nitryl fluoride by the reaction of fluorine with nitrogen dioxide, Hetherington and Robinson[3] found this method to be unsuitable because the highly exothermic reaction, often accompanied by a flame, yields a mixture of oxyfluorides contaminated with silicon tetrafluoride. Aynsley, *et al.*,[6] developed a simpler method of preparation in which anhydrous sodium nitrite was allowed to react with elemental fluorine in glass equipment. Although a nearly quantitative yield of nitryl fluoride was obtained, it was again necessary to control the reaction temperature by adjusting the fluorine flow. This was required to prevent the nitrogen dioxide, formed as an intermediate, from burning with a hot, yellow flame in the fluorine and causing considerable glass attack.

We have found that nitryl fluoride may be prepared very readily in high yields by passing nitrogen dioxide over a stirred bed of cobaltic fluoride at 300°. The crude product obtained in an 89.5% yield based on N_2O_4 was essentially pure nitryl fluoride containing only trace amounts of nitrogen dioxide. The cobalt difluoride formed in the reactor was reconverted to the trifluoride by treatment with fluorine.

As shown, this reaction, unlike the method of Aynsley and co-workers,[6] utilizes the fluorine quantitatively.

$$N_2O_4 + 2CoF_3 \longrightarrow 2FNO_2 + 2CoF_2$$

$$2CoF_2 + F_2 \longrightarrow 2CoF_3$$

An attempt to prepare nitrosyl fluoride by passing nitric oxide over heated cobaltic fluoride was unsuccessful. Either the nitric oxide or the expected product reacted completely with the cobalt fluoride, perhaps to form an addition compound, and no gaseous products were obtained.

Experimental

Nitrogen dioxide (40 g., 0.85 mole) was passed over a stirred bed of cobaltic fluoride (9 moles) at 300° during 30 min. The stirred monel reactor was identical with that described by Barbour, Barlow, and Tatlow.[7] Crude FNO_2 (50 g., 0.77 mole) was collected in liquid nitrogen-cooled traps.

The crude product was distilled from a copper flask held at −60 to −65° through copper tubing into a copper receiver maintained at −78°. The product (43 g.) distilled into the receiver. About 5 g. of product remained in the distillation flask, mainly in the vapor phase.

Anal. Calcd. for FNO_2: N, 21.6; F, 29.2. Found: N, 21.6; F, 28.6.

Attempts to determine the molecular weight of the FNO_2 were hindered by the very fast reaction of the product with the glass equipment.

The cobalt difluoride formed in the reactor was reconverted to the trifluoride by treatment with fluorine. The temperature of the reactor was maintained at 300° during this operation. The regeneration cycle was considered completed when the exit gases from the reactor would ignite cotton linters.

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[7] A. K. Barbour, G. B. Barlow, and J. C. Tatlow, *J. Appl. Chem.*, **2**, 127 (1952).

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Metal–Olefin Compounds. III. Some Compounds of Copper(I) Containing Cyclic Olefins[1]

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Received May 11, 1963

The reactions of copper(I) chloride and copper(I) bromide with olefinic and acetylenic hydrocarbons have received considerable attention[3,4] because of the similarity to the silver(I)–olefin complexes and possible commercial applications involving the separation of olefins *via* the formation of copper(I) compounds. Recent interest[5,6] in the copper–olefin compounds has been focused on the preparation of compounds containing cyclic olefins; however, very little information exists on the structures[7–9] of these compounds.

Our continuing interest in the properties and structures[10] of metal–olefin compounds prompted us to prepare a series of copper(I)–olefin compounds. An examination of the previously reported methods for the preparation of these compounds indicated that the products formed were polycrystalline materials unsuitable for single crystal X-ray diffraction studies or finely divided powders of poorly defined stoichiometry. We have found that suitable crystalline products can be isolated by treating an ethanol solution containing the appropriate copper(II) halide and an olefinic compound[11] with sulfur dioxide.

This procedure is particularly adaptable to the isolation of complexes containing cyclic polyolefins; however, cyclic monoolefins such as cyclohexene, cycloheptene, and cyclooctene also yield complexes. The complexes containing monoolefins were relatively unstable and reliable analytical results could not be obtained on this series.

Several factors have been noted that influence the composition, purity, yield, and crystallinity of the product isolated from this procedure. The quantity of ethanol used as a solvent appears to directly influence

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[1] For the previous paper in this series, see *J. Am. Chem. Soc.*, **83**, 2768 (1961).

[2] To whom communications concerning this paper should be addressed.

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[8] J. H. van den Hende, Abstracts, Annual Meeting, Am. Cryst. Assoc., 1962, p. 36.

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[10] The structures of several of the copper(I)–olefin compounds have been or are currently under investigation and the results of these studies will be reported in the near future.

[11] After completion of this phase of the problem, another preparative method was reported by Schrauzer and Eichler.[6] This technique has not been investigated by us as to suitability for preparing crystalline complexes of copper(I)–olefins for X-ray diffraction procedures.

