NOTES

Reactions of tetrakis(trifluorophosphine)nickel(o)

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IRVINE and WILKINSON⁽¹⁾ prepared Ni(PCl₃)₄ in 1951 by a simple replacement reaction using Ni(CO)₄ and PCl₃. The phosphorus trichloride complex has subsequently been used as the starting material for the preparation of the unusual compound Ni(PF₃)₄.^(2,3) Among the methods used for the preparation of this latter complex is the direct replacement reaction⁽²⁾ according to equation:

$$Ni(PCl_3)_4 + 4PF_3 \rightarrow Ni(PF_3)_4 + 4PCl_3$$
⁽¹⁾

Two interesting problems arise concerning the reactions of Ni(PCl₃)₄. The first concerns whether the replacement reaction of Equation (1) proceeds by means of ligand exchange or by halogen exchange. The second problem deals with the composition of the black residue that frequently accompanies this or other reactions of Ni(PCl₃)₄.

Most substitution reactions with zero valent metal complexes must, by the very nature of the ligands, proceed through a ligand exchange mechanism, and it might be argued that reaction 1 would be no exception. However, in the preparation of Ni(PF₃)₄ from Ni(PCl₃)₄ and fluorinating agents like SbF₃² and KSO₂F³ there may be no displacement of ligand and halogen exchange may take place. Since the Ni(PCl₃)₄-PF₃ reaction might take place in a similar fashion, it was studied with P³²—labelled Ni(PCl₃)₄.

The decomposition of many zero-valent metal compounds yields elemental metal plus the free ligand. When $Ni(PCl_s)_4$ reacts with PF_s or when it undergoes thermal decomposition, it yields a black material that looks as though it could be finely divided metal. However, the products' lack of ferro-magnetic properties makes the reaction worthy of further study. To avoid complications, the decomposition of the pure compound was studied.

EXCHANGE STUDIES

Unlabelled Ni(PCl_s)₄ was prepared by the method of SMITH⁽⁴⁾ on a reduced scale. The labelled compound was prepared by the same reaction but by quite different techniques. In a typical experiment, 0.7 g of Ni(CO)₄ (4 mmoles) and 3.0 g of P*Cl₃ (22 mmoles) were distilled *in vacuo* into a 300 ml flask. The contents of the flask were allowed to react for about 6 hr at room temperature and then 1 hr at 50–60°. During the reaction period, the flask was frequently cooled to -78° and the carbon monoxide that was produced was pumped off. Next, unreacted Ni(CO)₄ and PCl₃ were removed *in vacuo* and the non-volatile product dissolved in 30 ml diethyl ether containing about 5% PCl₃. The solution was filtered, the product precipitated at -78° and the crystals collected and vacuum dried. All of these operations were carried out in an inert atmosphere.

As both IRVINE and WILKINSON⁽²⁾ and SMITH⁽⁴⁾ have observed, Ni(PCl₃)₄ is more susceptible to decomposition when it has been recrystallized. The stability of the crude product is presumably due to the presence of PCl₃. The procedure described above allows the purification of the product while maintaining its stability.

The P³²Cl₃ was obtained from Nuclear of Chicago as a very active sample. By appropriate vacuum manipulation, it was diluted to suitable activity with non-radioactive PCl₃.

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The substitution reactions were carried out in Pyrex tubes 5 mm o.d. with an annealed constriction so that the evacuated tubes could be sealed off at a length of 150 mm. In a typical reaction, about $0.1 \text{ g of Ni}(P^*Cl_s)_4$ was placed in a tube and sufficient PF₃ was admitted to give 10–13 mm of liquid PF₃ present in the tube at low temperature. The sealed tubes were then heated to 50–80° for various periods of time. So long as care was taken to avoid getting too much PF₃ in the tubes, no explosions resulted.

At the completion of the reaction, the tubes were cooled to -195° , broken open, and the PF₃ removed at -78° . Next, the Ni(PF₃)₄ and PCl₃ were distilled from the tubes at room temperature into a trap at -78° and containing about 1 g of H₂O. After the PCl₃ had hydrolysed, the Ni(PF₃)₄ was recovered by vacuum distilling it through 4A Molecular Sieves. The Ni(PF₃)₄ was hydrolysed by dilute NaOH. The total hydrolysed samples of Ni(PF₃)₄ and PCl₃ were transferred to Planchets, evaporated, and counted.

Since the total quantities of phosphorus in the two products of the reaction of equation 1 are equal, only the ratio of counting rates under similar conditions need be considered. The ratio of the activity in the PCl_3 fraction to the activity in the $Ni(PF_3)_4$ fraction varies from 12:1 to 300:1 with the higher ratios applying to the shorter reaction times.

