

acceptor. The presence of the ring nitrogen atoms, the length of the conjugated pathway, and the fact that the ligand is attached at two sites to the metal would justify such a viewpoint. The amount of electron transfer would increase with decreasing effective nuclear charge on the metal as the group X becomes less electronegative. It is significant that k^2 , J , and B , which are all quite independent parameters, exhibit parallel trends in this respect (the B value for the thiocyanate complex being an exception).⁴⁹ The pyrazine series differs in its microstoichiometry (CoNX_3 rather than CoN_2X_2) from the phthalazine series. This ligand is known to be a good electron acceptor⁵¹ and can act as an electron sink to allow a greater cobalt-halogen covalent interaction. R exceeds unity in this series but not in the phthalazine series because of the greater number of heavy atoms surrounding the cobalt atom. It is significant that in the CoX_4^{2-} series R is

(51) A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, **4**, 810 (1965).

less than unity³⁷ ($k^2 < 1$)⁴¹ presumably because in the absence of a ligand such as pyrazine to act as an electron sink, the cobalt-halogen interaction is decreased.

The above discussion is speculative and further cobalt systems are under study to corroborate the approach. If K and R can be independently determined and their meaning clarified, they may prove to be most powerful probes into our understanding of transition metal chemistry.

Acknowledgments.—This work, carried out in part at York University and in part at the University of Texas, was supported by the Robert A. Welch Foundation, the U. S. Atomic Energy Commission, the National Science Foundation, and the National Research Council (Ottawa, Canada). We are also indebted to J. C. Donini for computer programming assistance, B. S. Ramaswamy for experimental assistance, and B. R. Hollebone for useful discussions.

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Methanolysis of Tetrakis(phosphorus trichloride)nickel(0)¹

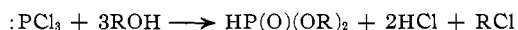
By DAVID F. BACHMAN, EDWIN D. STEVENS, THOMAS A. LANE, AND JOHN T. YOKE*

Received May 21, 1971

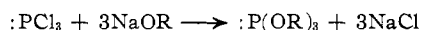
Methanolysis of $[\text{Ni}(\text{PCl}_2)_4]$ in hydrocarbon solvents is a slow heterogeneous oxidation-reduction process. Products typical of the methanolysis of uncoordinated phosphorus trichloride are formed; these include methyl chloride and dimethyl hydrogen phosphonate. The oxidation product is $[\text{Ni}(\text{CH}_3\text{OH})_6]^{2+}$. No hydrogen is formed, and the initial reduction product is methyl hypophosphite which decomposes to phosphine and other products. A hydridonickel intermediate is suggested by a transient ir absorption at 1610 cm^{-1} (shifted to 1135 cm^{-1} on deuteration), but no high-field nmr signal could be observed. When methoxide ion is made the nucleophile, the simple reaction product $[\text{Ni}(\text{P}(\text{OCH}_3)_3)_4]$ is obtained in high yield. Treatment of this with hydrogen chloride leads to slow hydrogen formation.

Introduction

Alcoholysis of phosphorus trichloride² results in an Arbuzov-type rearrangement, involving the lone pair of electrons and a change in the coordination number of phosphorus



The tertiary ester $:\text{P}(\text{OR})_3$ is commonly prepared by having a tertiary amine present to bind hydrogen chloride or may be obtained using sodium alkoxide in an inert medium



In tetrakis(phosphorus trichloride)nickel(0), $[\text{Ni}(\text{PCl}_2)_4]$, the coordination number of phosphorus is already four and the lone pair is involved in the coordinate bond. Smith³ reported that this compound "dissolves in alcohols but decomposition with the formation of green solutions is quite rapid."

A century ago,⁴ the methanolysis of phosphorus trichloride coordinated to platinum(II) and palladium(II) chlorides was reported to give the corresponding complexes of trimethyl phosphite. Similar synthesis of the trimethyl phosphite complex has been reported with gold(I)⁵ and copper(I).⁶ Since an Arbuzov rearrangement about phosphorus did not occur in those cases, retention of the metal-phosphorus bond during the reaction is implied.

We have studied the reaction of $[\text{Ni}(\text{PCl}_2)_4]$ with methanol and with methoxide ion in hydrocarbon solvents in some detail. Kruck and Höfler have reported⁷ the preparation of tetrakis(trimethyl phosphite)nickel(0) by the reaction of sodium methoxide with the analogous phosphorus trifluoride complex.

