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 drybox. The patterns were made with copper radiation in a 114-mm. Debye camera. The pattern was pseudocubic, 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,
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1,6-Diphenylhexatrieneiron Tricarbonyl

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

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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°

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[1] Partial support by the Asia Foundation is gratefully acknowledged.

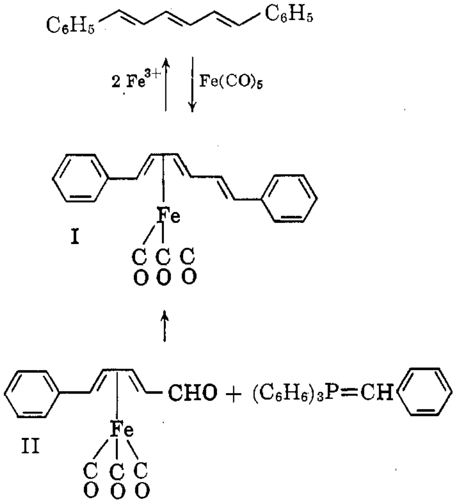
[2] Several polyene–iron carbonyl complexes of poorly defined structures have been described.[3-5]

[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).

for 28 hr. gave in 79% yield an air-stable complex which is formulated as I. An alternative preparation of I *via* Wittig reaction between *trans,trans*-5-phenyl-2,4-pentadienaliron tricarbonyl (II) and benzylidene triphenylphosphorane proceeded in good yield.



Retention of the diphenylhexatriene structure in I was shown by its smooth degradation to the starting olefin and 76% of three molar equivalents of carbon monoxide on treatment with ferric chloride.[6] Oxidation with ceric ion[7] produced three molar equivalents of carbon monoxide. Complexation of the iron tricarbonyl moiety unit with the triene moiety rather than with the aromatic rings was suggested by the upfield shift of two of the six olefinic protons (presumably those at C_1 and C_4) in the n.m.r. spectrum[8,9] of I. The assignment of *trans*-$\Delta^{1,2}$ and $\Delta^{3,4}$ as depicted in I is made by analogy with other diene–iron tricarbonyl complexes,[5] the *trans* nature of $\Delta^{5,6}$ is assigned on the basis of a 962 cm.$^{-1}$ band in the infrared spectrum of of I,[10] and the *s-trans* relationship between $\Delta^{3,4}$ and $\Delta^{5,6}$ is assigned on classical steric grounds.

We conclude that the presence of an additional conjugated double bond in acyclic diene–iron tricarbonyl complexes introduces no structural complexities. This is in agreement with the work of Murdoch and Weiss[11] on the reaction of 1,3,5-hexatriene with diiron enneacarbonyl.

Experimental

trans,trans-**5-Phenyl-2,4-pentadienaliron Tricarbonyl (II).**—A mixture of 3.0 g. of *trans,trans*-5-phenyl-2,4-pentadienal,[12] 26 ml. of iron pentacarbonyl, and 30 ml. of *n*-heptane was heated under reflux with stirring under nitrogen for 69 hr. The resulting black mixture was filtered, concentrated, and absorbed on a column of 250 g. of acid-washed alumina. Elution with chloroform and recrystallization from benzene–hexane (1:4) of the gray-green material contained in the second 300-ml. fraction gave 4.05 g. (72% yield) of the iron tricarbonyl complex II as yellow plates, m.p. 163–164°. The analytical sample was prepared by repeated recrystallization from benzene–hexane (1:4) as moderately air-stable yellow flakes, m.p. 166–166.5°.

Anal. Calcd. for $C_{14}H_{10}FeO_4$: C, 56.37; H, 3.38. Found: C, 55.93; H, 3.11.

N.m.r. Spectrum.—The n.m.r. spectrum showed aldehydic H as a doublet, $J = 5$ c.p.s. at δ 9.44, C_2–H as an incompletely resolved quartet centered at δ 1.60; C_3–H and C_4–H as a multiplet centered at δ 6.07; C_5–H as a doublet, $J = 10$ c.p.s., at δ 2.6; phenyl as a singlet at δ 7.34. All signals appeared in the correct intensity.

Infrared Spectrum.—The infrared spectrum showed aldehydic CH at 2820 and 2720 cm.$^{-1}$ (w), metal carbonyl at 2060 and 2000 cm.$^{-1}$ (vs), aldehyde carbonyl at 1670 cm.$^{-1}$ (s), a very weak band at 980 cm.$^{-1}$.

trans,trans,trans-**1,6-Diphenyl-1,3,5-hexatrieneiron Tricarbonyl (I). From Diphenylhexatriene and Iron Pentacarbonyl.**—A mixture of 1.50 g. of 1,6-diphenyl-1,3,5-hexatriene,[13] 6.4 g. (4.35 ml.) of iron pentacarbonyl, and 150 ml. of decalin was heated at 145–155° with stirring under nitrogen for 28 hr. The cooled reaction mixture was filtered and the solvent removed *in vacuo*. Crystallization of the brown residue from benzene–cyclohexane (1:4) gave 1.32 g. of the desired complex as rust-colored rods, m.p. 166–168°. Concentration and crystallization of the mother liquors with hand separation of the two types of crystals formed gave an additional 0.53 g. of the complex, m.p. 159–165°, and 0.033 g. of starting olefin. The analytical sample of I was prepared by repeated recrystallization from benzene–cyclohexane (1:4) as air-stable transparent rust-colored rods, m.p. 167–168.5°.

