

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA

## The Reactions of Diphosphorus Tetrachloride with Nickel Carbonyl and Boron Tribromide

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Diphosphorus tetrachloride displaces carbon monoxide from nickel carbonyl at 0°. With large excesses of P<sub>2</sub>Cl<sub>4</sub>, the P<sub>2</sub>Cl<sub>4</sub> reacts as a monofunctional base to form Ni(CO)<sub>2</sub>(P<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub> and probably Ni(CO)(P<sub>2</sub>Cl<sub>4</sub>)<sub>3</sub> and Ni(P<sub>2</sub>Cl<sub>4</sub>)<sub>4</sub>. With large excesses of nickel carbonyl, the P<sub>2</sub>Cl<sub>4</sub> reacts as a difunctional base to form (CO)<sub>3</sub>NiP<sub>2</sub>Cl<sub>4</sub>Ni(CO)<sub>3</sub>. With intermediate ratios of P<sub>2</sub>Cl<sub>4</sub> to Ni(CO)<sub>4</sub>, polymeric compounds containing both mono- and difunctional P<sub>2</sub>Cl<sub>4</sub> groups are formed. In reactions with nickel carbonyl, P<sub>2</sub>Cl<sub>4</sub> is a stronger base than PCl<sub>3</sub>. Diphosphorus tetrachloride decomposes in the presence of boron tribromide at 0° to form a phosphorus trihalide and a phosphorus subhalide, (PX)<sub>x</sub>. Halogen exchange occurs as completely as possible; with a sufficient excess of BBr<sub>3</sub>, the adduct PBr<sub>3</sub>·BBr<sub>3</sub> forms.

### Introduction

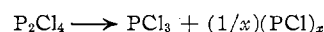
The purpose of this investigation was to study some reactions in which diphosphorus tetrachloride acts as a base. The reactions with nickel carbonyl and boron tribromide were chosen for study because of possible analogies to the reactions of these molecules with phosphorus trichloride<sup>2-5</sup> and to the reactions of nickel carbonyl with tetrasubstituted diphosphines.<sup>6-9</sup>

### Experimental<sup>10</sup>

**Apparatus and Experimental Methods.**—Sealed glass tubes with break-seals were used as reaction vessels, and a standard glass vacuum apparatus lubricated with KEL-F 90 grease (3M Company) was used for the transfer of reagents. Evolved CO was transferred with a Toepler pump and measured in a gas buret.

**P<sub>2</sub>Cl<sub>4</sub>.**—We prepared diphosphorus tetrachloride by using Sandoval and Moser's discharge method<sup>11</sup> in which white phosphorus reacts with PCl<sub>3</sub>. Our yield varied, but was generally about 2 g. in runs of 6–10 hr. Diphosphorus tetrachloride was identified by its melting point of -28°<sup>12</sup> and its mass spectrum. The identification was confirmed by molecular weight determinations (freezing point depression of benzene solutions) that gave values of 215 and 231 (calculated for P<sub>2</sub>Cl<sub>4</sub>, 204), and by allowing 217.3 mg. of P<sub>2</sub>Cl<sub>4</sub> to react with chlorine to yield 440.3 mg. of PCl<sub>3</sub> (calculated, 444.0 mg.). Diphosphorus tetrachloride decomposes at room temperature to a yellow solid and PCl<sub>3</sub>. At 0° it decomposes only very slowly. Two samples were kept at 0°

for 420 days. In one sample of P<sub>2</sub>Cl<sub>4</sub> (0.2367 g.), 7.3% (0.0913 mmole) of the P<sub>2</sub>Cl<sub>4</sub> decomposed, giving PCl<sub>3</sub> (0.0925 mmole) and traces of orange solid. In the other sample of P<sub>2</sub>Cl<sub>4</sub> (0.0314 g.), 40.0% (0.061 mmole) of the P<sub>2</sub>Cl<sub>4</sub> decomposed, giving PCl<sub>3</sub> (0.070 mmole) and orange solid. Thus, at 0° P<sub>2</sub>Cl<sub>4</sub> decomposes according to the equation



Because of this instability of P<sub>2</sub>Cl<sub>4</sub>, reactions were carried out at 0° or for short periods of time at room temperature.

