Photocondensation of *mer*-Trichlorotris(diethyl sulphide)iridium(III)

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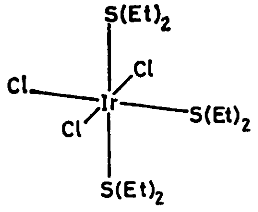
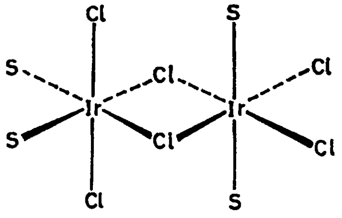
Photolysis of *mer*-$[IrCl_3(SEt_2)_3]$ (1) in benzene or toluene solution gives a mixture of di-μ-chloro-tetrachloro-tetrakis(diethyl sulphide)di-iridium(III) (2) and μ-chloro-pentachloro-μ(diethyl sulphide)-tris(diethyl sulphide)di-iridium(III) (3). The unusual bridging diethyl sulphide group in (3) is identified by the absence of rapid inversion at the sulphur atom.

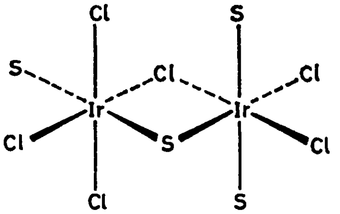
THE photochemistry of transition-metal complexes is currently a subject of considerable interest.[1,2] Several studies of the photochemistry of d^6 low-spin ions have now appeared, but these have been concerned mainly with complexes of nitrogen ligands, for which there is a reasonable amount of information on quantum yields and the stereochemistry of the products of photosubstitution as a result of irradiation in the *d–d*, or ligand-field, region of the spectrum.[3] Other complexes have been less well studied although the photoisomerisation of *mer*-$[IrCl_3L_3]$ (L = tertiary phosphine) is well established and has been used as a synthetic route to the *fac* isomer.[4] When it was observed, during the measurement of the dipole moment of *mer*-$[IrCl_3(SEt_2)_3]$ in benzene solution, that the solution darkened on exposure to light, it was considered of interest to isolate and examine the products.



(1)



(2)



(3)

EXPERIMENTAL

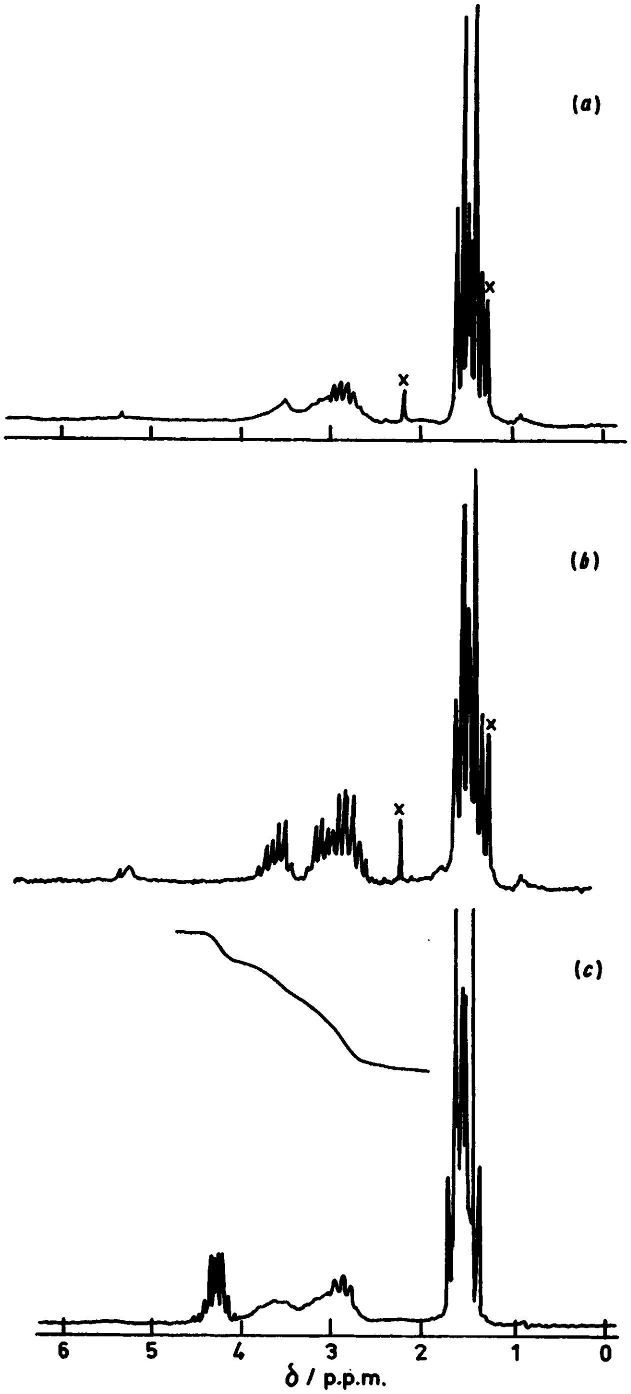
The compound *mer*-$[IrCl_3(SEt_2)_3]$ was prepared by the methods of Kauffman[5] and Allen and Wilkinson;[6] the latter method is preferable as there is no formation of the red ' isomer ' $[IrCl_2(SEt_2)_4][IrCl_4(SEt_2)_2]$.[7] A solution (*ca.* 10^{-2} mol dm^{-3}) of *mer*-$[IrCl_3(SEt_2)_3]$ in toluene or benzene was photolysed with a 75 W tungsten lamp at 10 cm from the reactant solution. During the photolysis the solution changes colour from yellow to orange-red. Pyrex-filtered sunlight or a low-pressure mercury lamp are equally effective. After photolysis the solvent is removed under reduced pressure leaving a red-brown residue containing (2), (3), and unreacted starting material. Although separation by fractional crystallisation is possible, separation by thin-layer chromatography is preferable. Using a cyclohexane–acetone (4 : 1) mixture on silica gel (Merck 60 F_{254}), the starting material moves fastest followed by (3) and then (2). Attempts to use column chromatography led to isomerisation of (3) into (2).

