$\sim$7 per bond,[9] the ratios given above are merely lower limits to the relative rates *if* H abstraction by alkyl also occurred; however, it has been estimated previously[7b] for the propane system that abstraction by CH_3 is unimportant even at much higher substrate concentrations. The rates relative to C=C addition (ethylene) for the three substrates are: primary/secondary/tertiary/C=C = 1:11:–:70 (propane) and 1:14:–:120 (butane); and for isobutane the ratios are 1:–:122:125. The average ratios are 1:12.5:122:125. The values were calculated with use of disproportionation and recombination rates[10] employed previously.[7a] A drastic change (to unity) in the assumed relative rates of all radical combinations is largely self-cancelling in its effect and does not alter the approximate magnitude of the abstraction ratios deduced.

The relative amounts of the two products, RCH_3 and $R'CH_3$, from reactions 6 and 7 would be expected to connote similar abstraction ratios. Instead, the amounts bear no correspondence to the numbers above. The ratios, $RCH_3/R'CH_3$, per bond are 1:3 (propane), 1:4 (*n*-butane), and 1:15 (isobutane). Also, the total amount of these products greatly exceeded the possible contribution from reactions 6 and 7, upper limits to whose magnitudes were calculated on the basis that ethane (less reaction 8b) arose from methyl recombination (reaction 5), and that propane arose from methyl reactions 5 and 9; *e.g.*, for RCH_3 products the calculated amounts are 0.11 (propane), 0.09 (*n*-butane), and 0.08 (isobutane), respectively, of the observed quantities. Nor are the amounts and ratios of the two products explicable in terms of a $^1CH_2$ component. Although there exists an incompletely understood concomitant process that could conceivably explain *some* of the higher products by successive chain-lengthening steps, this too is inadequate to explain the RCH_3 and $R'CH_3$ products. A simple explanation is that these products arise by insertion and spin inversion

$$RH + {}^3CH_2 \rightarrow RCH_3 \text{ and } R'CH_3 \qquad (12a,b)$$

Quite apart from whether this proposition is indeed proven, the fact remains that the older data[3,4] seem inadequate to disprove the occurrence of insertion[11] while the present results, at the least, simulate such a process.

On the basis of reactions 12 the following ratios may be calculated. Relative insertion rates are, for secondary/primary CH, 2.2 per bond (propane) and 3.5 per bond (butane); and for tertiary/primary CH, 10.9 per bond (isobutane). These numbers are averages for five to eight experiments. Some relative rates of abstraction/insertion are for primary CH: 0.38 (propane), 0.31 (*n*-butane), and 0.30 (isobutane), or an average of 0.33; secondary CH: 1.9 (propane) and 1.3 (*n*-butane), or an average of 1.5; tertiary CH: 3.0 (isobutane). These last three ratios (but not others above) decrease with increasing proportion of diazomethane, and approach limiting values about twice these, for mixture dilutions of 1:80.

Since $^1CH_2$ has recently been said to abstract hydrogen from C–H bonds in certain cases,[12] the qualitative (but not quantitative) parallelism of this roster of reactions of $^3CH_2$ and $^1CH_2$ with CH and C=C bonds may now be complete.

In view of the lesser magnitude of *D*(allyl H) relative to *D*(tertiary C–H), it continues plausible that a source of pentene products in butene systems is H abstraction by $^3CH_2$ followed by radical combination; some insertion could also occur.

Complete details and exposition of the rather complex product calculations will be submitted later.

Acknowledgment. We thank Mr. John Campbell for his assistance.

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[10] Based on $k_d/k_r = 2.2$ for *t*-Bu; a higher value[9] would raise this ratio. For the reasons that follow from the results cited in the next paragraph, and because of the complexity of triplet methylene systems, it is highly desirable that the R_2, R_2', RR′, and the RC_2H_5 and $R'C_2H_5$ products always be analyzed as diagnostics of abstraction amounts.

[11] For example, ref 4 reports no, or negligible, C_5 olefin products in the photosensitized decomposition of CH_2N_2 with butene-2. By contrast, we find such products of $^3CH_2$ to be of importance; *cf.* ref 2d.

(12) D. W. Setser, private communication.

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Anisotropic Electron Transport in Compounds Containing Polymeric Metal–Metal Bonds[1]

Sir:

A wide variety of complexes which contain metal–metal bonds have been synthesized since the recent realization that metal derivatives may be catenated.[2] We have become interested in the properties of the metal–metal bond because of our belief that compounds which possess a polymeric metal skeleton will exhibit many of the properties of the free metal. If this supposition is valid, one can anticipate that the *one-dimensional* polymeric arrangement of metal atoms in these compounds will result in unique solid-state properties, including *anisotropic* conductivity and photoconductivity.

Few physical measurements have been carried out on compounds which possess more than one metal–metal bond. The esr spectrum of the radical anion of dodecamethylcyclohexasilane indicates that the unpaired electron is delocalized over all six silicon atoms.[3] Likewise the catenation of silicon,[4] germanium,[5] tin,[6] and lead[6] is associated with the appearance of electronic transitions in the ultraviolet and visible regions. These observations provide the only definitive experimental evidence for the hypothesis that adjacent d and p orbitals in chains of metals will overlap to form delocalized band-type orbitals either in the ground or excited states.[7,8a] Seeking model compounds to test the con-

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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 ($\sigma_{\|}$) and perpendicular ($\sigma_{\perp}$) to the needle axis of the crystals. The ratios $\sigma_{\|} : \sigma_{\perp}$ 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.

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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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