The vapor pressure of P<sub>2</sub>Cl<sub>4</sub> was measured using an immersible mercury tensiometer at eight temperatures between 25 and 76°. The vapor pressure may be calculated, with an average deviation of ±2.9%, from the equation  $\log P_{mm} = 9.969 - 2958/T$ . The data yield an extrapolated boiling point of 144°, a heat of vaporization of 13.5 kcal./mole, and a Trouton constant of 32.4 e.u. Because of decomposition of P<sub>2</sub>Cl<sub>4</sub>, reaction of P<sub>2</sub>Cl<sub>4</sub> with the mercury, and the unusually high value calculated for the Trouton constant, these vapor pressure results should be considered as only approximate. The data disagree markedly with the values of Ross<sup>7</sup> (4 mm. at 0° and 10 mm. at 28°), Stock, Brandt, and Fischer<sup>14</sup> (5 mm. at 0°), and Besson and Fournier<sup>13</sup> (P<sub>2</sub>Cl<sub>4</sub> distilled at 180° or 20 mm. at 95–96°) and agree with Sandoval<sup>15</sup> (about 1 mm. at 25°).

### Results

**Reaction of P<sub>2</sub>Cl<sub>4</sub> with Ni(CO)<sub>4</sub>.**—When P<sub>2</sub>Cl<sub>4</sub> was allowed to react with Ni(CO)<sub>4</sub> at 0°, carbon monoxide was evolved. After a reaction period, usually of several days, the sample was frozen at -196°, and the carbon monoxide was measured. The sample was then allowed to warm, and unreacted P<sub>2</sub>Cl<sub>4</sub> or Ni(CO)<sub>4</sub> was removed and measured to determine the reacting ratio. Table I lists the data for representative runs involving various initial ratios of reactants.<sup>10</sup>

With large excesses of Ni(CO)<sub>4</sub> (run 1), 2 mmoles of Ni(CO)<sub>4</sub> reacted with every mmole of P<sub>2</sub>Cl<sub>4</sub>, giving 2 mmoles of CO and a yellow solid product having a composition close to P<sub>2</sub>Cl<sub>4</sub>[Ni(CO)<sub>3</sub>]<sub>2</sub>. After the CO and excess Ni(CO)<sub>4</sub> had been removed, the compound was stable at -63° but evolved CO and Ni(CO)<sub>4</sub> slowly even at -45° and very rapidly at room temperature. The samples turned black during this gas evolution, suggesting the formation of metallic nickel or possibly nickel phosphides. In run 1 (in which the initial unreacted Ni(CO)<sub>4</sub>, removed at -45°, indicated an empirical formula P<sub>2</sub>Cl<sub>4</sub>Ni<sub>2.00</sub>(CO)<sub>6.01</sub>) the sample

(1) Taken from a thesis presented by C. B. Lindahl for partial satisfaction of the requirements of the Ph.D. degree, University of California, Berkeley, 1964.

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

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

(4) E. Wiberg and K. Shuster, *Z. anorg. allgem. Chem.*, **213**, 94 (1933).

(5) R. R. Holmes, *J. Inorg. Nucl. Chem.*, **12**, 266 (1960).

(6) A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958).

(7) L. A. Ross, Ph.D. Thesis, Indiana University, 1962.

(8) R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964).

(9) W. Schweckendiek, German Patent 1,072,244 (Dec. 31, 1959); *Chem. Abstr.*, **55**, P12,355g (1961).

(10) For complete experimental details, the reader is referred to University of California Radiation Laboratory Report UCRL-11189, "Chemistry of Diphosphorus Tetrachloride," Jan., 1964.

(11) A. A. Sandoval and H. C. Moser, *Inorg. Chem.*, **2**, 27 (1963).

(12) Besson and Fournier<sup>13</sup> originally reported -28°, which was confirmed by Stock, Brandt, and Fischer,<sup>14</sup> Ross,<sup>7</sup> and Sandoval.<sup>15</sup> Finch<sup>16</sup> reported -34 to -35°.

(13) A. Besson and L. Fournier, *Compt. rend.*, **150**, 102 (1910).

(14) A. Stock, A. Brandt, and H. Fischer, *Ber.*, **58**, 643 (1925).

(15) A. A. Sandoval, Ph.D. Thesis, Kansas State University, 1963; see also *Dissertation Abstr.*, **24**, 1422 (1963).

(16) A. Finch, *Can. J. Chem.*, **37**, 1793 (1959).

