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The Preparation and Properties of Tetrakistribromophosphine Nickel and Tetrakistrifluorophosphine Nickel

BY GEOFFREY WILKINSON[1]

In 1936, the suggestion was made by A. A. Blanchard of this Institute that phosphorus trichloride might form a compound with nickel analogous to nickel carbonyl. The preparation of the crystalline non-volatile yellow compound, tetrakistrichlorophosphine nickel, $Ni(PCl_3)_4$, together with some of its properties, has been described in a previous paper.[2] It was also reported there that although phosphorus tribromide reacts with nickel carbonyl in the liquid phase with loss of carbon monoxide and formation of an orange solution, no compound of nickel with phosphorus tribromide could be isolated, presumably due to the ready decomposition of some intermediate replacement compound. Tetrakistribromophosphine nickel has now been made by the action of phosphorus tribromide on tetrakistrichlorophosphine nickel.

That phosphorus trifluoride might form a compound analogous to nickel carbonyl by the action of phosphorus trifluoride on nickel carbonyl was suggested by Chatt[3] following his preparation of phosphorus trifluoride complexes of divalent platinum chloride. The similarity of phosphorus trifluoride to carbon monoxide in its ability to form covalent complexes has been further demonstrated by the formation of an unstable ferrohemoglobin complex,[4] $HbPF_3$. The compound $Ni(PF_3)_4$, tetrakistriflucrophosphine nickel, has now been prepared both by direct fluorination of tetrakistrichlorophosphine nickel and by the action of phosphorus trifluoride on $Ni(PCl_3)_4$ and $Ni(PBr_3)_4$.

Tetrakistribromophosphine Nickel, $Ni(PBr_3)_4$.—The compound $Ni(PBr_3)_4$ is made by treating $Ni(PCl_3)_4$ with excess phosphorus tribromide. On warming the mixture to about 70°, the $Ni(PCl_3)_4$ dissolves and a deep orange-red color appears. Phosphorus trichloride is pumped off in a vacuum system, after which the residual solution is cooled to a temperature, just above the melting point of phosphorus tribromide (−38°). Small orange-red crystals separate; these are removed and recrystallized from phosphorus tribromide after which excess phosphorus tribromide is removed by washing with cold pentane. The solid is dried by aspiration of dry nitrogen, or by pumping in a vacuum system at room temperature. The yield of $Ni(PBr_3)_4$ is about 60% of the theoretical yield. Attempts to grow large crystals by slow cooling of the solutions have failed. The crystals are thermochroic like those of $Ni(PCl_3)_4$. The color changes from deep orange-red at room temperature to very pale yellow at −38°.

Qualitative analysis after removal of bromide by the persulfate or permanganate–acetone methods[5] showed the absence of chloride in the compound. Quantitative analysis of the compound after decomposition with sodium hydroxide was made as in the case[2] of $Ni(PCl_3)_4$ and gave Ni, 5.2 (calcd. 5.14); P, 10.7 (calcd. 10.84); Br, 83.5 (calcd. 83.9), confirming the formula $Ni(PBr_3)_4$.

The compound is notably less stable than $Ni(PCl_3)_4$. It begins to decompose thermally at about 80° to yield metallic nickel, phosphorus tribromide, and some nickel bromide. It is reasonably stable in a dry atmosphere and can be kept thus for several days.

Tetrakistribromophosphine nickel dissolves in inert organic solvents such as benzene, carbon tetrachloride, cyclohexane and xylene but decomposition rapidly follows with the disappearance of the characteristic orange color and with the slow formation of pale yellow or white flocculent precipitates of undetermined composition. In hot solutions blackening occurs at once. The solid is sparingly soluble in pentane and since at low temperatures decomposition is very slow, this solvent can be used for washing the solid free from phosphorus tribromide during its preparation. With the oxygenated solvents diethyl ether, ethyl acetate, ethanol and acetone, solution of the compound is accompanied by rapid decomposition.

The compound is, like $Ni(PCl_3)_4$, surprisingly stable toward water and dilute acids at room temperature, and even with 8 *N* nitric acid in the cold, the decomposition reaction takes several hours to accomplish. Sodium hydroxide solutions react readily to give a brown precipitate of undetermined composition and a solution of phosphorus acid; traces of phosphine also are liberated.