The separated isomers were removed from the silica gel by dissolution in dichloromethane. The products may be recrystallised by dissolving in the minimum volume of dichloromethane, adding a 10—20-fold excess of ethanol, and refrigerating (Found: C, 20.1; H, 4.3; Cl, 22.3; S, 13.4 for (2); C, 20.2; H, 4.3; Cl, 22.4; S, 13.5 for (3). Calc. for $C_{16}H_{40}Cl_6Ir_2S_4$: C, 20.1; H, 4.2; Cl, 22.2; S 13.4%). Melting points: 168 °C for (2), 174 °C for (3). Electrical conductivity measurements showed (2) and (3) to be neutral molecular species. Hydrogen-1 n.m.r. spectra in $CDCl_3$ solution were measured on a Varian X-L 100 spectrometer at 100 MHz. Shifts are quoted with respect to $SiMe_4$.

RESULTS AND DISCUSSION

The crystal structures of compounds (2) and (3) have been determined and will be published elsewhere.[8,9] The structures given above will be assumed in the following discussion.

Hydrogen-1 *N.M.R. Spectra*.—Rapid inversion at the sulphur atom of co-ordinated diethyl sulphide is well established[10,11] but was neglected in the previous discussions of the n.m.r. spectrum of (1).[7,12] Compounds (1), (2), and (3) all give blurred ^1H n.m.r. spectra at room temperature but on cooling to −20 °C the spectra may be resolved (see the Figure). The low-temperature spectrum of (1) may be simulated satisfactorily by two ABM_3 systems with intensity ratio 2 : 1 (corresponding to *mer* geometry) and that of (2) by two ABM_3 systems of equal intensity, in agreement with the crystal structure. The spectrum of (3) differs by the presence of a multiplet centred at $\delta = 4.2$ p.p.m., well resolved even at room temperature. The intensity of this multiplet corresponds to the methylene protons of one diethyl sulphide group, and we assign this to the bridging diethyl sulphide ligand. The other methylene resonances, assigned to unidentate SEt_2 groups, may be resolved on cooling as for (1) and (2). We suggest that the absence of inversion at a tetrahedrally co-ordinated sulphur atom may be used as a diagnostic for a bridging sulphur ligand.



^1H N.m.r. spectra: (*a*) (2) at 30 °C; (*b*) (2) at −20 °C; (*c*) (3) at 30 °C showing a well resolved low-field multiplet. Peaks marked with a cross are due to impurities

Photochemistry.—The effectiveness of Pyrex-filtered sunlight or a simple tungsten lamp in photolysing (1) suggests that the reaction is caused by excitation of the first spin-allowed *d–d* band of (1) at *ca.* 320 nm.[6] The electronic spectra of the products show a slight bathochromic shift and a considerable increase in intensity. The reaction is thus prevented from going to conclusion by the greater absorption of the products.

Two features of the photochemical reaction are of interest. Firstly, Adamson's rule that the axis labilised photochemically is that with the weakest average ligand field is not obeyed, since this would imply loss of chloride from (1).[13] We presume that this is due to the non-polar nature of the solvent which will not favour ionic dissociation or photosolvation. Solvent effects on photolysis of similar compounds have previously been reported.[14] Secondly, the photochemical behaviour of *mer*-$[IrCl_3(SEt_2)_3]$ is notably different from that of *mer*-$[IrCl_3L_3]$ (L = tertiary phosphine) where photolysis gives *fac*-$[IrCl_3L_3]$ in high yield.[4] No trace of products other than (2) and (3) was observed, and the absence of *fac*-$[IrCl_3(SEt_2)_3]$ suggests this compound to be unstable. In the presence of free diethyl sulphide the photolysis of (1) is stopped. Photolytic formation of dimers has previously been observed for $[RhCl_3(CO)(PPr^n_3)_2]$ with loss of CO to give $[Rh_2Cl_6(PPr^n_3)_4]$.[4]

The formation of dimers of formula $[\{MX_3L_2\}_2]$ (M = Rh or Ir; L = tertiary phosphine, tertiary arsine, or thioether) has frequently been reported,[15] and a structure similar to (2) was found for $[Rh_2Cl_6(PBu^n_3)_4]$ [16] and proposed for $[Rh_2Cl_6(SEt_2)_4]$.[17] In other cases halogen bridging between metal atoms has been assumed. The thioether bridged isomer (3) appears to be a kinetic product since isomerisation to (2) occurs on heating, and, to a certain extent, on a chromatography column. Thus, although bridging thioether groups are well known for platinum(II) compounds,[18] the bridging thioether linkage in (3) appears to be notably less stable than the double chloride bridge.

We are grateful to Dr. U. Burger and Mr. J.-P. Saulnier for obtaining the n.m.r. spectra. We acknowledge the assistance of the National Science Foundation Undergraduate Research Participation Programme (grant GY-9916) and the California State University, Fresno, Research Committee.

[9/786 *Received, 21st May*, 1979]

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