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 $n^{27}\text{D}$ 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: $\log_{10} p = 7.7830 - \frac{1595.5}{t°\text{C.} + 255}$ 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

BY GEOFFREY WILKINSON[1]

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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precipitate is obtained. The analyses[3] support the formula for bistrichlorostibine-triscarbonmonoxide iron, $Fe(CO)_3(SbCl_3)_2$: Fe, 10.4 (calcd. 9.37); Sb, 39.3 (calcd. 40.83); Cl, 34.4 (calcd. 35.70). The presence of carbon monoxide was shown qualitatively and a rough qualitative estimate of the gas evolved on thermal decomposition of the compound agrees with the other analyses. Like iron pentacarbonyl, the antimony trichloride complex is photosensitive, darkening on exposure to light, and consequently the reactions were carried out in absence of light.

Both the nickel and iron complexes are amorphous powders, insoluble in organic solvents such as benzene, pentane, cyclohexane and carbon tetrachloride. Carbon disulfide reacts, liberating carbon monoxide and leaving dark colored residues. With alcohols and acetone, decomposition occurs, carbon monoxide is evolved, and solutions of divalent nickel and iron result, leaving a precipitate of antimony oxychloride. With water, dilute acids and alkalies, similar rapid reactions occur with loss of carbon monoxide, giving nickelous or ferrous solutions or hydroxides, antimony oxychloride or antimonate. The compounds are decomposed on heating to give carbon monoxide and, in the case of the iron compound, some metal carbonyl together with antimony trichloride. On treating the compounds with phosphorus trichloride, there is a vigorous reaction evolving carbon monoxide and it is possible that further substitution occurs; the color of the residue is darker but no analyses have been made.

The great difference in properties between the antimony trichloride substitution compounds of nickel and those formed by the phosphorus halides may be due to the increasing inertness of the electron pair in the antimony halides compared with the phosphorus halides. Presumably there is also a lowered tendency to form π bonds with nickel which operate to stabilize metal complexes. Efforts to identify further antimony trichloride substitution products were without success.

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The Propargylic Rearrangement. IV. The Carbonation Products of Propargylmagnesium Bromide

BY JOHN H. WOTIZ, JOSEPH S. MATTHEWS AND JOHN A. LIEB

Recently it was found that primary propargylic bromides,[1] $R—C\equiv C—CH_2Br$ (I), where R signifies the normal propyl, butyl or amyl group, can be converted to Grignard reagents by means of amalgamated magnesium using a newly developed high dilution technique.[2] These Grignard reagents on low temperature carbonation yielded stable solid allenic acids, $\underset{\displaystyle CO_2H}{R—\overset{}{C}}=C=CH_2$ (II), liquid acetylenic acids, $R—C\equiv C—CH_2CO_2H$ (III) and unidentified dimeric acids. Secondary and tertiary propargylic bromides[3] were also converted into stable solid allenic acids by a similar procedure.

Prévost, *et al.*,[4] recently reported the conversion of propargyl bromide into a Grignard reagent which they carbonated at −80°. Upon hydrolysis they isolated a solid acid melting at 73° to which they assigned the structure $H—C\equiv C—CH_2CO_2H$ (IV) (*e.g.*, III where R equals H). They also found a liquid acidic portion and resins thought to be derived from the unstable butadienoic acid, $CH_2=C=CH—CO_2H$ (V) (*e.g.*, II where R equals H). Since these workers did not state the method used in assigning of structure of the solid acid, we thought they might be in error because: (a) the acid IV was previously prepared[5] by the oxidation of 3-butynol-1 and found to melt at 83°, (b) they regarded allenic acids (II) as unstable which is contrary to our findings.

We have repeated some of the above-described work treating propargyl bromide with amalgamated magnesium in the cyclic reactor,[2] and poured the formed Grignard reagent on Dry Ice. The yield of the crude acidic portion was 28% which is lower than the yields obtained (52 to 72%)[1] from I. On distillation a semi-solid was obtained which on repeated crystallization yielded 3-butynoic acid (IV), m.p. 83–84°, in form of white plates. Its structure was established by elementary analysis and infrared spectrum, Fig. 1, curve A. The spectrum shows a strong absorption band near 3270 cm.$^{-1}$ characteristic for the $H—C\equiv$ structure, and the absence of isomeric compounds. The mother liquor from IV was freed of solvent by redistillation. The distillate, b.p. 75–80° at 5 mm., had the same elementary analysis as IV. Its spectrum (Fig. 1, curve B) showed it to be a mixture of IV, the allenic

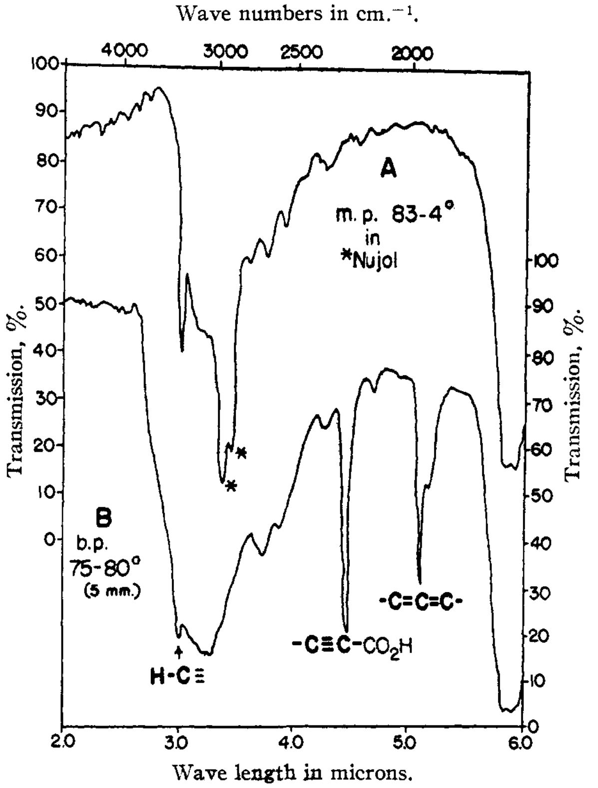

Fig. 1.

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