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Preliminary communication

THE SEPARATION OF PURE LATERAL AND DIAGONAL ISOMERS OF CYCLOPENTADIENYLDIBROMODICARBONYLRHENIUM

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Summary

Chromatography of $C_5H_5Re(CO)_2Br_2$ easily separates pure lateral and diagonal isomers which can be identified by the relative intensities of their symmetric and asymmetric $\nu(CO)$ bands.

Compounds of the types $C_5H_5MA_2B_2$ and $C_5H_5MA_2BC$ are known [1-3] to exist as pairs of lateral and diagonal isomers**. However, it has not been possible to separate pure lateral and diagonal isomers of the same compound by well-defined procedures, although a brief report [4] as well as more recent work [5] suggests the possibility of separating pure lateral and diagonal isomers of halide complexes of the type $C_5H_5Mo(CO)_2LX$ (L = $(CH_3)_3CNC$, C_6H_5NC, and $(C_6H_5)_3P$; X = Cl, Br, and I) by rather tedious and poorly described fractional crystallization procedures. We have now found that the reported [6] rhenium complex $C_5H_5Re(CO)_2Br_2$ can readily be separated into pure lateral and diagonal isomers by a simple and reproducible chromatographic procedure.

The reaction of $C_5H_5Re(CO)_3$ [7,8] with bromine in trifluoroacetic acid at room temperature was carried out according to the published procedure [6]. After quenching the reaction with water, the resulting brown solid was chromatographed on a Florisil column in dichloromethane solution. Elution with dichloromethane followed by evaporation of the eluates and recrystallization of the $C_5H_5Re(CO)_2Br_2$ fractions from mixtures of dichloro-

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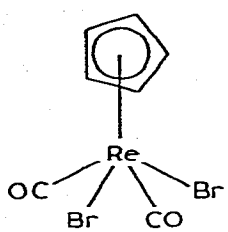
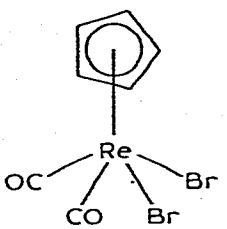
**The terms "lateral" and "diagonal" seem preferable to the more commonly used terms "*cis*" and "*trans*" for these pairs of isomers since in neither isomer are two ligands situated at 180° angles relative to each other as normally expected for *trans* isomers.

methane and carbon tetrachloride gave successively the following products: (a) Unreacted $C_5H_5Re(CO)_3$ (35% recovery); (b) Maroon plates of isomer A of $C_5H_5Re(CO)_2Br_2$ (39% conversion), m.p. 221-223°; infrared ν(CO) in $CHCl_3$: 2070 (*sym.*) and 2008 (*asym.*) cm^{-1}; proton NMR C_5H_5 in $(CD_3)_2CO$: τ 4.00; (c) Dark brown microcrystals of isomer B of $C_5H_5Re(CO)_2Br_2$ (13% conversion), m.p. 217-220°; infrared ν(CO) in $CHCl_3$: 2055 (*sym.*) and 1987 (*asym.*) cm^{-1}; proton NMR C_5H_5 in $(CD_3)_2CO$: τ 3.60. Both isomers of $C_5H_5Re(CO)_2Br_2$ gave correct C, H, and Br analyses within ±0.3%. Isomer B was considerably less soluble than isomer A in organic solvents such as dichloromethane.

Isomers A and B of $C_5H_5Re(CO)_2Br_2$ were identified as the diagonal (I) and lateral (II) isomers, respectively, by determination of the angles between



(I)



(II)

their two C—O bonds through the relationship [9] $\tan^2\theta = I_a/I_s$ where 2θ is the angle between the two C—O bonds, I_a is the area under the asymmetric ν(CO) band, and I_s is the area under the symmetric ν(CO) band with the ratio I_a/I_s being extrapolated to infinite dilution. Thus for isomer A the ratio I_a/I_s is 2.98 corresponding to an angle 2θ of 120° thereby indicating isomer A to be the diagonal isomer I. Similarly for isomer B the ratio I_a/I_s is 0.655 corresponding to an angle 2θ of 78° thereby indicating isomer B to be the lateral isomer II.

Both the diagonal (I) and lateral (II) isomers of $C_5H_5Re(CO)_2Br_2$ are stable in the solid state at room temperature with respect to isomerization. The diagonal isomer of $C_5H_5Re(CO)_2Br_2$ is also stable to isomerization in solutions in inert solvents even at temperatures as high as 110° (boiling toluene). The lateral isomer of $C_5H_5Re(CO)_2Br_2$ is stable in solution at room temperature over a period of days but readily isomerizes to the corresponding diagonal isomer in solution at elevated temperatures such as during several minutes in boiling chloroform. These observations suggest that the diagonal isomer I of $C_5H_5Re(CO)_2Br_2$ is more thermodynamically stable than the corresponding lateral isomer II possibly because of less steric interaction between the two relatively bulky bromine atoms in the diagonal isomer I relative to the lateral isomer II.

Further details on the isomerization of the lateral isomer of $C_5H_5Re(CO)_2Br_2$ to the corresponding diagonal isomer will be reported in a forthcoming full paper as well as reactions of the $C_5H_5Re(CO)_2Br_2$ with various ligands such as isocyanides and tertiary phosphites.

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