cept of anisotropic conductivity we have examined the square-planar d^8 complexes of the group VIII metals. While monomeric in solution, the short metal–metal distances and the dichroism exhibited by single crystals of these derivatives have been equated with polymeric metal interaction in the solid state.[8] In this communication we wish to report the verification of anisotropic electron transport in single crystals of dicarbonylacetylacetonatoiridium (I)[9] and dicarbonylacetylacetonatorhodium (II).[10]

The electrical conductivities of I and II have been measured using a number of single crystals of approximate dimensions 5 × 0.2 × 0.2 mm, with reproducible results. Silver paint was used to make direct contact to the crystal surface. The dc current–voltage characteristic was linear for I for voltages up to 100 v. In the case of II, linearity was only observed for lower voltages (<50 v). Where the conductivity of the crystals was high enough for ac measurements, ac current–voltage characteristics were obtained, and indicated barrier effects and crystal imperfections did not greatly influence the conductivity. At 25°, in a nitrogen atmosphere, the conductivities of I and II were determined to be 10^{-5} and 10^{-11} ohm^{-1} cm^{-1}, respectively. From a plot of ln conductivity *vs.* T^{-1}, the corresponding activation energies were determined to be 0.27 and 0.44 ev, respectively. To investigate the anticipated anisotropic conductivity, dc measurements were made both parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the needle axis of the crystals. The ratios $\sigma_{\parallel} : \sigma_{\perp}$ for I and II were determined to be greater than 500 and 100, respectively.[11]

Single-crystal X-ray analysis of I indicates a triclinic cell with a square-planar arrangement of the ligands about iridium. The metal atoms are arranged equidistantly (Ir–Ir = 3.20 A) along the cell edge, forming chains which extend throughout the crystal in the manner reported[2] for a number of other d^8 complexes. The fact that the crystal axis along which the metal atoms are aligned is also the axis of maximum conductivity provides strong evidence for associating the electron transport with the polymeric metal bonding. Likewise, while the X-ray analysis is not yet complete, the greater conductivity of I is consistent with current ideas on the strength of metal–metal bonds.[2] A detailed analysis of the conductivity of I and II, together with measurements on a number of other transition metal derivatives, will be reported elsewhere.

In concluding it must be pointed out that the extent of metal–metal interaction in d^8 complexes is an unknown quantity and probably does not represent the maximum attainable in a fully covalent intermetallic bond. This limitation, together with the fact that electron transport requires initial excitation of an electron from a fully occupied to an unoccupied molecular orbital of the metal chain, is the most likely reason why I and II exhibit semiconductor rather than metallic properties. Consequently we believe that the order of magnitude of electron transport in the above systems may be far exceeded in polymers containing metals linked by fully covalent bonds and in particular where the molecular orbitals are only partially occupied. Such systems may provide an opportunity to test the validity of the "one-dimensional superconductor" hypothesis.[12] Work is in progress to substantiate these ideas.

Acknowledgment. The authors are indebted to R. C. Corley, K. R. Skillern, and R. C. Strickland (R. T. I.) and to J. Y. Sun (U. N. C.) for technical assistance.

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(12) R. A. Ferrell, *Phys. Rev. Letters*, **13**, 330 (1964).

(13) Fellow of Alfred P. Sloan Foundation.

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Dichlorotris(tetrahydrofuran)-*p*-tolylchromium(III). Its Preparation and Crystal and Molecular Structure

Sir:

The isolation of a σ-bonded, monosubstituted organochromium(III) substance in crystalline form had eluded us until recent date.[1] Our interest in σ-bonded organochromium compounds in general and in particular their structural characteristics extends back to the first preparation of tris(tetrahydrofuran)triphenylchromium(III),[2] but these efforts until now have not presented the opportunity of determining the precise geometry and bond lengths of one of these molecules. The preparation and preliminary structural features of dichlorotris(tetrahydrofuran)-*p*-tolylchromium(III) are reported.

