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Preliminary communication

Syntheses of ruthenium tertiary phosphine complexes of type $[RuX_2(PR_3)_{3\ or\ 4}]$

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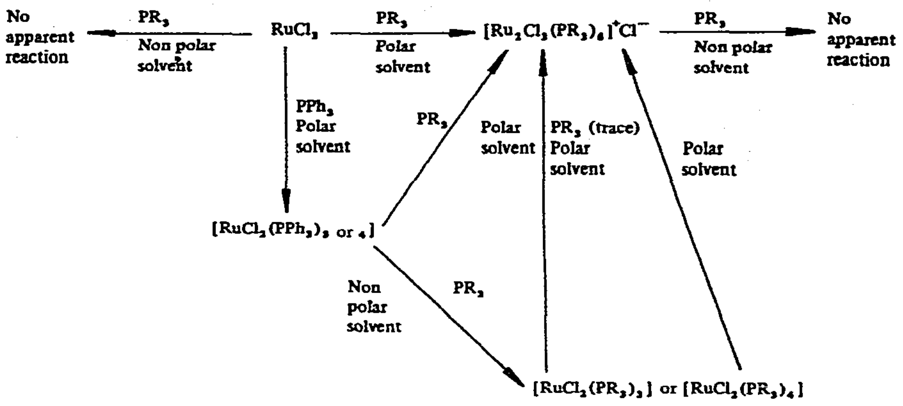
Since the preparation of $[RuX_2(PPh_3)_n]$ ($X = Cl, Br; n = 3,4$) in 1966[1], numerous papers have been published on the reactions of these compounds with carbon, sulphur, nitrogen and oxygen donor ligands[2] and on their usefulness as catalytic precursors in various olefin hydrogenation[3] and oxidation[4] reactions. A number of similar compounds of type $[RuX_2L_4]$ containing phosphorus donor ligands (L = secondary phosphine[5], tertiary phosphite[6]; L_2 = ditertiary phosphine[7]) have also been prepared, either by reaction between RuX_3 and L or by direct replacement of PPh_3 in $[RuX_2(PPh_3)_4]$. However, reaction of other tertiary phosphines with RuX_3 in either aqueous/ethanol[7] or 2-methoxyethanol[8] gives only the lemon-yellow dimeric triply halide-bridged cations $[Ru_2X_3(PR_3)_6]^+X^-$ ($PR_3 = PMe_2Ph, PMePh_2, PEt_2Ph, PEtPh_2, PPr_2Ph, PBu_2Ph, PEt_3$) which are not very useful starting materials in comparison with $[RuX_2(PPh_3)_{3\ or\ 4}]$.

In this note, we wish to report a convenient general synthetic method for the preparation of ruthenium tertiary phosphine complexes of type $[RuX_2(PR_3)_3]$ and $[RuX_2(PR_3)_4]$ which, on the indications of preliminary work, are excellent starting materials for the facile synthesis of a wide range of ruthenium(II) phosphine compounds. These complexes can be prepared by refluxing $[RuX_2(PPh_3)_4]$ in hexane or light petroleum (b.p. 60–80°) with an excess of tertiary phosphine, *e.g.*, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$ or $PClPh_2$. The ethylphosphine complexes are exclusively of type $[RuX_2(PR_3)_3]$ (orange or green) whereas the methylphosphine complexes are of type $[RuX_2(PR_3)_4]$ (yellow); chlorodiphenylphosphine forms the tris complex (X = Cl) and the tetrakis complex (X = Br). Examination of the low temperature ^1H NMR of $[RuCl_2(PMe_2Ph)_4]$ indicates a *cis*-configuration (*cf.* *cis*-$[RuH_2(PMe_2Ph)_4]$[9].

The compounds are soluble in most common organic solvents and are initially non-conducting. However, on standing, the conductivity slowly increases. This is particularly true for $[RuCl_2(PMe_2Ph)_4]$ where removal of dichloromethane solvent after ca. 5 h gives $[Ru_2Cl_3(PMe_2Ph)_6]$ Cl. For the other $[RuX_2(PR_3)_{3\ or\ 4}]$ compounds, refluxing gently in ethanol (with a small amount of free phosphine in the case of the tris compounds) readily gives the ionic species. If the reactions between $[RuX_2(PPh_3)_4]$ and

Scheme 1



(PR_3 = $PPhMe_2$, PPh_2Me, $PPhEt_2$, PPh_2Et)

excess PR_3 are carried out in CH_2Cl_2 or ethanol, the main product is the ionic dimer. Thus, these various reactions which are summarised in Scheme 1 effectively demonstrate the relative stabilities of these monomeric and dimeric ruthenium tertiary phosphine complexes and the importance of the solvent media in synthetic inorganic chemistry.

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