Technical Papers

The Preparation and Properties of Tetrakistrichlorophosphine Nickel[1]

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Trivalent phosphorus compounds have an electron pair available for the formation of dative covalent bonds. A number of complex compounds of divalent palladium and platinum have been prepared which contain phosphorus trihalides, trialkyls, trialkoxy derivatives, trihydroxide (phosphorous acid), and trihydride (phosphine) (*1, 2*). Since these compounds are analogous in many ways to the carbonyl complexes of divalent palladium and platinum halides (*1*), trivalent phosphorus might be expected to form analogs of other metal-carbonyl complexes and possibly analogs of the zero-valent metal carbonyls such as $Ni(CO)_4$. Such a possibility has recently been envisaged by Chatt (*2*) for phosphorus trifluoride.

In 1936, A. A. Blanchard, of MIT, predicted that phosphorus trichloride should form an analog of nickel tetracarbonyl, and from a consideration of the effective atomic number and molecular symmetry suggested that the compound would be volatile. At that time, at the suggestion of Professor Blanchard, one of the authors (JWI) made preliminary attempts to prepare the analog of nickel tetracarbonyl with active nickel (from the low-temperature reduction of nickel formate with hydrogen) and phosphorus trichloride vapor or liquid. A definite exothermic reaction occurred, but only small amounts of compound were recovered from several runs. Direct displacement of carbon monoxide from nickel tetracarbonyl in a sealed tube was then tried. The desired reaction occurred, as indicated by the yellow color that developed in the solution of phosphorus trichloride. When the reaction tube was cooled in liquid air prior to opening, the color faded and no product was isolated from the mixture. Subsequent observations of this system suggest a readily reversible equilibrium:

$$Ni(CO)_4 + 4PCl_3 = Ni(PCl_3)_4 + 4CO.$$

The equilibrium is shifted to the left at low temperatures, but the reaction goes readily if the CO is allowed to escape.

After noting the lack of volatility of the compound, work was discontinued until recently. We have now separated the compound, tetrakistrichlorophosphine nickel, and report some of its properties, together with a few studies on related syntheses. Complete replacement of the 4 dative groups in nickel tetracarbonyl has also been achieved by Hieber (*3*) with phenyl isocyanide.

Preparation. The light-yellow tetrakistrichlorophosphine nickel, $Ni(PCl_3)_4$, is readily formed by direct action in the liquid phase of phosphorus trichloride on nickel tetracarbonyl. Excess phosphorus trichloride is added to the carbonyl, whereupon CO is immediately evolved and the solution becomes pale-yellow in color; the reaction is completed by heating on a steam bath under a reflux condenser. Most of the excess of the phosphorus trichloride is removed by distillation to leave a yellow solution from which the coarsely crystalline precipitate may be obtained on cooling. The method of separation used, however, has been to dissolve the residue in pentane at room temperature and to crystallize the product as fine crystals by cooling the solution to $-60°$ C. Two crystallizations are sufficient to remove all phosphorus trichloride. The solid is dried on a porous plate. All crystallizing and drying operations are carried out in an atmosphere of dry CO_2.

Analysis. For determinations of phosphorus and nickel, the compound was destroyed by boiling with strong nitric acid, with the addition of a few drops of hydrogen peroxide. Gravimetric determinations were made (*4*) of nickel by the dimethylglyoxime method and of phosphorus by the ammonium molybdate method. For the determination of chloride, the compound was destroyed by boiling with strong sodium hydroxide, and, after acidification with nitric acid, the chloride was precipitated with silver nitrate from 3*N* nitric acid solution. The results of analyses are given in Table 1, the sum of the average percentages being 99.82%.

TABLE 1

Element	Determined %	Calcd for $Ni(PCl_3)_4$%
Ni	9.67 9.62	9.65
P	20.25 20.30	20.35
Cl	69.97 69.85	70.00

Properties. Tetrakistrichlorophosphine nickel is a thermochroic crystalline solid, being pale-yellow at room temperatures and white on cooling to about $-30°$ C. The compound is stable in air and unreactive with water at room temperatures over a period of several days. With dilute acids, concentrated sulfuric acid, or concentrated hydrochloric acid, it reacts very slowly in the cold. In hot solutions attack is quite rapid. Ammonium hydroxide reacts rapidly to give a brown solution. Sodium hydroxide reacts very slowly, giving a black precipitate and a solution of sodium phosphite. On heating, no decomposition occurs below 120° C; at higher temperatures blackening and loss of phosphorus trichloride occur, and there is evidence

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for the formation of nickel chloride and polymeric phosphorus dichloride. The tetrakistrichlorophosphine nickel appears to be nonvolatile.