Tetrakistrifluorophosphine Nickel, $Ni(PF_3)_4$.—The preparation of $Ni(PF_3)_4$ has been attempted in several ways. The direct interaction of nickel carbonyl and phosphorus trifluoride under pressure appears to give replacement of no more than two or three molecules of carbon monoxide, presumably because of a reversible equilibrium; this observation has also been made by Chatt.[6] The interaction of metallic nickel and phosphorus trifluoride at pressures up to 150 atm. and temperatures of 200° gave none of the desired product. Success was achieved by the direct fluorination of $Ni(PCl_3)_4$ suspended in a fluorinated hydrocarbon (Fluorolube FS, b.p. ~160°) with antimony trifluoride, using a trace of antimony pentachloride as a catalyst; small quantities of a volatile liquid, b.p. ~70°, were produced.

The most effective method of preparation yet found is the reaction of $Ni(PCl_3)_4$ or $Ni(PBr_3)_4$ with phosphorus trifluoride at 50 to 100 atm. pressure and at about 100°. Sealed tubes containing $Ni(PCl_3)_4$ and excess phosphorus trifluoride were heated in steam for about 24 hours; the tubes were then cooled in liquid nitrogen, opened, and the volatile components transferred to a high vacuum system. The excess phosphorus trifluoride was removed by distillation from a bath at −115°. On allowing the residue to warm up to 0°, the liquid separated into two phases which were mechanically separated. The upper phase is phosphorus trichloride and the lower $Ni(PF_3)_4$. The $Ni(PF_3)_4$ was purified from traces of phosphorus trichloride by fluorination with antimony trifluoride (and antimony pentachloride catalyst) and by fractionation in high vacuum. The yield of $Ni(PF_3)_4$ produced from $Ni(PCl_3)_4$ in the reaction is about 50% of the theoretical yield; the only other products are metallic nickel and phosphorus trichloride.

Samples of the compound were condensed into a weighed tube with a constriction joined to the vacuum system by a ground glass joint; the sample was sealed off, both parts of the tube reweighed, and the bulb of $Ni(PF_3)_4$ then broken under 6 *M* sodium hydroxide in a closed system. After complete absorption of the compound, the solution was made just acid and diluted to a known volume, and aliquots were taken for analysis. Nickel was determined by precipitation with dimethylglyoxime.[7] For determination of phosphorus, the phosphorous acid formed in hydrolysis of the compound was oxidized by boiling nitric acid to phosphoric acid which was then determined by the standard ammonium

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

[3] J. Chatt, *Nature*, **165**, 637 (1950).

[4] G. Wilkinson, *ibid.*, 1951, in press.

[5] R. K. McAlpine and B. A. Soule, "Prescott and Johnson's Qualitative Chemical Analysis," D. Van Nostrand, New York, N. Y., 1933.

[6] J. Chatt, private communication, December, 1950.

[7] N. H. Furman, Editor, "Scott's Standard Methods of Chemical Analysis," 5th Edition, Vol. I, D. Van Nostrand, New York, N. Y., 1939.

molybdate method.[7] Fluorine was determined by distillation of fluosilicic acid in superheated steam from concentrated sulfuric acid[8]; the distillate was collected in sodium hydroxide and aliquots of this solution were titrated with thorium solution using sodium alizarin sulfonate indicator, after adjusting the *p*H by a monochloroacetic acid buffer solution.[9] The thorium solution was standardized against sodium fluoride distilled as in the fluoride determinations. The results of analyses of $Ni(PF_3)_4$ gave Ni, 14.2 (calcd., 14.35); P, 30.55 (calcd., 30.15), and F, 55.0 (calcd., 55.5). No trace of chloride was found in the product.

The compound $Ni(PF_3)_4$ is a colorless, odorless, mobile and volatile liquid. The density was determined by a semimicro pycnometer method to be 1.800 ± 0.001 at 25°. The refractive index measured with an Abbe refractometer was $n^{27}D$ 1.3352. The boiling point determined by the Garcia micro method[10] is 70.7 ± 0.3° at 760 mm., and the melting point −55.0 ± 0.5°. The vapor pressure was measured over the temperature range −15 to 68° by the modified isoteniscope method[10] and the data fitted by the rapid graphical method[10] to the equation: $\log_{10} p = 7.7830 - \dfrac{1595.5}{t°\text{C.} + 255}$ By direct weighing of a bulb of vapor of $Ni(PF_3)_4$ at a known temperature and pressure, the molecular weight was found to be 409.2 (calcd. 410.8).

The chemical properties of $Ni(PF_3)_4$ and its thermal stability show that this compound is more stable than either nickel carbonyl or the compounds $Ni(PCl_3)_4$ and $Ni(PBr_3)_4$.

