derivatives are more stable than the corresponding bromo compounds and the cyclic polyolefin complexes possess greater stability than the cyclic monoolefin derivatives. In an attempt to obtain a more quantitative measure of the stability of the complexes a series of samples was placed in an evacuated tube and the change in pressure, with increasing temperature, was measured manometrically. The results were erratic and the pressures observed corresponded closely to the vapor pressures reported for the pure hydrocarbons. The decomposition temperatures of several of the copper(I) olefin complexes have been reported and in particular dicyclopentadienecopper(I) chloride reportedly[6] decomposed at approximately 115°. We have observed a change in the character of the crystals at this temperature; however, our pressure measurements indicated extensive decomposition had occurred as low as 50° and the reasons for the collapse of the crystals at 115° are obscure.

Experimental

Copper(I)–Olefin Compounds.—In a typical reaction 0.015 mole of the cyclic olefin was added to a solution containing 1.71 g. (0.01 mole) of copper(II) chloride dihydrate and 10–15 ml. of 95% ethanol. The solution was cooled to 0° and sulfur dioxide gas was bubbled into it, just until the initial precipitation of solid product was noted. The reaction mixture was kept at 0° for 2–3 hr., filtered, and the crystalline product was washed with 5 ml. of the olefin which had been previously cooled to 0°, followed by several 5-ml. portions of cold methanol. The copper(I) bromide derivatives were prepared by a similar procedure with the substitution of copper(II) bromide for copper(II) chloride hexahydrate.

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A New Cobalt Hydride

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In a recent paper, Chatt, *et al.*,[1] described a derivative of zero-valent cobalt with 1,2-bis-(diphenylphosphino)-ethane (L), of formula CoL_2, obtained by reduction of $CoBr_2L_2$ with sodium hydridoborate. At about the same time, while working on the hydrides of the metals of group VIII and studying the possibility of obtaining cobalt hydrides stabilized with tertiary phosphine or similar ligands, we isolated and characterized the cobalt hydride $CoHL_2$, where L is the same ligand used by Chatt, *i.e.*, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$. This hydride was prepared by mixing at room temperature, under nitrogen atmosphere, a solution of $CoBr_2$ and L in anhydrous tetrahydrofuran and by reducing the green suspension thus obtained with an excess of $LiAlH_4$.

$CoHL_2$ is a red crystalline solid, which rapidly decomposes in solution and in the solid state on exposure to air: it is slightly soluble in acetone, benzene, and ethanol and insoluble in pentane; it was recrystallized from benzene by addition of pentane.

The value of the atomic susceptibility of the metal in this hydride, *viz.*, the molar susceptibility of $CoHL_2$ corrected from the diamagnetism of other atoms, equals zero. This diamagnetic behavior completely agrees with the electronic structure d^8 of monovalent cobalt in a high ligand field.

The infrared spectrum of $CoHL_2$, in Nujol mull, shows at 1884 $cm.^{-1}$ a band of medium intensity ascribable to the stretching Co–H. This assignment was confirmed by comparing the infrared spectrum of $CoHL_2$ with that of $CoDL_2$ prepared under identical experimental conditions using $LiAlD_4$.

The deuteride does not show the band at 1884 $cm.^{-1}$, but a new band at 1358 $cm.^{-1}$ as expected for the Co–D stretching.

An analogous reaction was carried out with triphenylphospine as the ligand and $NaBH_4$ as the reducing agent, but the product so obtained, which was very unstable and had a poor solubility in organic solvents, could not be purified enough to measure the magnetic susceptibility. This compound shows an absorption at 1739 $cm.^{-1}$. The assignment of this band to Co–H stretching, although very probable, could not be confirmed on the deuteride because the reaction with $LiAlD_4$ (and $LiAlH_4$) takes place in this case to give complete decomposition.

Experimental

The 1,2-bis-(diphenylphosphino)-ethane was prepared by the method of Chatt and Hart.[2]

Melting points were determined in evacuated tubes. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer equipped with a rock salt prism. Susceptibilities were measured by the Gouy method.

