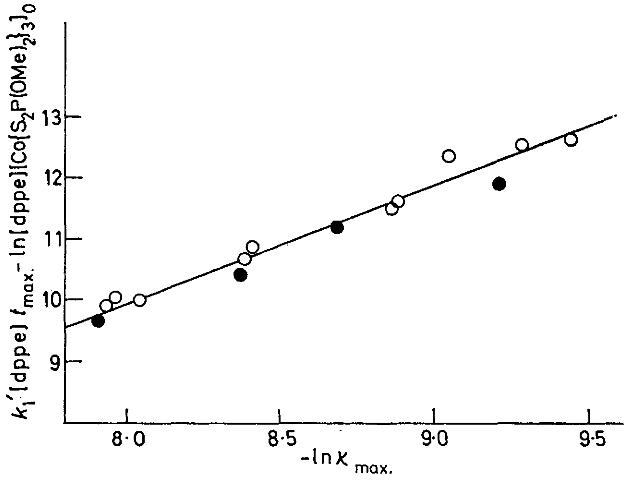
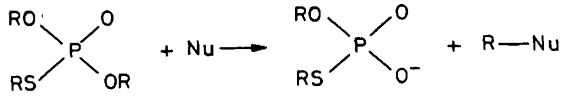
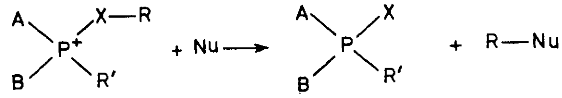


FIGURE 4 Left-hand side of equation (9) plotted against ln $\kappa_{max.}$ for varying initial $[Co\{S_2P(OMe)_2\}_3]$ at 35.3 ± 0.1 °C: [dppe] = $3 \times 10^{-2}$ (○) or $6 \times 10^{-2}$ mol dm$^{-3}$ (●)



(14)



(15)

However, it is well known that alkyl phosphorothioates are alkylating agents towards many nucleophiles [21] [see equation (14)]. Further, the second step of the Arbuzov rearrangement implies transfer to a nucleophile of an alkyl group of an alkoxyphosphonium ion [22] [see equation (15)]. Both reactions occur *via* nucleophilic attack on the P–O–C or P–X–C carbon atom of the transferred alkyl group, which has a positive charge. By reducing the electron density on the phosphorus atom of the dimethyl phosphorodithioate ion, co-ordination to a metal ion should also make the P–O–C carbon atoms more positive, thus favouring a nucleophilic displacement of the type shown above $\{Nu = [S_2P(OMe)_2]^-\}$.

[7/1573 *Received*, *5th September*, 1977]

---

[21] K. Pilgrim, *Tetrahedron*, 1966, **22**, 1241.

[22] W. Gerrard and W. J. Green, *J. Chem. Soc.*, 1951, 2550; G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, 1964, **18**, 38; G. Aksnes and R. Eriksen, *ibid.*, 1966, **20**, 2463; ref. 9, p. 135.