The compound is readily soluble in organic solvents. With dry, air-free, inert solvents such as benzene, carbon tetrachloride, pentane, and cyclohexane, there is only very slow decomposition at room temperatures. On heating the solutions, decomposition is rapid, to give black precipitates of nickel. The solubility in pentane at $-50°$ C is 0.9 g/100 g pentane. In solution in organic solvents such as alcohols and ketones, decomposition leading to green and brown solutions is quite rapid. With carbon disulfide, rapid blackening of the solution occurs; the products of this reaction have not been studied in detail, but the reaction appears to be similar to that reported for nickel carbonyl and carbon disulfide (*5*), where polymeric carbon monosulfide was formed.

Determination of the molecular weight by the method of freezing point depression in benzene gave a value of 600 ± 20, corresponding to the monomeric state of $Ni(PCl_3)_4$ (theoretical mol wt, 608).

Single hexagonal crystals of $Ni(PCl_3)_4$ several millimeters long can be grown by slow cooling of benzene solutions from 25° C to 10° C. The density of the compound, determined by the standard pycnometer method of weighing in water, is 2.10 ± 0.01 at 25° C.

The magnetic susceptibility of $Ni(PCl_3)_4$ at 25° C has been measured by the Gouy method. Air ($K = +0.029 \times 10^{-6}$ cgs) and water ($K = -0.72 \times 10^{-6}$ cgs) were used as standards, and as a check on the calibration curve of field vs. current, for the magnet used. In all cases the field was varied from about 5,000 to 9,500 oersteds, and the susceptibility values obtained were independent of field strength, showing the absence of ferromagnetic impurities. Measurements made after successive crystallizations from pentane solutions gave a value for the specific mass susceptibility χ for $Ni(PCl_3)_4$ of -0.355×10^{-6} cgs. For PCl_3 under the same conditions, χ is -0.455×10^{-6} cgs; the molar susceptibilities χ_m are then -216.0×10^{-6} cgs and -62.3×10^{-6} cgs for $Ni(PCl_3)_4$, and PCl_3, respectively. In the compound $Ni(PCl_3)_4$ the apparent molar susceptibility of nickel is hence $+33 \times 10^{-6}$ cgs. The measurements thus show complete filling of the nickel *d* orbitals and the absence of unpaired electrons, confirming that nickel is in the zero-valent state in the compound; the small paramagnetism may be of the temperature-independent type found in $KMnO_4$, $K_2Cr_2O_7$, etc.

Related reactions. Evidence has been obtained for intermediate replacement compounds in the reaction of nickel carbonyl and phosphorus trichloride, although these have not as yet been isolated. Preliminary investigations of the reaction of nickel carbonyl with phosphorus tribromide directly and in pentane solution have been made. At room temperature, the reaction is rapid, CO being evolved with effervescence, and a yellow solution is formed which later turns orange-red as the reaction proceeds. No bromide replacement compounds could be isolated from these solutions, however; if the orange-colored solution is warmed or allowed to stand for an hour or so, even at 0° C, decomposition occurs and a brown flocculent precipitate is produced.

Tetrakistribromophosphine nickel, $Ni(PBr_3)_4$, has been made by the reaction of PBr_3 and $Ni(PCl_3)_4$ and will be described subsequently, together with the preparation and properties of other complexes of nickel carbonyl and iron pentacarbonyl formed with the lower halides of phosphorus and antimony.

With AsF_3, $AsCl_3$, and $AsBr_3$, nickel carbonyl reacts readily in both liquid and vapor phases, liberating CO and forming black products; no definite compounds have been isolated.

No replacement compounds have yet been isolated from the reaction of PCl_3 with molybdenum, wolfram, and chromium hexacarbonyls at temperatures up to 150° C; solid products obtained appear to be mainly the metal phosphides.

References

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The Respiratory Effect of Ro 2-3198 (3-Hydroxy Phenyldimethylethylammonium Bromide) in Syncurinized Dogs[1]

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Most anesthesiologists find little use for neostigmine in the treatment of overdosage of curare products, being satisfied with augmented or controlled respiration for a period of time. Furthermore, the undesirable cholinergic effects and prolonged action of neostigmine have limited its use in anesthesia practice.

However, a short-acting anticurare drug with minimal undesirable cholinergic responses and low toxicity would most assuredly have a place in the treatment of depression from curare. A long series of phenolic quaternary ammonium salts has been studied, and among these derivatives Ro 2-2561 (3-hydroxy phenyltrimethylammonium bromide) (*1–4*), Ro 2-2017 (3-acetoxy phenyltrimethylammonium methylsulfate) (*5–7*), and Ro 2-3198 (3-hydroxy phenyldimethylethylammonium bromide) (*2–4*) were found to be effective in antagonizing curare activity.

We became interested in the response of the anticurare drug Ro 2-3198 to syncurine (bistrimethylammonium decane bromide) because its curarelike ac-

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[1] Preliminary report.