Experimental Section

Materials.—Tetrakis(phosphorus trichloride)nickel(0)³ was recrystallized from pentane or hexane immediately prior to use. Matheson nickel carbonyl and hydrogen chloride were used

(1) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; see Abstract No. INOR 97.

(2) G. M. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, Chapter 8; J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience, New York, N. Y., 1958, pp 372-373.

(3) W. C. Smith, *Inorg. Syn.*, **6**, 201 (1960).

(4) P. Schutzenberger, *C. R. Acad. Sci.*, **70**, 1414 (1870); *Bull. Soc. Chim. Fr.*, **14**, 178 (1870); **18**, 101 (1872).

(5) M. Levi-Malvano, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **17**, 847 (1909).

(6) T. L. Davis and P. Ehrlich, *J. Amer. Chem. Soc.*, **58**, 2151 (1936).

(7) T. Kruck and M. Höfler, *Angew. Chem.*, **79**, 582 (1967).

directly from the cylinders. Hydrocarbon solvents were dried over sodium. Methanol (reagent grade) and deuteriomethanol, CH₃OD (99% isotopic purity, Diaprep, Inc.), were distilled from magnesium. Methyl hypophosphite was prepared from hypophosphorous acid and trimethyl orthoformate⁸ and was purified by distillation in the high-vacuum line from a 5° trap to a -196° trap. Ir (CCl₄) (cm⁻¹): 2959, 2865, 1458 (C—H), 2392 (P—H), 1245 (P=O), 1011 (P—O—C). Nmr (neat): δ 7.08 (d, *J* = 573 Hz, PH), 3.83 (d, *J* = 13 Hz, POCH₃). Nickel(II) chloride⁹ was pumped on overnight in the vacuum line. Materials were transferred in a glove box under prepurified nitrogen. Carbon, hydrogen, and phosphorus microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Instrumental Methods.—Spectra were obtained with Beckman IR-8 and DK-2 and Coleman Hitachi 124 spectrophotometers. Proton nmr spectra were obtained with Varian A-60 and HA-100 spectrometers, and ³¹P nmr spectra were obtained at 40.5 MHz with the latter instrument. A temperature-programmed F and M Model 700 gas chromatograph was used with 20% Reoplex 400 on Chromosorb W columns.

Methanolysis Reactions.—Typically, about 200 ml of degassed hexane was condensed at -196° onto a weighed quantity of tetrakis(phosphorus trichloride)nickel(0) (about 10 mmol) in a 500-ml flask attached to the vacuum line. The mixture was then allowed to warm and stirred magnetically to give a light yellow solution. This was refrozen and methanol was condensed from a tared vacuum-line weighing bulb into the flask to give the desired reactant ratio. The mixture was allowed to warm to room temperature over the course of several hours, with stirring. Typically, a yellow solid suspension formed quickly. In a few minutes this changed to two liquid layers. The brown lower layer became red (30 min), olive green (several hours), and clear lime green (complete reaction, ca. 20 hr). Meanwhile, the top layer changed from yellow-green to colorless.

Reaction with Sodium Methoxide.—Sodium methoxide, 0.14 mol, in 50 ml of methanol, was added dropwise with stirring to a solution of 0.010 mol of tetrakis(phosphorus trichloride)nickel(0) in 250 ml of light petroleum ether (bp 30–60°) at 0° under nitrogen. The reaction mixture was refluxed for 30 min and filtered hot through a medium glass frit under nitrogen. The sodium chloride residue was washed three times with 20-ml portions of boiling petroleum ether (bp 30–60°). The volume of the combined filtrate and washings was decreased under a reduced pressure of nitrogen, to give a first crop of crystals. A second crop was obtained by cooling the remaining solution to -78°. The yellow crude product was recrystallized from petroleum ether (bp 30–60°) three times until colorless; yield 61%. Nmr (benzene): δ 3.60 (d, *J*_{POCH} = 10.5 Hz). *Anal.* Calcd for Ni(P(OCH₃)₃)₄: C, 25.97; H, 6.54; Ni, 10.58. Found: C, 26.24; H, 6.46; Ni, 10.24.

Reaction of Tetrakis(trimethyl phosphite)nickel(0) with Hydrogen Chloride.—A solution of 6 mmol of freshly prepared Ni(P(OCH₃)₃)₄ in 100 ml of hexane in a flask on the vacuum line at 0° readily absorbed hydrogen chloride gas (ca. 30 mmol) and turned yellow. A yellow precipitate formed in a few minutes. After 30 min this began to change to an olive green rubbery material from which bubbles of gas were evolved. After several hours a green solid remained and a large amount of noncondensable gas (hydrogen) had been formed.

