phine and the isolation of the known[5] $CH_3COCo(CO)_3P(C_6H_5)_3$.

A solution of 0.950 g. of $Co_2(CO)_8$ in about 50 ml. of hexane was stirred with mercury under carbon monoxide. After about 20 hr., the yellow solution was evaporated to dryness in a stream of carbon monoxide, giving a quantitative yield of $Hg[Co(CO)_4]_2$.

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CONTRIBUTION FROM THE
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Resolution of Chromium(III) Hexafluoroacetylacetonate by Gas Chromatography

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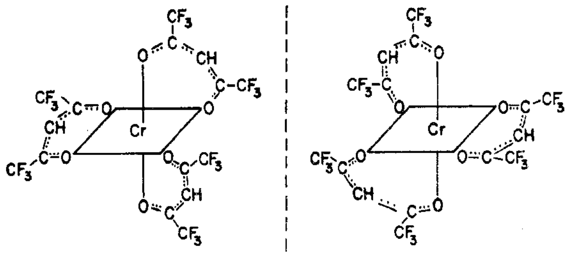
We wish to report the partial resolution of *dl*-tris-(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-chromium(III) (structure I) by gas–solid chromatography.



I

This complex can be prepared by allowing 1,1,1,5,5,5-hexafluoro-2,4-pentanedione to react with chromium(III) nitrate nonahydrate in absolute ethanol. Two g. (0.005 mole) of the chromium salt and 3.12 g. (0.015 mole) of the ligand were combined in 20 ml. of absolute ethanol and heated on a steam bath for 5 min. The solution was evaporated almost to dryness under an air stream, with the formation of green crystals. The product (yield, 1.5 g. or 42%) was separated by filtration and recrystallized from carbon tetrachloride. *Anal.* Calcd. for $Cr(C_{15}H_3F_{18}O_6)$: C, 26.76; H, 0.45; Cr, 7.73; F, 50.80. Found: C, 27.00; H, 0.93; Cr, 7.92; F, 50.57.

The complex is soluble in most common organic solvents and is moderately soluble even in hexane. It is remarkably volatile and sublimes rapidly at room temperature at 0.05 mm. and can even be steam distilled from boiling water. More impressively, the complex steam distils from boiling aqua regia. Increased volatility of the hexafluoroacetylacetonato complexes as compared with corresponding acetylacetonato complexes has been observed for a number of metal ions.[1–4]

A separation of optical isomers by gas chromatography is possible if the column employed is packed with an optically active substrate. In gas–solid chromatography the separation is based on the differences in the adsorptive tendencies of the isomers on the surface of the solid.

Experimental

A column packed with powdered *dextro* quartz (80–120 mesh) was used in this study. Large natural *dextro* quartz crystals were first broken down to pea-size pieces in a jaw crusher. The pieces were heated to 300° and then dumped into ice water.[5] The resulting thermal shock caused numerous ruptures and fissures, and consequently the grinding process was greatly facilitated. The powdered quartz was washed with hot concentrated hydrochloric acid and with distilled water several times. It was dried for 1 hr. at 200° and packed in a Teflon tube 12 ft. long with an inner diameter of 0.25 in. The tube was coiled and inserted in a constant temperature air bath in a Burrell Model K-7 gas chromatography apparatus. The column was conditioned for 1 week at 100° with a stream of purified helium.[6] For the remainder of the experiment the column temperature was maintained at 55°. The flash vaporizer chamber was thermostated at 125° and the detector cell at 150°. The flow rate of the carrier gas was 80 ml./min. Components in the effluent helium stream were collected in a trap immersed in liquid nitrogen.

The sample was taken from a saturated carbon tetrachloride solution of the chromium complex. Fifteen μl.

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[2] H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **78**, 2790 (1956).

[3] R. N. Haszeldine, W. K. Musgrave, F. Smith, and L. M. Turton, *J. Chem. Soc.*, 609 (1951).

[4] A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, *J. Am. Chem. Soc.*, **69**, 1819 (1947).

[5] The authors wish to thank Dr. L. Spialter for suggesting this procedure for pulverizing quartz.