TABLE I  
 REACTIONS OF P<sub>2</sub>Cl<sub>4</sub> WITH Ni(CO)<sub>4</sub>

Run	Initial ratio	CO evolved,	CO evolved,	Final press., atm.	Run time, hr.
	mmoles Ni(CO) <sub>4</sub> / mmoles P <sub>2</sub> Cl <sub>4</sub>	P <sub>2</sub> Cl <sub>4</sub> reacted, mmoles	Ni(CO) <sub>4</sub> reacted, mmoles		
1	12.5	1.99	0.995	0.15	21
2	1.02	1.86	1.84	...	619
3	0.89	1.83	1.99	0.96	3953
4	0.24	0.96	2.04	1.8	288
5	0.13	...	3.36	0.71	3644

was warmed to 0° for 21 hr., yielding a residue with a ratio CO:P<sub>2</sub>Cl<sub>4</sub> = 5.12. Four hours after warming this material to room temperature, the CO:P<sub>2</sub>Cl<sub>4</sub> ratio had fallen to 2.43; another 20 hr. at room temperature lowered the ratio to 2.00, and at the end of 1 week the ratio was 0.60. In another run with 1 atm. of CO pressure, there was no change in color in a 16-hr. period at 0°; the edges of the material turned gray in 30 min. at room temperature.

When roughly equal amounts of Ni(CO)<sub>4</sub> and P<sub>2</sub>Cl<sub>4</sub> were allowed to react (runs 2 and 3), a yellow solid of approximate empirical formula P<sub>2</sub>Cl<sub>4</sub>·Ni(CO)<sub>2</sub> formed. After standing for long periods of time at 0° or room temperature, this material evolved CO and small amounts of PCl<sub>3</sub>.

With large excesses of P<sub>2</sub>Cl<sub>4</sub> (runs 4 and 5), each mmole of Ni(CO)<sub>4</sub> reacted initially with 2 mmoles of P<sub>2</sub>Cl<sub>4</sub> to form a brownish yellow solid of approximate composition Ni(CO)<sub>2</sub>(P<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub>. When long reaction times were provided, and when the CO pressures were sufficiently low, the product continued to react slowly with P<sub>2</sub>Cl<sub>4</sub>. After removal of the initial evolved CO in three other runs, the reaction products were exposed to excess P<sub>2</sub>Cl<sub>4</sub> for an additional 6 to 17 weeks. The final ratios of the total CO evolved per Ni(CO)<sub>4</sub> were 3.63, 3.65, and 4.02. Apparently all four molecules of CO can be displaced from Ni(CO)<sub>4</sub>.

Three attempts were made to reverse the reaction of P<sub>2</sub>Cl<sub>4</sub> with Ni(CO)<sub>2</sub>(P<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub> by the application of CO pressures of up to 2.5 atm. for several days. The experimental errors in determining the CO absorbed were so great, however, that we can only say that, in these samples with about 3.6 CO replaced per Ni(CO)<sub>4</sub>, less than 0.3 mmole of CO was absorbed per mmole of Ni.

**Reactions of P<sub>2</sub>Cl<sub>4</sub> and PCl<sub>3</sub> with Ni(CO)<sub>4</sub>.**—Table II lists the results of our experiments at 0° on mixtures of PCl<sub>3</sub>, P<sub>2</sub>Cl<sub>4</sub>, and Ni(CO)<sub>4</sub> with ratios of both PCl<sub>3</sub>:Ni(CO)<sub>4</sub> and P<sub>2</sub>Cl<sub>4</sub>:Ni(CO)<sub>4</sub> of at least 2.3. In all cases most of the reaction was due to P<sub>2</sub>Cl<sub>4</sub>. In two cases, slightly more than 100% recovery was achieved, a

result attributable to some decomposition of P<sub>2</sub>Cl<sub>4</sub>. In another run excess P<sub>2</sub>Cl<sub>4</sub> was allowed to react with a sample formed by reaction of 4.97 mmoles of PCl<sub>3</sub> and 1.28 mmoles of Ni(CO)<sub>4</sub>. The solid reacted with 4.55 mmoles of P<sub>2</sub>Cl<sub>4</sub>, replacing 4.73 mmoles of PCl<sub>3</sub>.

**Reaction of P<sub>2</sub>Cl<sub>4</sub> with Boron Trihalides.**—Boron trifluoride was not absorbed by P<sub>2</sub>Cl<sub>4</sub> at 0° or room temperature. When an excess of BCl<sub>3</sub> was placed in a sealed tube with P<sub>2</sub>Cl<sub>4</sub> at 0°, the starting materials were recovered unchanged after 2 months.

When boron tribromide was mixed with P<sub>2</sub>Cl<sub>4</sub> at 0° or room temperature, a reaction occurred producing a yellow-orange nonvolatile solid, boron trichloride, and, in runs with BBr<sub>3</sub>:P<sub>2</sub>Cl<sub>4</sub> ratios greater than 1.42, a white volatile solid. Quantitative results were obtained in thirteen runs with BBr<sub>3</sub>:P<sub>2</sub>Cl<sub>4</sub> ratios of from 0.38 to 36. Representative results from five runs are presented in Table III.