Results

Final Reaction Products.—The methanolysis reaction was often allowed to proceed to completion (1–3 days) with an excess of methanol present (23.2–65.8 mol of methanol/mol of nickel(0) complex). In all cases, when the reaction mixtures were quenched to -196°, the pressure fell to zero; thus no hydrogen was formed. The components of the reaction mixtures were separated in a variety of ways. In addition to hexane and the excess of methanol, they were found to be [Ni(CH₃OH)₆]²⁺ as the chloride and the phosphite, methyl chloride, phosphine, dimethyl hydrogen phosphonate, and a mixture of unidentified organophosphorus compounds.

Separation and Analysis.—In certain cases, the highly volatile reaction products passing -78° traps were isolated from the bulk of solvent and other reaction components. From 6 to 10 mol of gas/mol of nickel complex was obtained, but quantitative separation of these highly volatile materials from their dilute solutions in hexane and methanol would not be expected. Only traces of hydrogen chloride were present (gas absorbed by sodium hydroxide). The gas mixture was proved to consist of methyl chloride and phosphine by vapor pressure (25 Torr at -130°, 40 Torr at -112°) and infrared spectral measurements (700–750 cm⁻¹, C—Cl; 2299 cm⁻¹, P—H; 2874 and 2959 cm⁻¹, C—H). These components reacted slowly at room temperature to give a solid deposit on the walls of the gas storage bulb.

In other cases, these highly volatile products and the hexane were stripped off in the vacuum line and discarded. Analysis of the remaining green methanol solution by gas chromatography showed the presence of dimethyl hydrogen phosphonate and of a complex mixture of components with similar and longer retention times. However, dimethyl methylphosphonate, the product of Arbuzov rearrangement of trimethyl phosphite, was absent. The green methanol solution was transferred to a volumetric flask in the drybox for quantitative analysis. Dimethyl hydrogen phosphonate was determined chromatographically by peak area integration relative to a 1.00% diglyme internal standard using a working curve based on standard solutions of an authentic sample. It was found that 30.1% of the phosphorus in the original nickel(0) complex appeared in this form.

The uv-visible spectrum of the green solution was exactly matched by that of a solution of anhydrous nickel(II) chloride in methanol, except that the former also contained an absorption peak at 32.3 kK. The spectrum was typical of octahedrally coordinated d⁸ nickel(II), with ³A_{2g} → ³T_{1g}(P), ν₃, at 24.3 kK (ε 8.39); ³A_{2g} → ³T_{1g}(F), ν₂, at 13.2 (sh) (ε 3.88), 14.5 kK. The following parameters were evaluated from literature tables:¹⁰ *Dq/B* = 0.862, *B* = 0.926 kK, 10*Dq* = 7.95 kK.¹¹ The ³A_{2g} → ³T_{2g} transition, ν₁, would then be expected at 1.26 μ in the near-infrared. Severe interference by a methanol absorption in this region was encountered, but a partly resolved peak at 1.23 μ was observed. Nickel was determined both by EDTA titration and spectrophotometry at 24.3 kK. Both methods indicated quantitative conversion of Ni(PCI₃)₄ to nickel(II), existing as [Ni(CH₃OH)₆]²⁺ in solution.

When all volatile material was stripped from the reaction mixture in the vacuum line, a green solid residue remained which turned yellow on prolonged pumping. *Anal.* Found: Ni, 19.20; Cl, 5.22; P, 26.88; C, 4.92; H, 3.07. This nickel(II) salt contained, therefore, only about one-quarter of the anionic charge as chloride ion and the rest as a phosphite-type anion with a small organic content. The residue was dissolved in the minimum amount of aqueous methanol, the solution was passed through a Dowex 50W-X4 (hydrogen ion) resin column, and the eluate was concentrated by evaporation. The ³¹P nmr spectrum

(10) A. B. P. Lever, *J. Chem. Educ.*, **45**, 711 (1968).

(11) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 2579 (1969), gave *B* = 0.949 kK and 10*Dq* = 8.37 kK without any experimental details.

(8) S. J. Fitch, *J. Amer. Chem. Soc.*, **86**, 61 (1964).

