amounts of carbonyl adduct used ranged from 0.2 to 1 g.; to this was added PF_3 to give a mole ratio of 1:2. Though attempts were made to increase the yield by altering concentrations and temperature, optimum results were obtained when the reaction was allowed to proceed at room temperature for 1 week under the conditions given. At lower temperatures the reaction proceeded slowly, while at higher temperatures excessive decomposition was observed. The bombs were then cooled and opened under anhydrous conditions. A white solid, black metal, and clear liquid were observed. None of the yellow carbonyl appeared to be present. The tubes were placed in a vacuum system, and the temperature was raised slowly from −196° to room temperature. A white solid intermediate (stable at −22°) was then collected. Subsequent fractionation gave a colorless, low-viscosity liquid collected in the range −100 to −78°. Though the product is reasonably stable at atmospheric pressure in a sealed system, it is somewhat unstable under reduced pressure, dissociating into free metal and PF_3. Yields were generally low (approximately 15% of theory). The product melted at approximately −100°.

Analysis.—The $[Pd(PF_3)_4]$ complex was first hydrolyzed in 0.25 *M* sodium hydroxide at ice temperature. Palladium was determined as the free metal[5] and fluorine as the insoluble calcium fluoride.[6]

Anal. Calcd.: Pd, 23.22; F, 49.75. Found: Pd, 24.65; F, 48.70.

Infrared Spectra.—Spectra were recorded with a Perkin-Elmer Model 21 infrared spectrophotometer using sodium chloride optics. Samples were contained in a 10-cm. gas cell at pressures up to 20 mm. With the exception of trace impurities such as SiF_4, which gave a band at 1027 cm.$^{-1}$, the rather complex spectrum consisted of stretching modes in the region of 890 cm.$^{-1}$ (see Table I). A band at 792 cm.$^{-1}$ appears to be characteristic of zerovalent complexes. Band intensities of coordinated PF_3 are substantially lower than those of free PF_3.

TABLE I

INFRARED SPECTRA[a]

PF_3	Obsd.	890 w	864 s	
	Lit.[2]	898	848	
$[Ni(PF_3)_4]$	Obsd.	903 w	864 s	793 m
	Lit.[2]	898	859	
$[Pd(PF_3)_4]$	Obsd.	888 w	861 s	792 m

[a] Frequency given in cm.$^{-1}$.

Nuclear Magnetic Resonance.—Magnetic resonance data were obtained on high resolution Varian equipment. P^{31} and F^{19} spectra were run at 24.288 and 56.445 Mc./sec., respectively. Phosphoric acid (85%) and trifluoroacetic acid were used as reference standards employing audio side-band techniques[7] for measurements. Samples were run as liquids in 5-mm. o.d. Pyrex sealed tubes. Bulk susceptibility corrections were assumed to be small and were not made. The P^{31} magnetic resonance spectra of $[Ni(PF_3)_4]$ and $[Pd(PF_3)_4]$ are very similar, both giving rise to a multiplet structure containing four lines with an intensity ratio of 1:3:3:1. F^{19} magnetic resonance spectra are made up of equal intensity doublets. Results are given in Table II.

Discussion

The relatively low stability of the palladium complex is expected when one considers its large d^{10}–d^{9} ionization potential.[8] This is reflected in the P^{31} magnetic resonance spectra of palladium and nickel complexes: δ_P and J_{P-F} in $[Pd(PF_3)_4]$ more closely approach those in PF_3. Only small perturbation of the ground state of PF_3 is expected for a weakly complexed system. This gives rise to correspondingly small changes in paramagnetic terms and coupling constants.[9]

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	δ_{CF_3COOH}, p.p.m.	$\delta_{H_3PO_4}$, p.p.m.	J_{P-F}, c.p.s.
PF_3	−42.3[a]	−97[b]	1441[c]
$[Ni(PF_3)_4]$	−60	−128	1300
$[Pd(PF_3)_4]$	−55	−116	1400

[a] H. S. Gutowsky and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953). [b] H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954). [c] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

It is probable that $[Pt(PF_3)_4]$ may be formed under conditions similar to those used to prepare the palladium complex and that its properties resemble those of the nickel and palladium compounds.

Acknowledgment.—The authors wish to acknowledge the use of nuclear magnetic resonance facilities of the Monsanto Chemical Company.

---

(5) N. H. Furman, "Standard Methods of Chemical Analysis," Vol. I, D. Van Nostrand Co., Inc., Princeton, N. J., p. 884.

(6) Reference 5, p. 460.

(7) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(8) R. S. Nyholm (Tilden Lecture), *Proc. Chem. Soc.*, 273 (1961).

(9) G. F. Svatos, being submitted for publication.

CONTRIBUTION FROM THE SPERRY RAND
RESEARCH CENTER, SUDBURY, MASSACHUSETTS

The Preparation and Crystallographic Properties of $KMnCl_3$

BY WILLIAM J. CROFT, MICHAEL KESTIGIAN,
AND FREDRIC D. LEIPZIGER

Received September 21, 1964

This note is concerned with the preparation and crystallographic properties of anhydrous $KMnCl_3$. The formation of this phase has been previously reported[1]; however, the compound has not been fully characterized. A viscosity study of the KCl–$MnCl_2$ system by Ermolenko and Vasil'eva[2] indicated the presence of a compound containing equimolar quantities of potassium chloride and manganous chloride.