The second column of Table III gives the mgrams of nonvolatile orange solid formed per mmole of P<sub>2</sub>Cl<sub>4</sub>; the values lie between the formula weights for PCl<sub>3</sub>, 66.4, and PBr<sub>3</sub>, 110.9. The third column of Table III gives the mgrams of solid (per mmole of P<sub>2</sub>Cl<sub>4</sub>) stopped by a -45° trap in a fractional condensation of the volatile products. The values lie between or near the molecular weights of PBr<sub>3</sub>, 521.2, and PBr<sub>4</sub>Cl<sub>2</sub>, 432.3. In addition, the white solids were analyzed by precipitation of silver halide, Volhard determination of total halogen, and treatment of the solid with chlorine followed by measurement of the liberated bromine and BrCl. Twenty-one determinations gave values for x (in PBr<sub>6-x</sub>Cl<sub>x</sub>) of 0-1.67, with the majority of the results in the range 0-0.5. On standing, these chlorine-containing samples continued slow halogen exchange until only stable PBr<sub>6</sub> (identical with the known adduct of PBr<sub>3</sub> and BBr<sub>3</sub><sup>5,17</sup>) remained. Solids containing chlorine had melting points depressed as much as 10-20° from the 61-62° melting point of pure PBr<sub>6</sub> and usually melted over a range of several degrees. The fourth column of Table III gives the mgrams of material (per mmole of BBr<sub>3</sub>) which passed a -78° trap in a fractional condensation of the volatile products in runs with excess P<sub>2</sub>Cl<sub>4</sub>. The results, in agreement with the molecular weight of BCl<sub>3</sub>, 117.2, and confirmed by infrared spectra which showed BCl<sub>3</sub> to be the principal component, indicated almost complete conversion of BBr<sub>3</sub> to BCl<sub>3</sub> in the presence of excess P<sub>2</sub>Cl<sub>4</sub>. With excess BBr<sub>3</sub>, infrared spectra showed

 TABLE II  
 REACTIONS OF PCl<sub>3</sub> AND P<sub>2</sub>Cl<sub>4</sub> WITH Ni(CO)<sub>4</sub> AT 0°

CO evolved Ni(CO) <sub>4</sub>	Final press., atm.	P <sub>2</sub> Cl <sub>4</sub> reacted, mmoles	PCl <sub>3</sub> reacted, mmoles	CO evolved, mmoles
2.09	0.64	1.58	(-0.23) <sup>a</sup>	1.63
1.99	1.22	2.77	0.21	3.20
2.57	0.69	1.09	(-0.14) <sup>a</sup>	1.36
2.11	0.63	1.82	0.32	1.22

<sup>a</sup> More PCl<sub>3</sub> was recovered than was put in the reaction vessel.

(17) J. Tarible, *Compt. rend.*, **116**, 1521 (1893).

TABLE III  
 PRODUCTS OF THE REACTION OF BBr<sub>3</sub> WITH P<sub>2</sub>Cl<sub>4</sub>

Initial ratio BBr <sub>3</sub> :P <sub>2</sub> Cl <sub>4</sub>	mg. of nonvol. prod. mmole of P <sub>2</sub> Cl <sub>4</sub>	mg. of white solid mmole of P <sub>2</sub> Cl <sub>4</sub>	mg. of vol. at -78° mmole of BBr <sub>3</sub>
35.9	94	524	<i>a</i>
3.35	69	484	<i>a</i>
2.10	96	435	<i>a</i>
1.42	71	0	117
1.30	96	0	106

<sup>a</sup> Inseparable mixed boron trihalides.

the presence of the four possible BCl<sub>2</sub>Br<sub>3-x</sub> compounds which are rapidly formed in any BCl<sub>3</sub>-BBr<sub>3</sub> mixture.

