Formation of *trans*-Bis(triphenylphosphine)chlorotricarbonylrhenium by Incorporation of Chlorine from a Perchlorate Ion

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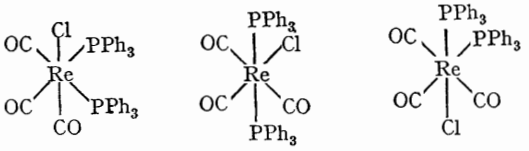
FEW ligand-substituted derivatives of the hexacarbonylrhenium cation have been reported to date, and of these [v-triars $Re(CO)_3]^+$ was prepared[1] by direct action of the arsine upon $Re(CO)_6^+$, and [*trans*-$(Ph_3P)_2Re(CO)_4]^+$ was prepared[2] by the carbonylation of $(Ph_3P)_2Re(CO)_3Cl$. We have also obtained a cationic product [diphos $Re(CO)_4]^+$ from the direct interaction of hexacarbonylrhenium and 1,2-bis(diphenylphosphino)ethane. In very marked contrast, however, the action of triphenylphosphine upon hexacarbonylrhenium perchlorate has yielded the neutral complex bis(triphenylphosphine)chlorotricarbonylrhenium $(Ph_3P)_2Re(CO)_3Cl$, characterised by elemental analysis, i.r. spectrum [ν_{CO} at 2050 (w), 1954 (vs), and 1905 (m) cm.$^{-1}$], M (osmometric) in chloroform: found 780; required 830; and electrical conductivity $\Lambda_{0\cdot001M} = 0\cdot33$ ohm^{-1} cm.^{2} mole^{-1}).

In addition to its unexpected formation, we find that the product has a different stereochemistry from the previously reported[3] bis(triphenylphosphine)chlorotricarbonylrhenium. The three possible structures for the compound are (I), (II), and (III). The previously reported isomer of



(I) (II) (III)

$(Ph_3P)_2Re(CO)_3Cl$, designated[3] the *cis*-structure (I), has three i.r. modes of almost equal intensity and is not the isomer prepared in the present work, which we call the *trans*-isomer. We find, however, that like the corresponding manganese compounds[4] the *cis*-isomer can be converted into the *trans*, but as reported by Freni,[5] vigorous conditions (150° in the presence of an excess of triphenylphosphine) are required, as compared with the manganese isomerization.[4] The *trans*-isomer we obtain by this thermal method is identical with that obtained from the hexacarbonylrhenium perchlorate and we favour (II) rather than (III) for this, by analogy[4] with the spectrum of the corresponding manganese compound, whose dipole moment strongly suggests (II).

To explain the formation of a chloro-complex in high yield, and its stereochemistry, it is possible that initially the hexacarbonylrhenium cation undergoes substitution to give $[(Ph_3P)_2Re(CO)_4]^+$ which is known in a *trans*-configuration.[2] Subsequent attack by chloride, generated *in situ* by the triphenylphosphine reduction of the perchlorate, with evolution of carbon monoxide could produce the observed *trans*-$(Ph_3P)_2Re(CO)_3Cl$. As the reactions were carried out in chlorine-free solvents, the only source of chlorine appears to be the perchlorate anion by a somewhat unexpected reduction. This source of chlorine has been confirmed by the preparation of ^{36}Cl labelled $[Re(CO)_6]ClO_4$, which reacted with triphenylphosphine to produce *trans*-$(Ph_3P)_2Re(CO)_3Cl$ with over 95% incorporation of ^{36}Cl.

The postulated mechanism is given support by the observation that it is also possible to obtain (II) by the action of triphenylphosphine upon *trans*-bis(triphenylphosphine) tetracarbonyl perchlorate under analogous conditions.

We further note that when triphenylphosphine and sodium perchlorate in diglyme are heated for a short time, triphenylphosphine oxide and chloride ion are detectable in the solution.

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