[6] When the column was used without prolonged conditioning, the adsorptive ability of the quartz was greatly reduced. Retention times were considerably longer after conditioning for 1 week as compared with 1 day. It is suspected that mono- or poly-layers of adsorbed water are responsible for the erratic adsorptive behavior of the quartz.

of the solution (containing 0.3 mg. of the complex) was injected into the flash vaporizer chamber. One minute after the sample was injected, carbon tetrachloride appeared in the trap. Most of the carbon tetrachloride was eluted in the first 6 min., but small amounts appeared as late as 25 min. after sample injection. At this point the chromium complex began to be eluted. It was eluted rapidly at first and then much more slowly. Tailing was very extensive, and very small quantities of the complex were still being eluted several hours later. After 20 hr. the column was dismantled and examined to see if any of the complex remained adsorbed or had decomposed. Only 60 to 70% of the complex could be accounted for in the eluted fractions. Attempts to extract the chromium complex from the quartz with chloroform and ethanol were unsuccessful. However, destructive oxidation with potassium permanganate in sulfuric and nitric acids and subsequent treatment with sodium azide, ammonium hydroxide, and freshly prepared diphenylcarbazide showed a positive test for chromium.[7]

An early fraction of the eluate, collected over the period from 25 to 35 min. after injection, was dissolved in carbon tetrachloride and checked for optical activity. The observed rotation was +0.043 ± 0.008° at the sodium D line at 25°. The concentration of the complex was determined spectrophotometrically at 359 mμ, and the apparent specific rotation was calculated to be +260°. It is concluded that at least a partial resolution was accomplished.

The experiment was repeated several times under somewhat different conditions. Observed rotations ranged from +0.034 ± 0.003° to +0.051 ± 0.006° and apparent specific rotations varied between +80 and +190°.

Acknowledgment.—The authors wish to thank Dr. B. W. Ponder for his helpful suggestions.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Infrared Spectral Evidence for Dative π-Bonding in Ethynylsilanes

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Many observations of the physical and chemical properties of aryl silicon compounds indicate that dative π-bonding can take place from the filled aromatic π-orbitals into the vacant 3d orbitals of silicon.[1] The direction of additions to vinylsilanes provides indirect evidence which suggests that similar π-bonding may take place involving olefinic π-electrons.[2] In R_3Si compounds, it is probable that a degenerate pair of orbitals (d_ϵ) is available on silicon for dative π-bonding.[3] Such back-bonding might be especially favorable in ethynylsilanes, for in these compounds two equivalent dative π-bonds might be formed involving both of the acetylenic π-orbitals.

Accordingly, a study was undertaken of some of the vibrational frequencies of ethynylsilanes, and of the properties of these compounds as proton acceptors and proton donors in hydrogen bonding.[4] The C≡C and C–H stretching frequencies of the ethynylsilanes suggest substantial dative π-bonding in these compounds. This interpretation is substantiated by the hydrogen bonding results, which show that ethynylsilanes are better proton donors and poorer proton acceptors than 1-alkynes. Ethynyltrimethylstannane was studied for comparative purposes, but the results do not provide definite indication of dative π-bonding in this compound.

Experimental

Spectra.—Infrared frequencies were measured with a Perkin-Elmer Model 112 spectrophotometer using a lithium fluoride prism. Acetylenes were studied as approximately 0.06 *M* solutions in reagent grade carbon tetrachloride. For the studies of acetylene basicity, phenol was present at 0.02 *M*, and the acetylene at 1 *M*; the path length was 3 mm. In the studies of hydrogen bonding acidity, the acetylenes were present at 0.6 *M* and the concentration of N,N-dimethylacetamide was 2 *M*; the path length was 1 mm. Frequency shifts were determined from logarithmic plots of the per cent transmission spectra as described previously.[4a]

Materials.—Methods used for the purification of phenol, N,N-dimethylacetamide, and the various acetylenes have been reported previously.[4a] Commercial acetylene gas was purified by passing through a cold trap at −80° and then through towers containing either concentrated sulfuric acid or alumina. 3,3-Dimethyl-1-butyne was prepared by the method of Cleveland and Murray[5] and was shown to be pure by gas chromatography. Bistrimethylsilylacetylene was prepared according to the method of Frisch and Young.[6] Boiling points and refractive indices of both of these acetylenes agreed with those reported in the literature.

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