Experimental

The compound $KMnCl_3$ was prepared by heating an intimate equimolar mixture of KCl and $MnCl_2 \cdot 4H_2O$ in an atmosphere of dry hydrogen chloride transported by dry argon carrier gas. The sample, contained in a platinum (or dense graphite) vessel, was slowly heated to above its melting point and the temperature maintained for 2 hr. Single-crystal growth experiments were carried out by use of the horizontal Bridgman technique. Nominally, a 100° temperature gradient between the hot and cool temperature zone and a furnace travel rate of 0.05 in./hr. were used. Single-crystal growth experiments were also carried out utilizing an evacuated sealed ampoule technique, by use of the vertical Bridgman and temperature gradient methods.

---

(1) C. Sandonnini and G. Scarpa, *Atti accad. nazl. Lincei*, **22**, II 163 (1913).

(2) N. F. Ermolenko and G. I. Vasil'eva, *Uch. Zap. Belorussk. Gos. Univ., Ser. Khim.*, 295 (1956).

TABLE I
X-RAY DATA FOR $KMnCl_3$

Tetragonal indices *hkl*	d_{calcd}, Å.	d_{obsd}, Å.	I_{obsd}
200	5.012	5.007	m+
002	4.986		
220	3.544	3.537	m
202	3.534		
311	3.021	3.015	w
113	3.010		
222	2.889	2.891	s−
320	2.780	2.778	w
302	2.776		
203	2.770		
321	2.678	2.680	w
132	2.675		
123	2.670	2.665	w
400	2.506	2.506	s
004	2.493	2.493	s
240	2.241	2.236	w
402	2.239		
024	2.232		
422	2.044	2.043	m
224	2.039	2.031	m−
404	1.767	1.767	m
440	1.772		

Analysis.—A sample was weighed and dissolved in water. The chlorine was precipitated as AgCl, dried at 110°, and weighed. The potassium was precipitated as potassium tetraphenylboron, dried, and weighed. The manganese was oxidized with $NaBiO_3$ and titrated with $FeSO_4$.

Anal. Calcd. for $KMnCl_3$: K, 19.5; Mn, 27.4; Cl, 53.1. Found: K, 19.9; Mn 27.5; Cl, 51.3.

Crystallography

Crystals were examined on a microscope heating stage in polarized light. The heating chamber was continuously flushed with helium that had passed through a trap cooled with liquid nitrogen. The crystal rested directly on a transparent aluminum oxide plate which was heated from below by a platinum coil.

The original fragments were orange in color, translucent, polycrystalline, and extremely fine grained. The compound melts congruently at 507° [±5°] as indicated by its sharpness of melting on a hot stage microscope. The original material and the melted recrystallized material give the same X-ray diffraction powder pattern. The material grew as flat orthogonal plates which were isotropic just below the melting temperature. On further cooling, the crystals became anisotropic at 458° [±5°]. This is a completely reversible transformation although the pattern of complex twinning varies in the same sample each time the temperature goes above and below the transition. At about 150°, in the cooling cycle, the crystals develop a series of orthogonal cracks. These are probably due to the differing expansion of the crystals and the sapphire substrate. The sapphire plate is slightly etched by the molten salt. The room temperature birefringence is quite low (approximately 0.005).

The crystals are extremely hygroscopic. Exposure of fragments (0.1 mm.) to moist air (relative humidity 80%) results in complete dissolution in a few minutes. The material can be crystallized as a hydrate at room temperature in an atmosphere of dry helium. The hydrate is anisotropic with high birefringence and can be heated to form the original anhydrous salt.

The X-ray diffraction data were obtained by loading the powdered sample into a capillary which was sealed with paraffin. This was done in a nitrogen-filled dry-box. The patterns were made with copper radiation in a 114-mm. Debye camera. The pattern was pseudo-cubic, but because of the observed splitting of the 400 and 422 reflections it could be indexed on the basis of a tetragonal unit cell with a = 10.024 Å. and c = 9.972 Å. (c/a = 0.995). Further evidence of the distortion from cubic symmetry is the observed optical anisotropy. The crystals showed parallel extinction and very low birefringence. The density was measured in toluene on a modified Berman balance and gave a value of 2.67. For a unit cell containing eight units of $KMnCl_3$ the theoretical density is 2.69. The X-ray diffraction data are presented in Table I.

Summary

The formation of anhydrous $KMnCl_3$ was confirmed by chemical analysis. X-Ray diffraction data obtained from powdered samples indicate the compound to have tetragonal symmetry at room temperature with a_0 = 10.024 Å. and c_0 = 9.972 Å. Upon heating, the material becomes isotropic at 458° [±5°]. It is this transition that prevents the growth of large single crystals of the room temperature phase. The antiferromagnetic properties of $KMnCl_3$ are reported elsewhere.[3]

---

(3) R. W. Kedzie, J. R. Shane, M. Kestigian, and W. J. Croft, Decennial Conference on Magnetism and Magnetic Materials (presented Nov. 1964; to be published in *J. Appl. Phys.*).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

1,6-Diphenylhexatrieneiron Tricarbonyl

BY H. W. WHITLOCK, JR., AND YOW NAN CHUAH[1]

Received September 21, 1964

As a preliminary to a study of the position-fixation of metal carbonyl groups attached to polyene chains, we wish to report the preparation of a well-defined acyclic triene–iron tricarbonyl complex[2] by two independent methods.

Reaction of *trans,trans,trans*-1,6-diphenyl-1,3,5-hexatriene with iron pentacarbonyl in decalin at 145–155°

---

(1) Partial support by the Asia Foundation is gratefully acknowledged.

(2) Several polyene–iron carbonyl complexes of poorly defined structures have been described.[3-5]

(3) J. Xavier, M. Thiel, and E. R. Lippincott, *J. Am. Chem. Soc.*, **83**, 2403 (1961).

(4) A. Nakamura and M. Tsutsui, *J. Med. Chem.*, **7**, 335 (1964).

(5) A recent review of olefin–iron carbonyl complexes: R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).