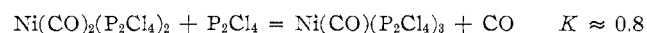
### Discussion

**Reaction of P<sub>2</sub>Cl<sub>4</sub> with Ni(CO)<sub>4</sub>.**—It appears that either one or both phosphorus atoms of P<sub>2</sub>Cl<sub>4</sub> can act as donors to nickel and that one to four CO molecules can be displaced from nickel carbonyl by the phosphorus atoms of P<sub>2</sub>Cl<sub>4</sub>. Thus in the presence of a large excess of Ni(CO)<sub>4</sub>, the binuclear complex (CO)<sub>3</sub>NiP<sub>2</sub>Cl<sub>4</sub>Ni(CO)<sub>3</sub> forms; in the presence of a large excess of P<sub>2</sub>Cl<sub>4</sub>, mononuclear complexes such as (CO)<sub>2</sub>Ni(P<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub>, (CO)-Ni(P<sub>2</sub>Cl<sub>4</sub>)<sub>3</sub>, and Ni(P<sub>2</sub>Cl<sub>4</sub>)<sub>4</sub> form. When there is no large excess of either reactant, we believe that polymeric materials, in which nickel atoms are bridged by P<sub>2</sub>Cl<sub>4</sub> molecules, are formed. For all of these compounds, or mixtures of compounds, the approximate average sum of the P<sub>2</sub>Cl<sub>4</sub> groups and Ni atoms per molecule may be calculated from the function  $(a + b)/(a - ab + b)$ , where  $a = \text{CO evolved}/\text{P}_2\text{Cl}_4 \text{ reacted}$  and  $b = \text{CO evolved}/\text{Ni(CO)}_4 \text{ reacted}$ .<sup>18</sup> In runs with a large excess of either reagent, the function has values fairly close to 3 (*e.g.*, 3.0 in run 1 and 2.9 in run 4 of Table I), corresponding to P<sub>2</sub>Cl<sub>4</sub>Ni(CO)<sub>3</sub> or Ni(CO)<sub>2</sub>(P<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub>. Values of 14 and 22 are obtained for runs 2 and 3, suggesting the formation of polymeric materials when there was no large excess of either reagent.

In fifteen runs involving an excess of P<sub>2</sub>Cl<sub>4</sub>, the only runs in which significantly more than two molecules of CO per Ni(CO)<sub>4</sub> were displaced by P<sub>2</sub>Cl<sub>4</sub> molecules were those runs of long duration in which the final pressure of carbon monoxide was less than about 0.8 atm. Whenever the final pressure of carbon monoxide was greater than 0.8 atm., the CO evolved/Ni(CO)<sub>4</sub> reacted was, within experimental error, equal to 2.

(18) This formula is based on the assumption that there are no ring structures formed.

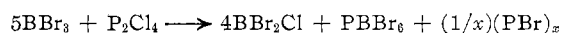
This result suggests that an equilibrium is achieved in mixtures containing CO, P<sub>2</sub>Cl<sub>4</sub>, Ni(CO)<sub>2</sub>(P<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub> groups, and Ni(CO)(P<sub>2</sub>Cl<sub>4</sub>)<sub>3</sub>. Although three experiments in which we attempted to reach this equilibrium by reaction with excess CO were inconclusive (possibly due to slowness of the reaction), we write



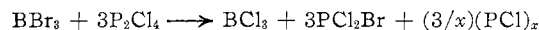
It should be made clear, however, that some of the coordinated P<sub>2</sub>Cl<sub>4</sub> molecules in this equation may form bridges to other nickel atoms.

**Reactions of P<sub>2</sub>Cl<sub>4</sub> and PCl<sub>3</sub> with Ni(CO)<sub>4</sub>.**—The data indicate that P<sub>2</sub>Cl<sub>4</sub> is a stronger Lewis base than PCl<sub>3</sub> in reactions with Ni(0), as might have been predicted from a consideration of the inductive effect.

**Reaction of P<sub>2</sub>Cl<sub>4</sub> with Boron Trihalides.**—The reaction of P<sub>2</sub>Cl<sub>4</sub> with BBr<sub>3</sub> involves both the quantitative<sup>\*</sup> disproportionation of the P<sub>2</sub>Cl<sub>4</sub> to PCl<sub>3</sub> and (PCl)<sub>x</sub> and the quantitative conversion, as far as possible, of PCl<sub>3</sub> and (PCl)<sub>x</sub> to PBr<sub>3</sub> and (PBr)<sub>x</sub> and of BBr<sub>3</sub> to BCl<sub>3</sub>. The disproportionation and halogen-exchange reactions cannot be separated, however. In the presence of a large excess of BBr<sub>3</sub>, the net reaction is



In the presence of a large excess of P<sub>2</sub>Cl<sub>4</sub>, the reaction is



We initially studied this reaction with the hope of making P<sub>2</sub>Cl<sub>4</sub>·2BBr<sub>3</sub>; indeed, this adduct may be an intermediate in the complicated reaction observed. In this regard it is interesting to note that the weaker acids BF<sub>3</sub> and BCl<sub>3</sub> neither react with P<sub>2</sub>Cl<sub>4</sub> nor accelerate its decomposition.

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