Journal of Organometallic Chemistry, 60 (1973) C63–C66
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Preliminary communication

ortho-Metallation reactions involving some triphenyl phosphite complexes of osmium

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(Received September 3rd, 1973)

SUMMARY

Osmium triphenylphosphine complexes, $OsH_4(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$ react with triphenyl phosphite in boiling organic solvents to yield triphenyl phosphite derivatives which subsequently undergo *ortho*-metallation reactions.

Cyclometallation reactions involving cleavage of carbon–hydrogen bonds in coordinated organo-phosphorus and -nitrogen ligands have been observed for an extensive range of platinum metal complexes[1]. In particular, intramolecular *ortho*-metallation of coordinated triphenyl phosphite ligands affords products containing sterically favoured five-membered chelate rings, and numerous examples of *ortho*-metallation reactions involving these ligands have been described[2]. We have reported reactions of this type for triphenyl phosphite derivatives of ruthenium[3], iridium[4], palladium and platinum[2], and now discuss the first reported examples involving the corresponding osmium complexes.

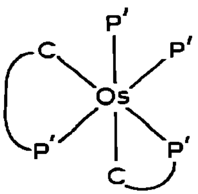
The osmium triphenyl phosphite complexes suitable for use in the present work were unknown, and were therefore generated *in situ* by treatment of the appropriate triphenylphosphine derivatives, $OsH_4(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$, with an excess of triphenyl phosphite in boiling organic solvents. In several instances mixed phosphine/phosphite species, arising from the stepwise displacement of the triphenylphosphine ligands, were observed and isolated; however, in other cases, *ortho*-metallation of the incoming triphenyl phosphite ligands occurred readily, and only the *ortho*-metallated products could be satisfactorily characterised. No evidence for the metallation of the residual triphenylphosphine ligands was found. The reactions observed are summarised below (Schemes 1, 2 and 3). Intermediates postulated but not isolated or characterised are given in brackets; all other products were isolated and were fully characterised by infrared, proton and phosphorus NMR and analytical data. The presence of *ortho*-metallated triphenyl phosphite ligands was confirmed using previously established infrared criteria[2].

The conversion of $OsH_4(PPh_3)_3$ to the dimetallated product $Os[(C_6H_4O)P(OPh)_2]_2[P(OPh)_3]_2$ by treatment with excess triphenyl phosphite in boiling decalin (Scheme 1) must involve a series of ligand substitution and *ortho*-metallation reactions; however in the absence of characterisable intermediates the exact reaction sequence cannot be determined. The final product $Os[(C_6H_4O)P(OPh)_2]_2[P(OPh)_3]_2$, isolated from this reaction, is the first example of a dicyclometallated osmium derivative. Its ^{31}P NMR spectrum shows the presence of four non-equivalent phosphorus nuclei and is therefore indicative of stereochemistry (I). A similar stereochemistry (II) has recently been established for the closely related, dimetallated iridium(III) complex $IrCl[(C_6H_4O)P(OPh)_2]_2[P(OPh)_3]$[5].

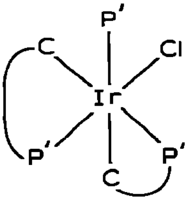
Scheme 1.

$$\mathrm{OsH_4P_3} \xrightarrow[\text{boiling decalin } 1\tfrac{1}{2}\text{h}]{\text{excess P}'} \mathrm{Os(P'{-}C)_2P'_2}$$