Hydrido-di-[1,2-bis-(diphenylphosphino)-ethane]-cobalt, CoH-$[C_2H_4(P(C_6H_5)_2)_2]_2$.—A solution of 1,2-bis-(diphenylphosphino)-ethane (8 g., 0.01 mole) in dry THF (30 ml.) was added, under nitrogen, to a stirred solution of $CoBr_2$ (2.2 g., 0.01 mole) also in THF (20 ml.). The resulting green suspension was treated with a suspension of $LiAlH_4$ (1.2 g., 0.03 mole) in THF (30 ml.). After a few minutes red crystals separated. They were filtered under nitrogen, washed with dry THF, and dried under vacuum. The compound was recrystallized from benzene by addition of pentane. The purified compound is moderately stable to air, darkening in a few hours; m.p. 265°, dec. 280°.

Anal. Calcd. for $C_{52}H_{49}CoP_4$: C, 72.9; H, 5.76; P, 14.46. Found: C, 72.4; H, 5.6; P, 14.6.

Deuterido-di-[1,2-bis-(diphenylphosphino)-ethane]-cobalt, CoD-$[C_2H_4(P(C_6H_5)_2)_2]_2$.—This compound was prepared in the same way as the analogous hydride derivative but using $LiAlD_4$ in dry THF; m.p. 264° dec.

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[1] J. Chatt, F. A. Hart, and D. T. Rosevear, *J. Chem. Soc.*, 5504 (1961).

[2] J. Chatt and F. A. Hart, *ibid.*, 1378 (1960).

Anal. Calcd. for $C_{52}H_{48}DCoP_4$: C, 72.8; H, 5.9. Found: C, 72.1; H, 5.65.

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Convenient Methods for Preparing $S_3N_2Cl_2$ and S_4N_3Cl

BY WILLIAM L. JOLLY, KEITH D. MAGUIRE, AND
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When a suspension of ammonium chloride in S_2Cl_2 is refluxed, the principal reaction products are NSCl and HCl.[1]

$$NH_4Cl + 2S_2Cl_2 \longrightarrow 3S + NSCl + 4HCl$$

If a sufficiently large amount of ammonium chloride is used, transparent orange crystals of $S_3N_2Cl_2$ soon begin to form in the condenser above the level of the refluxing liquid. When practically all the S_2Cl_2 has been consumed, the $S_3N_2Cl_2$ which has formed in the condenser may be removed. However, if S_4N_3Cl is the desired product, the reaction flask is removed, and a flask containing carbon tetrachloride is attached to the condenser containing the crystals of $S_3N_2Cl_2$. The carbon tetrachloride is boiled so that the refluxing liquid washes the crystals into the flask. During this process the crystals first turn green (S_3N_2Cl) and finally yellow (S_4N_3Cl).

It is believed that the vapors of S_2Cl_2 and NSCl react to form the $S_3N_2Cl_2$.

$$2NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2$$

This reaction does not begin immediately upon refluxing the mixture of ammonium chloride and S_2Cl_2 because of the presence of chlorine[2] in the effluent gases. Chlorine is known[1] to react with $S_3N_2Cl_2$ according to the equation

$$Cl_2 + S_3N_2Cl_2 \longrightarrow 2NSCl + SCl_2$$

However, when the concentration of sulfur in the S_2Cl_2 increases sufficiently to prevent, or almost prevent, the evolution of chlorine,[4] the $S_3N_2Cl_2$ deposition begins. Two types of experiments attest to this interpretation of the delayed deposition of $S_3N_2Cl_2$. First, when relatively small amounts of ammonium chloride are used, no $S_3N_2Cl_2$ is deposited even when the refluxing is continued until the ammonium chloride is completely consumed. (In such cases, the concentration of sulfur never becomes high enough to prevent effectively the evolution of chlorine.) Second, when sulfur is added to the reaction mixture, the time to the first appearance of $S_3N_2Cl_2$ is greatly reduced. Indeed $S_3N_2Cl_2$ is produced when sulfur is added to a reaction mixture that ordinarily does not produce $S_3N_2Cl_2$.