One of the facts which emerges is the significant lengthening of the chromium–oxygen bond *trans* to the σ-bonded *p*-tolyl group, relative to the other two Cr–O bonds. In this may lie the explanation of the selective loss of one tetrahydrofuran ligand from tris(tetrahydrofuran)triphenylchromium(III).[3] The *trans* effect on bond lengths has also been observed in platinum complexes containing metal–carbon σ bonds.[4]

Dichlorotris(tetrahydrofuran)-*p*-tolylchromium(III), prepared by the interaction of equimolar ratios of *p*-tolylmagnesium chloride and $Cr^{III}Cl_3(THF)_3$ in tetrahydrofuran, was obtained as well-formed, pale green crystals. *Anal.* Calcd for $C_{19}H_{31}O_3Cl_2Cr$: C, 53.0; H, 7.3; Cl, 16.5; Cr, 12.1. Found: C, 52.1; H, 7.1; Cl, 17.3; Cr, 12.6.

The compound has ν_{max} (Nujol) *1905*, *1818*, *1739*, 1613, 1330, 1300, 1250, 1176, 1098, 1080, 1042, 1026, 913, 866, *793*, 730, 694, 678, 570, and *490* cm^{-1}, and is paramagnetic to the extent of 3.87 BM, in agreement with a chromium valency of three.[5] The substance

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(1) R. P. A. Sneeden and H. P. Throndsen, *Chem. Commun.*, 509 (1965).

(2) W. Herwig and H. H. Zeiss, *J. Am. Chem. Soc.*, **79**, 6561 (1957); **81**, 4798 (1959).

(3) J. Hähle and G. Stolze, *Z. Naturforsch.*, **19b**, 1081 (1964).

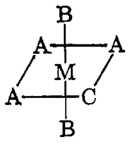
(4) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966); M. A. Bennett, G. J. Erskine, J. Lewis, R. Mason, R. S. Nyholm, G. B. Robertson, and A. D. C. Towl, *ibid.*, 395 (1966).

(5) This value was kindly determined by Drs. G. and S. Olivé of MRSA, Zürich, for a tetrahydrofuran solution, and based on a molecular weight of 430.26.

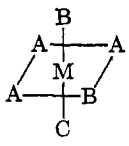
reacts with mercuric chloride to give *p*-tolylmercuric chloride, mp and mmp 236–238°. Unlike the corresponding dichlorotris(pyridine)benzylchromium(III),[1] the σ-bonded *p*-tolylchromium compound absorbs only weakly in the visible region (λ_{max} (THF) 445 mμ (ϵ 137)), is rapidly hydrolyzed, and does not reduce Fe^{III} salts in perchloric acid solution. The pure, crystalline solid is stable under nitrogen, only undergoing decomposition between 130 and 190° to give *p,p'*-ditolyl as the main organic product.

The crystals of dichlorotris(tetrahydrofuran)-*p*-tolyl chromium(III) are orthorhombic with $a = 10.396$, $b = 18.447$, $c = 22.396$ A, $d_m = 1.315$, $Z = 8$, $d_c = 1.331$; the space group is Pbca. Since the crystals are unstable to the atmosphere, they were sealed in Lindemann glass capillaries before exposure to X-rays. The intensities were measured with the aid of a Hilger and Watts linear diffractometer; the 2661 strongest reflections produced by Mo Kα radiation were used in the analysis. The structure was solved by three-dimensional Patterson and Fourier methods. The current value of R is 0.136.

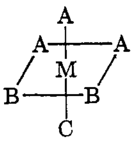
There are three possible isomers of octahedrally coordinated compounds of the type MA_3B_2C. The



I



II



III

configuration of the present compound is depicted by I.

The molecule projected down the *a* axis is shown in Figure 1. In the solid state the ligands adopt an orientation which precludes the symmetry $\bar{1}$ or m in the molecule, and so, since the space group contains symmetry centers and glide planes, there are equal numbers of *d* and *l* molecules in the unit cell. The *p*-tolyl group is σ bonded to the chromium through one carbon atom. The bond lengths in the octahedron at the chromium atom are at present: $Cr–O_1 = 2.04$, $Cr–O_2 = 2.05$, $Cr–O_3 = 2.21$, $Cr–C = 2.01$, $Cr–Cl_1 = 2.31$, $Cr–Cl_2 = 2.33$ A. Refinement is continuing and final details of the molecular structure will be published.

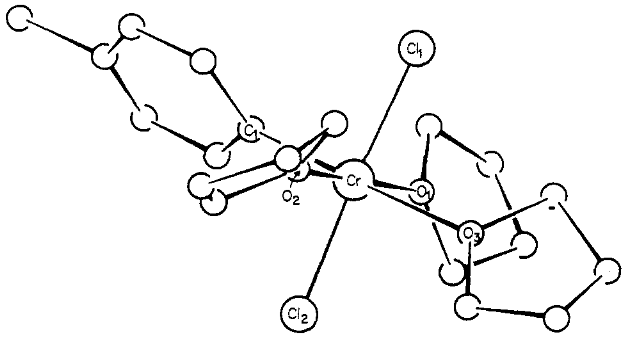


Figure 1.