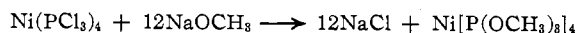
(9) A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).

consisted of a doublet, -5.62 ppm from H_3PO_4 , $J_{\text{P-H}}$ 704 Hz, characteristic of phosphorous acid.¹²

Intermediate Reaction Products.—In some experiments, in which an excess of methanol was again used, samples were removed at various times from the reaction mixture by syringe under nitrogen. The ir spectra showed a strong sharp peak at 1610 cm^{-1} , which developed during about the first 0.5 hr and then slowly disappeared. This peak was shifted to 1135 cm^{-1} when CH_3OD was used. The proton nmr spectra were also obtained, especially in the high-field region up to τ 40. No hydridic signal could be observed.

In other experiments, in which a deficiency of methanol was used (12.1–14.4 mol/mol of nickel(0) complex), the reaction was terminated after 8–12 hr by removal of all volatile materials from the reaction flask in the vacuum line. The nearly black nonvolatile residue was found to contain: Ni, 13.31; Cl, 53.09; P, 20.67; C, 2.64; H, 1.46. (Subsequent lengthy treatment of this with an excess of methanol and evaporation gave an orange residue. *Anal.* Found: Ni, 22.34; Cl, 18.88; P, 17.79; C, 9.27; H, 3.58. This great change demonstrated clearly that the initial degree of methanolysis was very incomplete.) Evidence was found for the presence of the unstable intermediate methyl hypophosphite in the final portion of the material volatilized. This colorless liquid fraction was isolated separately in a trap. In one case it decomposed on standing overnight at room temperature, to give a gas which was partly noncondensable at -196° and copious amounts of a yellow solid. In another case, this fraction was removed and stored at -20° prior to nmr studies. The ^{31}P nmr spectrum was complex and showed peaks in addition to those of dimethyl hydrogen phosphonate. In the proton spectrum, the phosphonate signal¹³ was cleanly resolved from another doublet at δ 7.05, in good agreement with our authentic methyl hypophosphite spectrum (except that, for reasons that are not understood, the apparent coupling constant was lower, $J_{\text{P-H}}$ 514 Hz). In addition, the methoxy resonance of the hypophosphite was partly resolved.

Reaction with Sodium Methoxide.—This reaction showed totally different behavior, with the product tetrakis(trimethyl phosphite)nickel(0) being obtained according to the equation

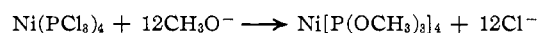


Discussion

Although tetrakis(trimethyl phosphite)nickel(0) was obtained in good yield by the treatment of tetrakis(phosphorus trichloride)nickel(0) with sodium methoxide, this known compound would normally be synthesized from more readily available reagents, nickel(II) halides and trimethyl phosphite.¹⁴ However, it is of interest to consider the possible mechanism of the sodium methoxide reaction in relation to that of the more complicated methanolysis reaction.

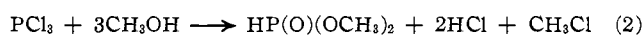
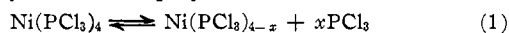
For the sodium methoxide reaction, a dissociation mechanism, $\text{Ni}(\text{PCl}_2)_4 \rightleftharpoons \text{Ni}(\text{PCl}_2)_3 + \text{PCl}_2$, would be in accord with the known formation of the tertiary phosphite ester with methoxide ($\text{PCl}_2 + 3\text{CH}_3\text{O}^- \rightarrow$

$\text{P}(\text{OCH}_3)_3 + 3\text{Cl}^-$) but would require that the free phosphite return with high efficiency to the coordination sphere of the nickel at each of four stages of dissociation, since $\text{Ni}[\text{P}(\text{OCH}_3)_3]_4$ was formed in high yield (over 60% after extensive purification). Twelve steps of direct substitution on phosphorus remaining coordinated to nickel



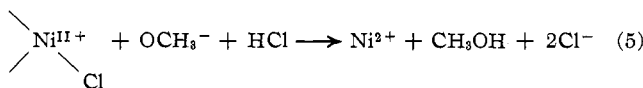
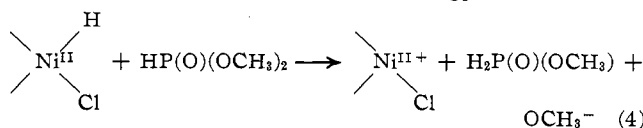
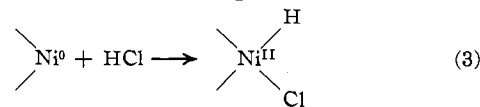
would more simply account for the observed results. Compounds of the type $\text{Ni}[\text{P}(\text{OCH}_3)_x\text{Cl}_{3-x}]_4$, which would be intermediates in such a process, have previously been prepared.¹⁵