Tetrakistrifluorophosphine nickel is insoluble in water, does not react with it in the cold, and can be volatilized in steam with little hydrolysis. The compound can be distilled in nitrogen atmosphere at its normal boiling point with inappreciable decomposition. There is no attack on glass or mercury at temperatures up to the boiling point. On igniting in air or oxygen, the vapor of $Ni(PF_3)_4$ explodes forming metallic nickel. The compound reacts with aqueous solutions containing strong oxidizing agents such as potassium permanganate and potassium dichromate, which oxidize it slowly in the cold; hot solutions of silver nitrate and mercuric chloride are also very slowly reduced; there is no reaction with acidified sodium iodide solutions. With concentrated nitric acid, $Ni(PF_3)_4$ reacts violently; with cold concentrated sulfuric acid there is no reaction, but on heating decomposition occurs and nickel sulfate is formed. Ammonium hydroxide solutions rapidly decompose $Ni(PF_3)_4$ in the cold to give a brown solution which on warming is reduced to metallic nickel. Sodium hydroxide reacts rapidly in the cold to give a yellow precipitate and a solution containing phosphite and fluoride; the yellow precipitate is reduced on heating the solution to metallic nickel.

Tetrakistrifluorophosphine nickel is very soluble in benzene and toluene, somewhat less soluble in pentane and cyclohexane, and still less soluble in chlorinated hydrocarbons such as carbon tetrachloride. It is sparingly soluble in carbon disulfide, and unlike $Ni(CO)_4$ and $Ni(PCl_3)_4$ does not react with it even on heating. The compound is insoluble in ethanol, but reacts on heating to give a colorless solution; it is soluble in acetone and ether with no apparent reaction. Although $Ni(PF_3)_4$ is sparingly soluble in cold pyridine, it reacts on warming to form a greenish-yellow solution, and on standing, a greenish-blue precipitate; although complete analyses of this precipitate have not been made, it contains phosphorus trifluoride, nickel and pyridine and hence is probably a partially substituted compound similar to the compounds formed by nickel carbonyl and pyridine. Bromine reacts vigorously with $Ni(PF_3)_4$ forming nickel bromide and probably PF_3Br_2; iodine reacts slowly to give nickel iodide. Phosphorus trichloride and phosphorus tribromide do not react with $Ni(PF_3)_4$ in the cold but on heating $Ni(PF_3)_4$ with phosphorus tribromide a yellow solution is formed; no substitution compounds have been formally characterized yet but there is qualitative evidence for the formation of a volatile yellow compound, probably $Ni(PF_3)_3(PBr_3)$.

For the metal carbonyls, Pauling[11] and others have advanced the idea of multiple covalent bonding to the central metal atom by the use of subvalence orbitals, and Chatt[3] has discussed the role of the ligand as an acceptor system. The tetrakistrihalogenophosphine nickel compounds are probably rather similar in structure to nickel carbonyl and $Ni(PCl_3)_4$ has been shown to be diamagnetic[2] suggesting that the nickel atom has an effective atomic number of 36 like $Ni(CO)_4$. The very strongly electronegative fluorine in phosphorus trifluoride is probably more effective than chlorine in phosphorus trichloride in freeing by ionic resonance a stable orbital on the phosphorus atom for use in forming π bonds with *d* electrons from the central nickel atom. The decreasing stability of $Ni(PX_3)_4$ from phosphorus trifluoride to phosphorus bromide is, in the main, probably due to decreasing availability of stable orbitals in the phosphorus atom and a consequent increase in the polar nature of the Ni–P bond.

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Antimony Trichloride Substitution Compounds with Nickel and Iron Carbonyls

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Previous studies[2a,b] have led to the characterization of the tetrakistrihalogenophosphine compounds $Ni(PX_3)_4$, formally analogous to nickel carbonyl. Stability decreases from the volatile PF_3-compound through the non-volatile PCl_3- and PBr_3-compounds. This paper reports efforts that have been made to produce similar compounds by the interaction of antimony trichloride with nickel carbonyl and iron pentacarbonyl, which have led to the identification of mixed carbonyltrichlorostibine products.

By the interaction of nickel carbonyl with excess antimony trichloride in a cyclohexane solution at ordinary temperatures, partial replacement of carbon monoxide occurs and a pale buff precipitate was obtained. This was removed, washed with cyclohexane, and dried in a stream of dry nitrogen. Analyses[3] were in agreement with the formula for the compound trichlorostibine-triscarbonmonoxide nickel, $Ni(CO)_3SbCl_3$: Ni, 16.0 (calcd. 15.85); Sb, 32.3 (calcd. 32.8); Cl, 28.7 (calcd. 28.8); the presence of carbon monoxide in the compound was shown qualitatively.

A similar reaction occurs between iron pentacarbonyl and antimony trichloride in benzene solution, and a pale yellow

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[3] N. H. Furman, Editor, "Scott's Standard Methods of Chemical Analysis," 5th Edition, D. Van Nostrand Co., New York, N. Y., 1939.