Anal. Calcd. for $C_{21}H_{18}FeO_3$: C, 67.75; H, 4.34; Fe, 15.02. Found: C, 68.00; H, 4.44; Fe, 14.28.

N.m.r. Spectrum.—The hydrogens at C_1 and C_4 appeared as a multiplet centered around δ 2.35, the aromatic rings as a doublet centered around δ 7.25, and the remaining olefinic hydrogens as a multiplet stretching from δ 6.9 to δ5.3. The areas of the peaks were in the appropriate ratio and the spectrum was unchanged on going from room temperature to 60°.

Infrared Spectrum.—The infrared spectrum showed metal–carbonyl bands at 2060 and 2000 cm.$^{-1}$ (vs), *trans*-CH=CH– at 962 cm.$^{-1}$ (s), and monosubstituted benzene rings (two types) at 755, 745, and 687 cm.$^{-1}$ (s).

Complex I ***via*** **the Wittig Reaction.**—To a suspension of 166 mg. (0.42 mmole) of benzyltriphenylphosphonium chloride in 5 ml. of dry ether contained under nitrogen in a 25-ml. flask was added a solution of 25 mg. (0.39 mmole) of butyllithium in 0.250 ml. of hexane. The resulting red suspension was stirred under nitrogen at 25° for 2 hr. A suspension of 48 mg. of aldehyde–iron tricarbonyl complex II in 8 ml. of dry ether was added and the mixture was heated under reflux with stirring for 15 hr. The reaction mixture was poured into water, the ether layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and evaporated to afford 230 mg. of a brown wax which was adsorbed on a column of 20 g. of acid-washed alumina. Elution with hexane, followed by trituration of the yellow eluate with benzene–cyclohexane (1:4), gave 48.6 mg. (81% crude yield) of oily crystals. These were recrystallized twice from cyclohexane–benzene to give 33 mg. (55% yield) of diphenylhexatriene–iron tricarbonyl complex I, m.p. 166.5–168°. A mixture of this with the sample prepared above had m.p. 166.5–168°.

Oxidation of Complex I.—To a solution of 144 mg. (0.39 mmole) of I in 25 ml. of acetonitrile and 2 ml. of water was added a solution of 382 mg. (2.26 mequiv.) of anhydrous ferric chloride in 15 ml. of acetonitrile. After 210 min. 19.5 ml. of gas (STP) (calcd. for 3 molar equiv. of CO, 25.8 ml.) had been evolved. The reaction mixture was poured into water and the aqueous layer was extracted with chloroform. The combined chloroform

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(6) J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

(7) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

(8) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

(9) J. E. Mahler and R. Pettit, unpublished results quoted in ref. 5.

(10) Whereas *trans,trans*-5-phenyl-2,4-pentadienal has a strong out-of-plane C–H deformation band at 10.2 μ, its iron tricarbonyl complex II does not. We observe the same phenomenon for *trans,trans*-1,4-diphenyl-1,3-butadiene and its iron tricarbonyl compound.

(11) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **46**, 1588 (1963).

(12) A. Luttringhaus and G. Schill, *Ber.*, **69**, 2078 (1936).

(13) W. Stilz and H. Pommer, German Patent 1,092,472 (1960); *Chem. Abstr.*, **56**, P413e (1962).

extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated. Crystallization of the residue from benzene–cyclohexane gave 66 mg. (74% yield) of 1,6-diphenyl-1,3,5-hexatriene, m.p. and m.m.p. 204–205°. The use of ceric ammonium nitrate instead of ferric chloride led to the rapid production of the theoretical amount of gas but apparently overoxidized the complex, since no hexatriene could be recovered from the reaction mixture.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Pressure and Polymorphism in the Rare Earth Sesquioxides[1]

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Investigations of the temperature ranges of stability of the three polymorphs of the lanthanide sesquioxides, R_2O_3,[2,3] have been summarized in Figure 1.[4]