A dissociation mechanism is clearly indicated for the heterogeneous reaction of methanol itself with tetrakis(phosphorus trichloride)nickel(0). Even though this compound shows a monomeric molecular weight in benzene,¹⁶ occurrence of a slight reversible dissociation has been demonstrated by halophosphine ligand exchange studies¹⁷ as well as by the effect of excess PCl_3 on the catalysis of olefin polymerization.¹⁸



While the solubility of methanol in hexane is limited, we are working within the solubility limit here. The separation of the reaction mixture into two phases is presumably due to the formation of dimethyl hydrogen phosphonate, which is known to be insoluble in hexane.

After formation of a highly reactive coordinatively unsaturated nickel(0) species, oxidation-reduction occurs to give nickel(II) and methyl hypophosphite. The latter is known⁸ to disproportionate readily to phosphine and a mixture of unidentified organophosphorus compounds. A reasonable mechanism for the oxidation-reduction would be by oxidative addition of hydrogen chloride (or nascent hydrogen), followed by hydride transfer to dimethyl hydrogen phosphonate with displacement of methoxide, *e.g.*



The ir evidence, development and decay of an absorption at 1610 cm^{-1} (shifted to 1135 cm^{-1} when CH_3OD is used), indicates some sort of hydrogen-containing intermediate. It is, however, mysterious that no hydridic nmr spectrum could be obtained and that the ir frequency observed is very different from the 1800–2000- cm^{-1} value expected for a Ni–H species.^{19–23}

(15) P. Cassoux, *et al.*, *J. Chim. Phys.*, **64**, 1813 (1967).

(16) J. W. Irvine and G. Wilkinson, *Science*, **113**, 742 (1951).

(17) R. J. Clark, P. I. Hoberman, and E. O. Brim, *J. Inorg. Nucl. Chem.*, **27**, 2109 (1965).

(18) J. R. Leto and M. F. Leto, *J. Amer. Chem. Soc.*, **83**, 2944 (1961).

(19) E. H. Brooks and F. Glockling, *J. Chem. Soc. A*, 1030 (1967).

(20) K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **8**, 519 (1969).

(21) K. Jonas and G. Wilke, *ibid.*, **9**, 312 (1970).

(22) R. A. Schunn, *Inorg. Chem.*, **9**, 394 (1970).

(23) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 4217 (1970).

(12) M. M. Crutchfield, *et al.*, " ^{31}P Nuclear Magnetic Resonance," Interscience, New York, N. Y., 1967, p 290.

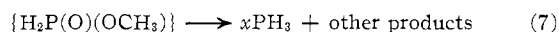
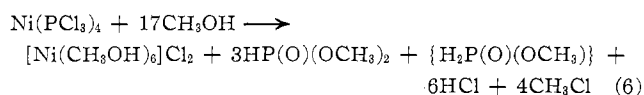
(13) L. J. Goodell and J. T. Yoke, *Can. J. Chem.*, **47**, 2461 (1969).

(14) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, **3**, 1062 (1964).

Conceivably, this is due to some special coordinate geometry; thus Jonas and Wilke²¹ found no Ni-H absorptions in the usual region for hydrido-bridged binuclear nickel complexes, and an unusual example of an Ir-H stretch at 1634 cm⁻¹ has been reported.²⁴

A nondissociative mechanism involving formation of Ni(P(OCH₃)₃)₄ and its subsequent reaction with hydrogen chloride can be ruled out, since we find that these compounds react to form hydrogen gas (*cf.* ref 23, 25).

A summation of the methanolysis and oxidation-reduction processes is represented by the equations



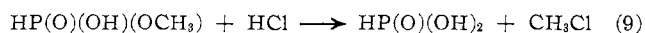
Accompanying these steps is the known process²⁶ of cleavage of the organophosphorus esters by hydrogen chloride, *e.g.*



(24) L. Malatesta, M. Angoletta, and G. Caglio, *Proc. Int. Conf. Coord. Chem.*, 8th, 1964, 210 (1964).

(25) W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, Jr., *Inorg. Chem.*, 9, 392 (1970).

