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UCRL-10840

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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May 1963

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Diphosphorus tetrachloride can act either as a monofunctional or as a difunctional Lewis base.

The nature of the product resulting from the reaction of nickel carbonyl and P_2Cl_4 at 0° depends on the relative amounts of the reactants. A large excess of $Ni(CO)_4$ with P_2Cl_4 forms a yellow-white solid $P_2Cl_4[Ni(CO)_3]_2$ which decomposes rapidly when warmed to room temperature and decomposes slowly even at -45° after the evolved CO and excess $Ni(CO)_4$ are removed. Large excesses of P_2Cl_4 with $Ni(CO)_4$ form a brownish-yellow solid $Ni(CO)_2(P_2Cl_4)_2$. When there is no large excess of either reactant, a yellow mixture of compounds (whose apparent composition approaches $P_2Cl_4 \cdot Ni(CO)_2$ when equal amounts of reagents are employed) forms.

Diphosphorus tetrachloride does not react, or reacts only extremely slowly, at 0° with $Fe(CO)_5$, $Cr(CO)_6$ or $Mo(CO)_6$.

With a large excess of BBr_3 at 0°, P_2Cl_4 reacts to form $Br_3B \cdot PBr_3$, boron chloro- bromo-trihalides and phosphorus subhalides. Boron trichloride and BF_3 show no reaction with P_2Cl_4 at 0°. This is consistent with the order of Lewis acid strengths $BBr_3 > BCl_3 > BF_3$.

Diphosphorus tetrachloride reacts with B_2H_6 causing slow decomposition producing H_2, BCl_3 and $BHCl_2$.

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* Speech to be given at the ACS Meeting, September 8-13, 1963 by Charles B. Lindahl.

Some Reactions of Diphosphorus Tetrachloride

By Charles B. Lindahl and William L. Jolly

Diphosphorus tetrachloride, with a lone pair of electrons on each phosphorus atom, can behave as a Lewis base. The reactivities of P_2Cl_4 with the compounds $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, BBr_3, BCl_3, BF_3 and B_2H_6 have been investigated in order to compare the acid-base reactions of P_2Cl_4 with those of PCl_3 and to determine whether P_2Cl_4 can act as either a monofunctional or a difunctional base.

Phosphorus trichloride[1] displaces as many as four molecules of carbon monoxide per nickel carbonyl to give $Ni(PCl_3)_4$. The literature also contains three reports on reactions of $Ni(CO)_4$ with organic diphosphines. Burg and Mahler[2] report the reaction of $P_2(CF_3)_4$ with $Ni(CO)_4$ to yield $P_2(CF_3)_4\ [Ni(CO)_3]_2$. The preparation of $P_2(C_6H_5)_4\ [Ni(CO)_3]_2$[3] from $ClP(C_6H_5)_2$ and sodium in boiling xylene has been reported in a German patent by Schweckendiek. Ross[4] reports the preparation of $P_2(CH_3)_4\ [Ni(CO)_3]_2$ with an excess of $Ni(CO)_4$ over $P_2(CH_3)_4$ and $[P_2(CH_3)_4\ Ni(CO)_2]_x$ with equal amounts of reagents or an excess of $P_2(CH_3)_4$.

Reactions with $Ni(CO)_4$:

When P_2Cl_4 is allowed to react with $Ni(CO)_4$ at 0°, carbon monoxide is readily evolved. After a reaction period, usually of several days, the sample was frozen at -196° and the carbon monoxide measured. The sample was then allowed to warm and unreacted P_2Cl_4 and $Ni(CO)_4$ were removed to determine the ratio of reactants. Table I lists a series of reactions using varying ratios of reactants.

Table I.

Reactions of $Ni(CO)_4$ with P_2Cl_4

Run	Ratio of Reactants: mmoles $Ni(CO)_4$ / mmoles P_2Cl_4	mmoles CO evolved / mmole $Ni(CO)_4$ reacted	mmoles CO evolved / mmole P_2Cl_4 reacted	Ratio in Products: mmoles $Ni(CO)_x$ / mmole P_2Cl_4
1	12.48	0.995	1.99	2.00
2	4.968	0.987	1.99	2.02
3	3.170	1.20	1.96	1.63
4	1.015	1.84	1.87	1.02
5	0.8879	1.87	1.78	0.947
6	0.4930	1.96	1.55	0.791
7	0.3859	1.98	1.22	0.615
8	0.2388	2.04	0.956	0.468