TABLE I

PROPERTIES AND ANALYSIS OF COPPER(I)–OLEFIN COMPOUNDS

Coordinated olefin	Complex formula	Yield, %	Analysis[a]				Color	Density,[a] g. cm.$^{-3}$	Remarks
			Cu	X[b]	C	H			
Norbornadiene	C_7H_8CuCl	52	33.24	18.55	43.99	4.22	Light	1.77	Tetragonal ($P\bar{4}2_1C$)
			33.06	18.59	43.05	4.23	yellow	1.76	8(C_7H_8CuCl)/cell
	C_7H_8CuBr	34	26.97	33.92			Tan		
			26.86	33.40					
1,5-Cyclooctadiene	$C_8H_{12}CuCl$	81	30.67	17.11	46.38	5.84	White		
			30.26	16.94	46.44	5.83			
	$C_8H_{12}CuBr$	96	25.25	31.76	38.18	4.81	Tan		
			25.67	31.83	38.64	5.20			
Cyclooctatetraene	C_8H_8CuCl	55	31.28	17.45	47.30	3.97	Yellow-	1.78	Orthorhombic (Pbca)
			31.84	17.79	45.02	3.85	orange	1.77	8(C_8H_8CuCl)/cell
	C_8H_8CuBr	76	25.66	32.28	38.81	3.26	Light		
			25.74	32.57	38.60	3.68	yellow		
cis-Cyclooctene	$C_8H_{14}CuCl$	..	30.37	16.95	45.93	6.75	White		Product relatively
			30.80	17.30	44.46	6.58			unstable
Dicyclopentadiene	$C_{10}H_{12}CuCl$	69	27.48	15.34	51.95	5.23	White	1.46	Tetragonal cell
			26.26	14.70	53.22	5.34		1.42	32($C_{10}H_{12}CuCl$/cell)
	$C_{10}H_{12}CuBr$	82	23.05	28.99	43.57	4.39	Tan		Product relatively
			22.79	26.96	45.61	4.86			unstable
cis,trans,trans-Cyclododecatriene	$C_{12}H_{18}(CuCl)_2$	42			40.01	5.04	White		
					38.09	3.95			
	$C_{12}H_{18}(CuBr)_2$	..			32.09	4.04	Tan		
					32.46	3.94			
trans,trans,trans-Cyclododecatriene	$C_{12}H_{18}(CuCl)_2$	25	35.30	19.72	40.01	5.04	White		
			33.95	19.10	40.13	5.14			
1,3-Cyclooctadiene	$C_8H_{12}(CuCl)_3$	..	47.05	26.25	23.71	2.99	White		Product relatively
			46.02	26.36	20.31	2.51			unstable

[a] First line for each substance is calculated %; second line is found. [b] X is % halogen in compound.

the yield of the desired compounds. The highest yields were obtained by using the minimum amount of ethanol necessary to obtain a homogeneous mixture of the solvent, olefin, and copper salt. Unfortunately, the products isolated from concentrated solutions were often finely divided materials of low purity. The quantity of solvent necessary to obtain products of the desired purity and crystallinity was determined by trial and error and the yields reported in the Experimental section are for conditions that gave macroscopic crystals of reasonable purity.

The quantity of sulfur dioxide added to the reaction media also influences the purity and crystallinity of the isolated product. Large quantities of sulfur dioxide usually resulted in a finely divided powder of low stability and purity. In general, the addition of sulfur dioxide was carried out until the first traces of precipitation were noted or a perceptible color change occurred in the solution. The quantity of sulfur dioxide added was quite critical in the formation of the norbornadiene and cyclooctatetraene complexes, where the addition of relatively large amounts not only yielded finely divided products but also complexes of different stoichiometry.

Attempts to purify the complexes by recrystallization were unsuccessful due to the low solubility of many of the complexes and the extensive decomposition of soluble compounds. Washing the crystalline products with a minimum amount of cold methanol or a small amount of the chilled olefin followed by a methanol solution of sulfur dioxide usually yielded, upon drying, pure samples of the complexes. The use of chlorinated hydrocarbons, ethers, or alcohols other than methanol for washing the complexes often resulted in extensive decomposition.

The compounds decomposed upon prolonged drying under vacuum or in an inert atmosphere over calcium chloride or phosphorus(V) oxide. The complexes of low stability were dried as thoroughly as possible on the filter and stored at −78°. The relatively stable compounds may be stored in an inert atmosphere over anhydrous calcium sulfate at 0°.

Reduced temperatures and conditions of low humidity were usually advantageous in isolating the copper(I) complexes. Decomposition rates were markedly increased under conditions of high humidity, presumably due to the oxidation of copper(I) to copper(II).

A variety of complexes can be formed between copper(I) and norbornadiene or cyclooctatetraene. Using the procedure described by Abel, Bennett, and Wilkinson,[5] we also have isolated a norbornadienecopper(I) bromide complex that approximates 1:2 stoichiometry. A product of similar stoichiometry also was isolated by the rapid addition of sulfur dioxide to an ethanolic solution of copper(II) bromide containing norbornadiene. A similar occurrence was noted in the chloride series in which compounds containing norbornadiene or cyclooctatetraene with 1:1 or approximately 1:2 stoichiometry were isolated by slight alterations in experimental conditions. The infrared spectra of the 1:1 and 1:2 cyclooctatetraene copper(I) chloride complexes are distinctly different and the 1:2 complex has the same spectrum as the 1:2 compound reported by Schrauzer and Eichler.[6]

Qualitative observations indicate that the chloro 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.

Acknowledgment.—This research was carried out with the aid of a grant from the U. S. Army Research Office, Durham, for which we are grateful. H. L. H. wishes to acknowledge the receipt of an Ethyl Corporation Fellowship.

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A New Cobalt Hydride

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Received May 31, 1963

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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