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NOTE

HYDRIDO COMPLEXES OF OSMIUM(II): *trans*-[$OsH_2(Ph_2P{-}CH_2{-}PPh_2)_2$] AND THE Os–H BOND IN *trans*-[$OsHCl(Ph_2P{-}CH_2{-}PPh_2)_2$]·$C_6H_6$

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The reduction of *cis*-[$OsCl_2(Ph_2P{-}CH_2{-}PPh_2)_2$] with lithium aluminium hydride in tetrahydrofuran was reported to give a hydridochloride of osmium(II) which crystallises from benzene as the solvent adduct, *trans*-[$OsHCl(Ph_2P{-}CH_2{-}PPh_2)_2$]·$C_6H_6$ (I). The Os–H stretching vibration was not observed in the infrared and only appeared, as a weak band at 2077 cm^{-1}, when benzene was removed under high vacuum[1].

We have tried to repeat the preparation of (I) in order to make an X-ray study of the interaction between the hydride ligand and the molecule of benzene.

We find that the reduction of *cis*-[$OsCl_2(Ph_2P{-}CH_2{-}PPh_2)_2$] with commercial lithium aluminium hydride (100% excess) in tetrahydrofuran does give the hydridochloride of osmium(II), *trans*-[$OsHCl(Ph_2P{-}CH_2{-}PPh_2)_2$], but with a medium intensity band in the infrared (nujol mull) at 2088 cm^{-1} which we assign to the Os–H stretch. This band differs in position from the value of 2077 cm^{-1} in the earlier report[1] and is not suppressed when the complex crystallises from benzene as the complex, *trans*-[$OsHCl(Ph_2P{-}CH_2{-}PPh_2)_2$]·$\frac{1}{2}$ C_6H_6, m.p. 286–288°. (Found: C, 61.8; H, 4.75; Cl, 4.17. $C_{53}H_{48}ClOsP_4$ calcd.: C, 61.6; H, 4.7; Cl, 3.44%.) The Os–H bond assignment is confirmed by ^1H NMR which shows a quintet of bands at τ 27.0, [$J(P{-}H) = 15$ Hz] for the hydride ligand.

Deuteration experiments using lithium aluminium deuteride as reducing agent give the deutero analogue, *trans*-[$OsDCl(PPh_2{-}CH_2{-}PPh_2)_2$]·$\frac{1}{2}$ C_6H_6, mp 280°, with Os–D stretching vibration at 1494 cm^{-1}. The isotopic shift factor, $\nu(Os{-}H)/\nu(Os{-}D) = 1.398$. (Found: C, 61.54; H, 4.78; Cl, 3.13. $C_{53}H_{47}ClDOsP_4$ calcd.: C, 61.5; H, 4.54; Cl, 3.43%.)

When ethyl acetate is used as solvent, the complex crystallises as [$OsHCl(Ph_2P{-}CH_2{-}PPh_2)_2$]·$\frac{1}{2}$ EtOAc, m.p. 273–274°. (Found: C, 60.1; H, 4.92; Cl, 3.25. $C_{52}H_{49}ClOOsP_4$ calcd.: C, 60.1; H, 4.75; Cl, 3.42%.) The Os–H stretch is at 2074 cm^{-1} and the ethyl acetate bands occur at 1735, 1235 and 1048 cm^{-1} in the infrared as was reported by Chatt and Hayter[1]. The Os–Cl stretch is assigned to a band at 362 cm^{-1}.

If a large excess of lithium aluminium hydride (10 times excess) is used for the reduction of *cis*-[$OsCl_2(Ph_2P{-}CH_2{-}PPh_2)_2$], the complex obtained is *trans*-[OsH_2-

$(Ph_2P\text{-}CH_2\text{-}PPh_2)_2]$, which crystallises from benzene as yellow rhombs, m.p. 255° (dec.). (Found: C, 63.07; H, 4.92; $C_{50}H_{46}OsP_4$ calcd.: C, 62.5; H, 4.8%.) *trans*-$[OsH_2(Ph_2P\text{-}CH_2\text{-}PPh_2)_2]$ is reported here for the first time. The Os–H stretch shows up in the infrared as a very strong band at 1712 cm^{-1}, which is consistent with the value of 1720 cm^{-1} for Os–H stretch in the complex *trans*-$[OsH_2(Et_2P\text{-}o\text{-}C_6H_4\text{-}PEt_2)_2]$[1]. The deutero analogue has the Os–D bond stretch at 1228 cm^{-1} and the isotopic shift factor, $\nu(Os\text{-}H)/\nu(Os\text{-}D)$ is 1.394. We were unable to obtain a reliable ^1H NMR for the hydride ligand because the complex was not sufficiently soluble in an inert solvent.

Our results confirm the existence of a benzene solvate of the complex *trans*-$[OsHCl(Ph_2P\text{-}CH_2\text{-}PPh_2)_2]$, but cast some doubts on several reports in recent years which have justified conclusions on the existence of metal hydrides in absence of a metal–hydrogen stretch in the infrared by reference to the complex *trans*-$[OsHCl(Ph_2P\text{-}CH_2\text{-}PPh_2)_2]\cdot C_6H_6$.

REFERENCE

1 J. Chatt and R. G. Hayter, *J. Chem. Soc.*, (1961) 2605.