With a large excess of $Ni(CO)_4$ (Runs 1 and 2), one millimole of P_2Cl_4 reacts with two millimoles of $Ni(CO)_4$ giving two millimoles of CO and a product of empirical formula $P_2Cl_4 \cdot [Ni(CO)_3]_2$. This material is a yellow solid when in the presence of excess $Ni(CO)_4$ at 0°, and is yellowish-white at -45° after the CO and excess $Ni(CO)_4$ are removed. When the CO and excess $Ni(CO)_4$ are removed, the compound evolves CO and $Ni(CO)_4$ slowly even at -45° and very rapidly at room temperature. For example in run 2, after removing the unreacted $Ni(CO)_4$ in three hours at -45°, it was found that apparently 2.02 millimoles of $Ni(CO)_4$ had reacted per millimole P_2Cl_4. After 42 more hours at -45°, further evolution of small amounts of CO and $Ni(CO)_4$ indicated an empirical composition of $P_2Cl_4 \cdot [Ni(CO)_3]_{1.71}$ for the residue. Run 1 (from which initial removal of unreacted $Ni(CO)_4$ at -45 gave an apparent ratio of 2.00 $Ni(CO)_4$ reacted per P_2Cl_4) was warmed to 0° for 21 hours evolving small amounts of CO and $Ni(CO)_4$ giving a residue of empirical composition $P_2Cl_4 \cdot [Ni(CO)_3]_{1.78}$. Warming this to room temperature caused it to evolve large amounts of CO and turn black rapidly indicating the presence of large amounts of metallic nickel. Within four hours the material had fallen from a ratio of 5.12 CO per P_2Cl_4 (corresponding to 1.78 $Ni(CO)_4$ reacted per P_2Cl_4) to 2.43 CO per P_2Cl_4. Another 20 hours lowered it to 2.00 CO per P_2Cl_4 (corresponding to the empirical formula $P_2Cl_4 \cdot Ni(CO)_2$). Carbon monoxide continued to be slowly evolved. At the end of one week the ratio was 0.60 CO per P_2Cl_4 in the sample. Thus the composition of the material changes rapidly from 6 to 2 CO per P_2Cl_4, and then slowly evolves most or all the remaining CO at room temperature.

When roughly equal amounts of $Ni(CO)_4$ and P_2Cl_4 are allowed to react (Runs 4 and 5), a yellow solid of approximate empirical formula $P_2Cl_4 \cdot Ni(CO)_2$ forms.

With a large excess of P_2Cl_4 (Run 9), one millimole $Ni(CO)_4$ reacts with two millimoles of P_2Cl_4 with evolution of two millimoles of CO. A brownish yellow solid with the empirical formula $Ni(CO)_2(P_2Cl_4)_2$ remains.

The results may be explained by assuming that in all cases a transient intermediate of composition $P_2Cl_4 \cdot Ni(CO)_3$ formed. In the presence of excess $Ni(CO)_4$, the reaction

$$Ni(CO)_4 + P_2Cl_4 \cdot Ni(CO)_3 \longrightarrow (CO)_3Ni \cdot P_2Cl_4 \cdot Ni(CO)_3 + CO$$

took place. In the presence of excess P_2Cl_4, the reaction

$$P_2Cl_4 + P_2Cl_4 \cdot Ni(CO)_3 \longrightarrow P_2Cl_4 \cdot Ni(CO)_2 \cdot P_2Cl_4 + CO$$

took place. When there was neither a large excess of P_2Cl_4 nor of $Ni(CO)_4$, the concentration of the intermediate was relatively large and some polymerization took place. Probably a complex mixture of products containing species such as $P_2Cl_4 \cdot Ni(CO)_2 \cdot P_2Cl_4 \cdot Ni(CO)_3$, $(CO)_3Ni \cdot P_2Cl_4 \cdot Ni(CO)_2P_2Cl_4 \cdot Ni(CO)_3$, etc. was formed. With equal amounts of reagents, the products tend toward the empirical formula $Ni(CO)_2P_2Cl_4$. Even a 100% or 200% excess of P_2Cl_4 or $Ni(CO)_4$ produced a mixture. This suggests that the formation of a phosphorus nickel bond to be dependent only upon local concentration effects, with no subsequent rearrangements to reach an equilibrium.

It is interesting that no more than two molecules of carbon monoxide were ever displaced from nickel carbonyl. This is in contrast to the reaction with PCl_3, which can displace all four carbon monoxide molecules. It is not clear whether this is due to a steric effect or to a weaker basicity on the part of P_2Cl_4. (Although P_2Cl_4 would be expected to be a better

Lewis base than PCl_3 on the basis of a simple inductive effect, it is possible that some double bond character in the P-P linkage causes a weakening of the base strength.)