$(P = PPh_3;\ P' = P(OPh)_3;\ P'{-}C = (C_6H_4O)P(OPh)_2)$



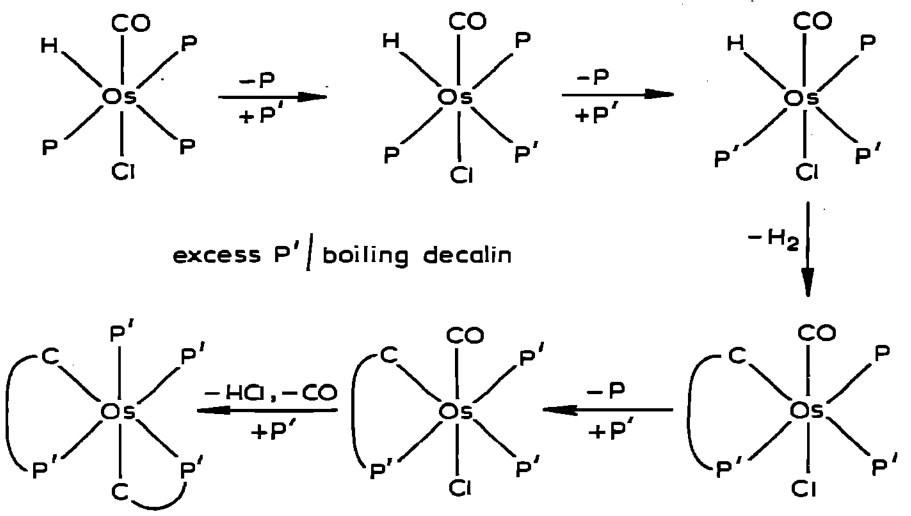
(I)



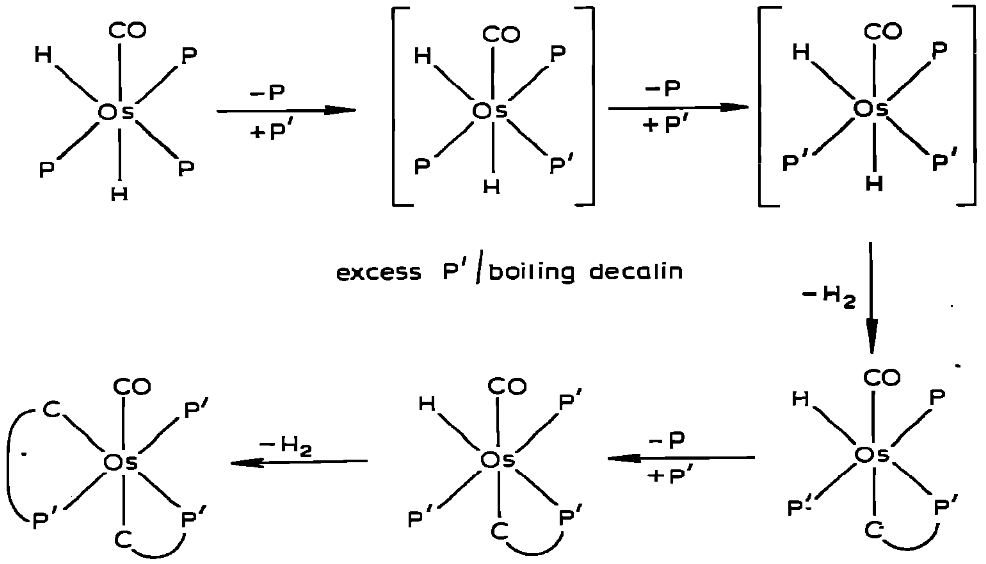
(II)

The prolonged reaction of $OsHCl(CO)(PPh_3)_3$ with triphenyl phosphite in boiling decalin also gave the dimetallated complex $Os[(C_6H_4O)P(OPh)_2]_2[P(OPh)_3]_2$ (I) as final product (Scheme 2). Hydrogen chloride (1 mol per mol of complex) was eliminated during this reaction and was estimated as silver chloride. Under less vigorous conditions, the intermediates shown (Scheme 2) could be isolated and characterised; however the fully substituted species $OsHCl(CO)[P(OPh)_3]_3$ could not be detected.

The vigorous conditions necessary to induce reaction between $OsH_2(CO)(PPh_3)_3$ and triphenyl phosphite (Scheme 3) are sufficient to cause *ortho*-metallation to occur; simple substitution products could not, therefore, be detected. However, the metallated species (III) and (IV) were isolated and fully characterised. These complexes, on prolonged reaction with triphenyl phosphite in boiling decalin, afford a further product which we tentatively formulate as the dimetallated species (V) but we were unable to isolate it in a pure form.



Scheme 2



(V) (IV) (III)

Scheme 3

ACKNOWLEDGEMENT

We thank the S.R.C. for financial support of this work.

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