It would thus appear that the reaction is proceeding via ligand exchange and not halogen exchange. This conclusion is enhanced when the exchange

$$P^*Cl_3 + PF_3 \rightarrow P^*F_3 + PCl_3 \tag{2}$$

is considered. That this exchange does take place to some extent is shown by the presence of mild activity in the hydrolysis products of the excess PF_3 gas. Radioactive phosphorus trifluoride, which would appear after the reaction has gotten underway, can then enter into the main reaction of equation 1 resulting in activity in the Ni(PF_3)₄ fraction. Without this added exchange reaction, activity would only appear in Ni(PF_3)₄ when halogen exchange is taking place. That the ratio is as high as 300:1; is clear evidence that not only is the reaction proceeding mainly by ligand exchange, but in addition, the halogen exchange between PCl_3 and PF_3 is relatively slow.

It cannot be concluded that a large portion of the P^*Cl_3 comes from the simple thermal decomposition of Ni(PCl_3)₄. Under the conditions used, most of the starting material was consumed, and little or none of the black residue that accompanies thermal decomposition was produced.

DECOMPOSITION STUDIES

The thermal decomposition of $Ni(PCl_3)_4$ was first studied by determining the weight loss in a sample heated in an inert atmosphere on a thermogravimetric balance. Next separate studies were made on samples heated to temperatures representative of temperatures above each of the three zones of loss.

A sample heated to 200° was extracted with water in an inert atmosphere yielding a solution having a Cl to Ni mole ratio of about 2.5:1 plus a trace of phosphorus. A black, pyrophoric residue containing only Ni and P was left from the extraction. The residue from this temperature was amorphous to X-rays.

A sample heated to 400° was qualitatively similar.

A sample heated to above 700°C *in vacuo* was studied as representative of the third zone. Two types of products were observed. One was a yellow sublimate, identified by X-ray diffraction analysis as NiCl₂ and the other was a black residue whose X-ray diffraction pattern fit that of a mixture of Ni₂P and Ni₇P₃. A few lines were unidentified. The mole ratio of Ni to P in this material was about 2.3:1.

In the absence of phosphorus trifluoride, Ni(PCl₃)₄ undergoes three steps of thermal decomposition on being heated to 1000° at atmospheric pressure of an inert gas. The three temperature ranges are 100–150° during which 79.6% of the weight is lost, 250–400° with another 1.9% of the original weight being lost, and finally 650–875° with a loss of somewhat greater than 8 per cent. The final figure was low owing to the deposition of an indeterminant quantity of yellow solid on the weighing arm of the balance.

The three main products from decomposition appear to be phosphorus trichloride, nickel chloride and nickel phosphide. The phosphorus trichloride is formed at the first stage of decomposition.

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The weight loss at the highest temperature is the sublimination of anhydrous NiCl₂ leaving a mixture of Ni₂P₃ and Ni₂P.

The nature of the small but definite weight loss at the intermediate temperature has not been determined.

No evidence for metallic nickel was ever found although the metal can easily be postulated as an intermediate in the formation of the nickel chloride and phosphide.

Department of Chemistry Florida State University Tallahassee, Florida and Tonawanda Laboratories Union Carbide Corporation-Linde Division Tonawanda, New York R. J. Clark* P. I. Hoberman †

E. O. BRIMM ‡

- * To whom inquiries should be sent, Florida State University.
- † Dade County Junior College, Miami, Florida.
- ‡ Union Carbide Europa, S.A., 40 Rue du Rhone, Geneva, Switzerland.

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BX₃ complexes of some pyridine N—oxides

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IN RECENT years several publications concerned with the electron acceptor properties of boron trihalides and borane have indicated that the trends in acidity of these species are not in accord with simple electronegativity arguments.⁽¹⁻⁵⁾ BROWN and HOLMES⁽¹⁾ have suggested that resonance structures involving $p\pi$ - $p\pi$ overlap between the empty boron p-orbital and the filled p-orbitals of the fluorine and chlorine atoms could be responsible for BF_3 being less acidic than BCl_3 . With BH_3 and BF_a the trend appears to vary with the choice of reference base; $BF_a > BH_a$ for ethers⁽⁸⁾ and $BH_a >$ BF_{3} for thioethers^(2,3) and pyridine,⁽⁴⁾ These reversals for BF_{3} and BH_{3} cannot be explained solely on the basis of back bonding.^(8,5) TAMRES and his coworkers^(3,7) have advanced the idea that the mutual polarization of acid and base may be one reason for these and other unexpected trends. PEARSON'S recent classification of acids and bases as "soft" and "hard" also implies that the mutual polarization of acid and base is important in determining the strength of the interaction.⁽⁸⁾ Accordingly, an increase in polarization of the base might favour association with BH₃ relative to BF₃, since the former would be expected to be a softer acid. Since pyridine appears to be a soft base we thought it would be of interest to study the interactions of BF₃, BH₃, and BCl₃ with pyridine N-oxide (PyO), p-methyl, and p-nitro pyridine N-oxides (MePyO, NO₂PyO) all of which are less basic than pyridine⁽⁹⁾ and also probably less polarizable than pyridine.

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