X-Ray Molecular Structure of $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$; a Complex with a Co-ordinated Tertiary Phosphineiminato(1−) Ion

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Summary *X*-Ray structure analysis has shown that $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ contains a co-ordinated $Et_2PhP{=}N^-$ ligand with an essentially linear arrangement of Ru–N–P.

GRIFFITH and PAWSON have recently reported[1] that triphenylphosphine reacts with $[OsNCl_4]^-$ to give $Os(NPPh_3)Cl_3(PPh_3)_2$. Further work[2] has shown that a wide range of phosphines R_3P will react with $MNX_3(AsPh_3)_2$ (M = Os, Ru; X = Cl, Br) to give $M(NPR_3)X_3(PR_3)_2$. We now present *X*-ray structural data on $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ which, since it shows the presence of a co-ordinated $Et_2PhP{=}N^-$ ligand, confirms the suggestion[1] that nucleophilic attack on the nitride ligand by the phosphine has occurred. This unusual behaviour of osmium and ruthenium nitrido complexes in functioning as electrophilic deprotonated nitrenes is in contrast to the nucleophilic behaviour of some rhenium complexes, *e.g.* $ReNCl_2(PEt_2Ph)_3$.[3]

The title compound crystallises from acetone as black prisms. The crystals are orthorhombic, a = 19·870, b = 11·933, c = 14·194 Å, U = 3365·5 Å^3, D_m = 1·41, Z = 4, D_c = 1·42, space group $P2_12_12_1$. *X*-Ray intensity data were collected on a Siemens four-circle diffractometer. Using Cu-K_α radiation a total of 3591 independent reflections were measured (to θ = 70°), of which 45 were judged to be unobserved. The structure was solved by Patterson and Fourier methods and least-squares refinement has now reached R = 0·035.

The Figure shows that the ruthenium atom has a slightly

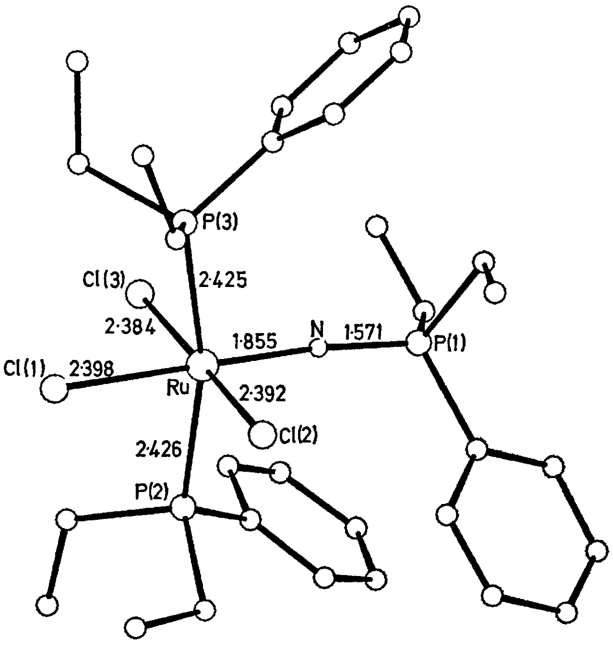

FIGURE. Molecular structure of $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$. The estimated standard deviations are: Ru–P, 0·002; Ru–Cl, 0·002; Ru–N, 0·005; N–,P 0·005 Å.

distorted octahedral co-ordination with a mean Ru–P distance of 2·426 Å, and a mean Ru–Cl (*trans* to Cl) distance of 2·388 Å. An Ru–Cl (*trans* to N) distance of 2·398 Å suggests that the $NPEt_2Ph$ group exerts little, if any, *trans*-influence.

A structurally novel part of the molecule is the phosphineiminato ligand which is co-ordinated to the metal atom in an essentially linear fashion, with an Ru–N–P angle of 175·0(4)°. The P–N distance of 1·571 Å is typical of a P=N double bond,[4] whereas the Ru–N distance of 1·855 Å may be compared to those of 1·720 and 1·725 Å found in two other Ru(IV) complexes, $M[Ru_2NCl_8(H_2O)_2]$ (where M = K[5] or NH_4[6]), in which the nitride ligand plays a bridging role.

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