Reactions with Other Carbonyls:

When P_2Cl_4 was placed in a sealed tube with $Mo(CO)_6$ for 40 days at 0°, less than 0.002 CO per P_2Cl_4 and less than 0.009 CO per $Mo(CO)_6$ was evolved. No CO was evolved when P_2Cl_4 was placed with $Cr(CO)_6$ for 43 days at 0°. Iron pentacarbonyl placed with P_2Cl_4 gave about 0.02 CO per $Fe(CO)_5$ or P_2Cl_4 in one run of 39 days at 0°. Subsequent warming of this sample to room temperature for 37 days gave an additional 0.02 millimoles CO per $Fe(CO)_5$ or P_2Cl_4. During this time at room temperature part of the P_2Cl_4 undoubtedly also decomposed. Another run of 77 days at 0° produced 0.05 CO per P_2Cl_4 and 0.10 CO per $Fe(CO)_5$. Both runs produced reddish brown solids which suggest that at least part of the carbon monoxide was produced by the known decomposition of $Fe(CO)_5$. Thus we conclude that P_2Cl_4 reacts only extremely slowly or not at all with $Fe(CO)_5$, $Mo(CO)_6$ and $Cr(CO)_6$. Schweckendiek[3] reports the preparation of $P_2(C_6H_5)_4$ $[Fe(CO)_4]_2$ by reaction for several hours at 170-180°. Such conditions would readily decompose P_2Cl_4. Irvine and Wilkinson[1] report no replacement compounds of PCl_3 with molybdenum and chromium hexacarbonyls at temperatures up to 150°.

Reactions with Boron Halides:

When a large excess of BBr_3 is allowed to react with P_2Cl_4 at 0° or room temperature in a sealed tube, $PBr_3 \cdot BBr_3$, other volatile chlorine containing PBX_6 compounds (which yield $PBr_3 \cdot BBr_3$, BCl_3, $BBrCl_2$, BBr_2Cl and presumably phosphorus trihalides), and a yellow orange non-volatile phos

phosphorus subhalide mixture which contains some boron halides are formed.

We suggest the following mechanism.

$$P_2Cl_4 + 2BBr_3 \longrightarrow P_2Cl_4 \cdot 2BBr_3$$

$$P_2Cl_4 \cdot 2BBr_3 \longrightarrow PCl_2Br \cdot\cdot BBr_3 + \frac{1}{x}(PCl_2BBr_2)_x$$

$$\frac{1}{x}(PX_2BX_2)_x \longrightarrow \frac{1}{x}(PX)_x + BX_3$$

Boron tribromide probably causes the rupture of the phosphorus-phosphorus bond in P_2Cl_4 by forming a Lewis adduct which is unstable. This decomposes to the boron trihalide-phosphorus trihalide addition compound and a reduced phosphorus-boron species which rearranges and decomposes in part to give boron trihalide. Halogen exchange occurs in all products producing the materials $PBr_3 \cdot BBr_3$ and BCl_3 and an appropriate mixture of BBr_2Cl and $BBrCl_2$ depending on the excess of BBr_3. Exchange of Cl and Br between phosphorus and boron is also found in the complex $PCl_3 \cdot BBr_3$[5] which decomposes on standing to yield BCl_3 and PBr_3. When an excess of BCl_3 is placed in a sealed tube with P_2Cl_4 at 0°, the reactants can be recovered unchanged even after two months. No change in pressure of BCl_3 vapor is observed when it is exposed to P_2Cl_4 at 0° or room temperature. No change in pressure of BF_3 vapor is observed when it is exposed to P_2Cl_4 at 0° or room temperature. The fact that neither BCl_3 nor BF_3 forms an adduct or otherwise reacts with P_2Cl_4 is consistent with the order of Lewis acid strengths $BBr_3 > BCl_3 > BF_3$.

Reaction With Diborane:

When B_2H_6 is exposed to P_2Cl_4 at 0°, a slow increase in pressure, due primarily to evolution of H_2, continues over a long period of time. This

experiment was terminated after 17 days of continuous H_2 evolution. Boron trichloride and $BHCl_2$ (identified by their infrared spectra) were also evolved. Evidently P_2Cl_4 reacts with B_2H_6 causing slow decomposition rather than any recognizable complex formation.

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