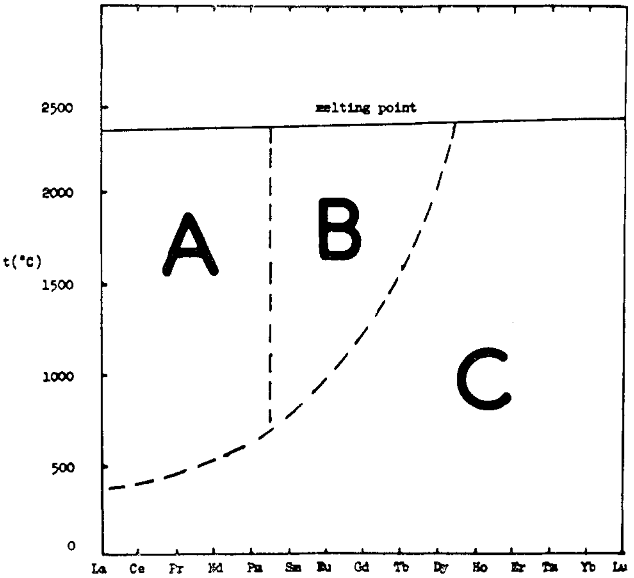

Figure 1.—Fields of stability for the polymorphic forms of M_2O_3: A, hexagonal; B, monoclinic; C, cubic.

The structures of each of the polymorphic forms are built up either from a single type of coordination polyhedron (MO_6 in the cubic C type and MO_7 in the hexagonal A form) or from a mixture of MO_6 and MO_7 polyhedra as in the monoclinic B form. The observed regions of stability of the various forms correlate well with the idea that it is the cation size (lanthanide contraction) and the temperature which determine the type of sesquioxide existing under ordinary conditions of pressure. For the different structures the densities are markedly different, with $\rho_A > \rho_B > \rho_C$: it therefore seemed possible that the transformation temperature for C → B and for B → A might be reduced by the application of high pressure. In particular, it might be possible to convert: (1) the B form of the sesquioxides of Sm through Dy to the A form; and (2) the C form sesquioxides of the heavy lanthanides (beyond Dy) and yttrium to the B form. We have, accordingly, investigated the effect of pressure on the following sesquioxides: B form: Sm_2O_3; C form: Pr_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and Y_2O_3; and A form: Pr_2O_3, Nd_2O_3.

Experimental

The starting materials all had a nominal purity of 99.9 + %: 1 to 2.5 g. of each oxide was dried by heating at 1000° for 24 hr. The phases were characterized by X-ray diffraction using a Guinier focusing camera. Each sample was tightly packed into a hole drilled in a steel cylinder. The open end of each cylinder was sealed by welding a steel rod into the hole—using a helium atmosphere and with the lower part of the cylinder in cold water. The cylinders were machined into cylindrical projectiles weighing 14.2 g. and then fired (at a velocity of $\sim$1.5 km. sec.$^{-1}$) into a hole in a steel receiver.[5] When cool, the projectile was separated from the receiver, opened, and the contents examined in the Guinier camera. On the basis of observed changes of state in phosphorus and other materials in similar experiments, it is estimated[6] that the samples were subjected to a static pressure (during impact) of 10–20% of the theoretical, *i.e.*, $3 \pm 1 \times 10^5$ atm. Since there was no evidence that the steel projectiles had melted, the maximum temperature attained was presumably below $\sim$1500°.

Results

The starting materials were sufficiently well-crystallized to give sharp diffraction patterns; whereas, after firing, all the powder patterns were composed of broad diffuse lines, with a rapid decrease in line intensity with increasing Bragg angle. Two transformations only were observed: C-type Pr_2O_3 was completely converted to the A modification and C-type Ho_2O_3 partly ($\sim$20%) converted to the B form. This latter conversion has not been reported previously: heating the C form of holmia at atmospheric pressure and up to its melting point has failed to effect it.[4] We therefore attribute the present observation to the effect of high pressure.

The identification of B form Ho_2O_3 follows from the fact that the powder pattern of the sample could be indexed completely as a two-phase mixture of: (1) a b.c.c. phase with $a_0 = 10.610 \pm 0.008$ Å. and (2) monoclinic phase, isostructural with the other B form sesquioxides and having the lattice parameters: $a_0 = 13.90 \pm 0.05$, $b_0 = 3.505 \pm 0.005$, $c_0 = 8.630 \pm 0.008$ Å., $\beta = 100.2 \pm 0.1°$.

In an attempt to improve the line quality of the film, a portion of the sample was annealed at 417° for 4 days. All lines due to the B form disappeared: the C form pattern sharpened considerably. The latter suggests that (at this low annealing temperature) the process is one of relief of microstrain produced in the original crystallites during impact, rather than an increase in crystallite size. Annealing at 715° for 3 days gave a monophasic, perfectly crystalline sample of C form

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(1) Work supported by the U. S. Atomic Energy Commission.

(2) R. S. Roth and S. J. Schneider, *J. Res. Natl. Bur. Std.*, **64A,** 309 (1960).

(3) I. Warshaw and R. Roy, *J. Phys. Chem.*, **65**, 2048 (1961).

(4) L. Eyring and B. Holmberg, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p. 46.

(5) We are indebted to Dr. A. L. deLisle of Scottsdale, Ariz., for preparing and firing the projectiles, using techniques which he has developed.

(6) A. L. deLisle, private communication.