When $S_3N_2Cl_2$ is heated to 80–95° *in vacuo*, greenish black S_3N_2Cl is formed.[1]

$$3S_3N_2Cl_2 \longrightarrow 2S_3N_2Cl + 2NSCl + SCl_2$$

We believe that this pyrolysis is the best method for preparing S_3N_2Cl. When S_3N_2Cl is heated to 130–150° *in vacuo*, a variety of products, including NSCl and SCl_2, are evolved, and a residue of pure S_4N_3Cl is formed. In view of these facts and the fact that a dark green intermediate is observed during the refluxing of carbon tetrachloride with $S_3N_2Cl_2$, we believe that the over-all conversion of $S_3N_2Cl_2$ to S_4N_3Cl by boiling carbon tetrachloride proceeds *via* S_3N_2Cl. Meuwsen[5] carried out this same conversion, but he stated that the reaction proceeds smoothly only in the presence of S_2Cl_2, and he did not report the intermediate formation of S_3N_2Cl.

Experimental

Preparation of S_4N_3Cl.—NH_4Cl (50 g.) and 25 ml. of S_2Cl_2 were placed in a 500-ml. round-bottomed flask fitted with an air condenser (75 cm. long and 22 mm. in diameter) to the top of which a calcium sulfate drying tube was attached. The mixture was refluxed gently using a heating mantle. The heating was adjusted so that the level of the refluxing S_2Cl_2 was just above the neck of the flask. During approximately 16 hr. of refluxing, orange crystals of $S_3N_2Cl_2$ collected in the air condenser. At the end of this time the heating was stopped and the apparatus was allowed to stand overnight so that most of the liquid adhering to the crystals could drain away. (This liquid contained appreciable amounts of dissolved hydrogen chloride which, if not removed, resulted in a product contaminated with ammonium chloride.) The reaction flask was removed and *immediately* replaced with a similar flask containing 100 ml. of *dry* carbon tetrachloride (freshly distilled from $CaSO_4$). The carbon tetrachloride was then refluxed up into the air condenser over the crystalline deposit. The material first turned dark green and partly bright yellow and fell into the flask. Shaking the assembly or even inserting a long glass rod down the air condenser was sometimes necessary in order to assist the sublimate down into the reflux flask. The carbon tetrachloride was boiled until all the dark material was converted into a bright yellow solid (approximately 4 hr.). The solid S_4N_3Cl was filtered from the carbon tetrachloride while it was still warm; it was washed with dry carbon tetrachloride, and finally dried in a vacuum desiccator; yield 4.5 g.

Anal. Calcd. for S_4N_3Cl: N, 20.38; S, 62.34; Cl, 17.24. Found: N, 21.02; S, 62.09; Cl, 17.58. The infrared spectrum (KBr disk) showed peaks at 8.55, 10.0, and 14.75 μ, and was identical with the infrared spectrum of a sample of S_4N_3Cl prepared in the usual way.[6]

Preparation of $S_3N_2Cl_2$.—The orange $S_3N_2Cl_2$ which formed in

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[1] K. D. Maguire, J. J. Smith, and W. L. Jolly, to be published.

[2] Most of the chlorine probably arises from the decomposition of the S_2Cl_2. When S_2Cl_2 is fractionally distilled at atmospheric pressure, SCl_2 comprises the first fraction. Because SCl_2 is known to decompose appreciably to chlorine,[3] and because in these syntheses the more volatile vapors are being carried away by a stream of hydrogen chloride, it is reasonable to expect chlorine in the initial off-gases.

[3] J. W. George, *Progr. Inorg. Chem.*, **2**, 33 (1960).

[4] Presumably sulfur reduces the concentrations of SCl_2 and Cl_2 in the liquid S_2Cl_2 by shifting the equilibria $S_2Cl_2 = S + SCl_2$ and $S_2Cl_2 = 2S + Cl_2$.

[5] A. Meuwsen, *Ber.*, **65**, 1724 (1932).

[6] M. Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin, 1957, p. 155.