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The Reaction of Chloroformates with Silver Fluoroborate in Chlorobenzene

Sir:

The unique chemistry of diazonium ions[1] (I) and isocarboxonium ions[2] (II) has been of continuing practical and theoretical interest. We wish to report attempts to generate carboxylium ions[3] (III), another member of

$$\underset{\text{I}}{[R{-}N{\equiv}N]^+} \qquad \underset{\text{II}}{[R{-}O{=}C]^+} \qquad \underset{\text{III}}{[R{-}O{=}C{\equiv}O]^+}$$

this family, by the reaction of chloroformates with silver fluoroborate in chlorobenzene. Our results suggest that the formalism relating I and III has chemical significance.[4]

The classic work of Bartlett and Knox[5] established that deamination of 1-aminoapocamphane yields bridgehead substitution products whereas the corresponding 1-chloroapocamphane is remarkably inert even to forcing conditions.[6] This difference in reactivity has generally been ascribed to the exceptional behavior of the diazonium ion.[1,7]

We have found that treatment of 1-apocamphane chloroformate (IV) with an equimolar amount of silver fluoroborate in chlorobenzene at room temperature for 8 hr also yields bridgehead substitution products. Under these conditions the products are silver chloride (92%), carbon dioxide (70%), 1-fluoroapocamphane (V; 52%), and isomers of 1-chlorophenylapocamphane (VI; 24%). The chloroformate IV was stable in chlorobenzene in the absence of silver fluoroborate, and 1-chloroapocamphane was unreactive toward boron trifluoride and silver fluoroborate in chlorobenzene. The fluoride V was identified by infrared, proton, and

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[1] H. E. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961.

[2] P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959), and subsequent references; J. Landgrebe, *Tetrahedron Letters*, 105 (1965).

[3] Carbalkoxylium ions[3c] have been postulated as intermediates in the reaction of chloroformates with silver nitrate to give nitrate esters: (a) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959); see, however, D. N. Kevill and G. H. Johnson, *Chem. Commun.*, 235 (1966); in the solvolysis of chloroformates: (b) M. Green and R. F. Hudson, *J. Chem. Soc.*, 1076 (1962), and earlier work; A. Kivinen, *Acta Chem. Scand.*, **19**, 845 (1965); and in the hydrolysis of N,N'-dicarbalkoxy-N,N'-dialkoxyhydrazines: (c) R. J. Crawford and R. Rapp, *J. Org. Chem.*, **28**, 2419 (1963). These ions can be considered as a ramification of some of the mechanistic proposals for the rearrangement and eliminations of chloroformates: (d) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1961 (1961); K. L. Oliver and W. G. Young, *ibid.*, **81**, 5811 (1959); K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1955); and in the Friedel-Crafts reactions of chloroformates: (e) W. H. Coppock, *J. Org. Chem.*, **22**, 325 (1957); (f) C. Friedel and J. M. Crafts, *Compt. Rend.*, **84**, 1450 (1877); F. A. Drahowzal, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 644.

[4] In this context chemical significance implies a reactant-product analogy and not a mechanistic analogy. The carboxylium ions which may be proposed to rationalize the following results are at best a unifying concept which represents a starting point for more detailed mechanistic work.

[5] P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939).

[6] The reaction of a structurally similar bridgehead chloride has been achieved with aqueous silver nitrate at 205° for 19.5 hr: W. von E. Doering and E. F. Schoenewaldt, *J. Am. Chem. Soc.*, **73**, 2333 (1951). However, the same chloride is stable toward ethanolic silver nitrate at 160° for 21 hr and toward aqueous zinc chloride at 205° for 91 hr. The recently reported reaction of 1-chloronorbornane with antimony pentafluoride in sulfur dioxide appears to be unique: P. von R. Schleyer, W. E. Walts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

[7] For recent discussions see (a) D. Y. Curtin, B. H. Klanderman, and D. F. Tavares, *J. Org. Chem.*, **27**, 2709 (1962); (b) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 27P.