(26) W. Gerrard, *J. Chem. Soc.*, 85 (1944).



Thus, the analytical result in one experiment that 30.1% of the original phosphorus appeared in the form of HP(O)(OCH₃)₂ is fortuitous, depending on the particular extent of ester cleavage. Similarly, the hydrogen chloride and methyl chloride balance of eq 6 is greatly changed by eq 8 and 9. It is also apparent why, after evaporation of the reaction mixture to dryness, the nonvolatile residue is a mixture of nickel(II) salts, chloride and phosphite with a small organic content.

In conclusion, when the donor atom changes from phosphorus to oxygen during methanolysis in this system, spontaneous oxidation of nickel(0) occurs, with reduction of part of the organophosphorus ester. This is in interesting contrast to the nickel(II)-trialkyl phosphite system studied by Vinal and Reynolds.¹⁴ There, with phosphorus as the donor atom, spontaneous reduction of nickel(II) occurs, with oxidation of part of the organophosphorus ester.

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Complexes with Six-Membered Chelate Rings. IV. Preparation of Some Complexes of 1,3-Diaminopropan-2-ol and 2-Chloropropane-1,3-diamine with Platinum and Palladium

By T. G. APPLETON AND J. R. HALL*¹

Received March 1, 1971

Preparations are reported for the complexes M(tnOH)Cl₂, M(tnCl)X₂, Pt(diamine)(NH₃)₂²⁺, M(diamine)₂²⁺, *trans*'-Pt(diamine)Cl₂(OH)⁺, Pt(diamine)Cl₄, *trans*'-[Pt(tnOH)(NH₃)₂Cl₂]₂Cl₂, and *trans*-[Pt(tnOH)₂Cl₂]₂Cl₂, where M = Pt or Pd, X = Cl or Br, and diamine = 1,3-diaminopropan-2-ol (tnOH) or 2-chloropropane-1,3-diamine (tnCl). Some complexes, M(tnCl)X₂, show an unusual polymorphism.

Introduction

In previous papers we have described the preparation² and pmr spectra^{3,4a} of some complexes of platinum and palladium with trimethylenediamine (propane-1,3-diamine, tn) and some methyl-substituted derivatives. This work has now been extended to the hydroxy- and chloro-substituted trimethylenediamines 1,3-diaminopropan-2-ol (NH₂CH₂CHOHCH₂NH₂, tnOH) and 2-chloropropane-1,3-diamine (NH₂CH₂CHClCH₂NH₂, tnCl), respectively. This paper describes the preparation of some complexes of these ligands and the following paper^{4b} describes their pmr and infrared spectra. A few complexes of the ligand 2-bromopropane-1,3-diamine (tnBr) have also been prepared for comparison.

(1) Address correspondence to this author.

(2) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 9, 1800 (1970).

(3) T. G. Appleton and J. R. Hall, *ibid.*, 9, 1807 (1970).

(4) (a) Part III: T. G. Appleton and J. R. Hall, *ibid.*, 10, 1717 (1971); (b) part V: T. G. Appleton and J. R. Hall, *ibid.*, 11, 117 (1972).

Experimental Section

Ligands. 1,3-Diaminopropan-2-ol.—This was obtained as a highly deliquescent, pale yellow solid from Koch-Light. Its dihydrochloride, a white solid, was prepared in the usual way² (some tar was always formed when the diamine was neutralized, but this could be removed by boiling aqueous solutions with charcoal). *Anal.* Calcd for (tnOH)(HCl)₂, C₃H₁₂Cl₂N₂O: C, 22.1; H, 7.4; N, 17.2; Cl, 43.5. Found: C, 22.1; H, 7.7; N, 17.2; Cl, 43.5.

2-Chloropropane-1,3-diamine.—Approximately 13.6 g of tnOH was mixed in a flask with 44.8 g of phthalic anhydride (molar ratio 1:2). The flask was fitted with an air condenser and heated in a fume hood, at first gently and then more strongly, as the whole mass melted and became brown. The solid obtained on cooling was extracted from the flask with hot chloroform and the solution was evaporated to dryness. After two recrystallizations from glacial acetic acid, followed by recrystallization from a large volume of 95% ethanol, 32.6 g of pure 2-hydroxypropane-1,3-diphthalimide was obtained in long silky crystals (50.6% based on tnOH). When the product is merely being used as a preparative intermediate, a single recrystallization from acetic acid suffices.