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Preliminary communication

CRYSTAL AND MOLECULAR STRUCTURES OF *cis*-DICHLOROBIS(TRIFLUOROPHOSPHINE)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II), *cis*-$RuCl_2(PF_3)_2(PPh_3)_2$, AND DICHLORO(2,7-DIMETHYLOCTA-2,6-DIENE-1,8-DIYL)(TRIFLUOROPHOSPHINE)RUTHENIUM(IV), $RuCl_2(PF_3)(C_{10}H_{16})$

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Summary

The first structures of trifluorophosphine complexes of transition metals in an oxidation state greater than +1 are reported.

Although many transition metal complexes of trifluorophosphine have been characterised [1-3], very little structural work on them has been reported, and in no case are there details on complexes in which the oxidation state of the metal exceeds +1. In view of current interest [4, 5] in the nature of the metal—phosphorus bond in transition metal phosphine complexes we have recently synthesised [6, 7] the complexes $RuCl_2(PF_3)_2(PPh_3)_2$ (I) and $RuCl_2(PF_3)(C_{10}H_{16})$ (II) [($C_{10}H_{16}$ = 2,7-dimethyl-2,6-diene-1,8-diyl] in which the oxidation state of the ruthenium atom is formally +2 and +4, respectively. We describe below their molecular structures (Figs. 1 and 2) as determined by a single crystal X-ray crystallographic analysis.

I crystallises in space group $P2_1/n$, a special setting of $P2_1/c$. The unit cell has dimensions a = 18.540(8), b = 16.067(7), c = 12.415(5) Å and β = 102.64(3)°. A final R factor of 3.4% was attained, based on 2310 significant reflections. II crystallises in space group $C2/c$ with unit cell dimensions a = 12.575(10), b = 9.591(7), c = 12.051(9) Å and β = 106.70(6)°. Refinement converged at R 3.9%, based on 1112 significant reflections.

In complex I the *cis*-arrangement of the two trifluorophosphine ligands within a slightly distorted octahedral structure confirms our previous suggestion based on NMR studies on the related dihydride complex [6]. The ruthenium—triphenylphosphine distances are found to be 2.471 and 2.456 Å respectively, while the metal—trifluorophosphine bond lengths are very much shorter (2.180 and 2.160 Å). Standard deviations in Ru—P bond lengths are 0.002Å.

The structure of II is based on a trigonal bipyramid in which the axial posi-

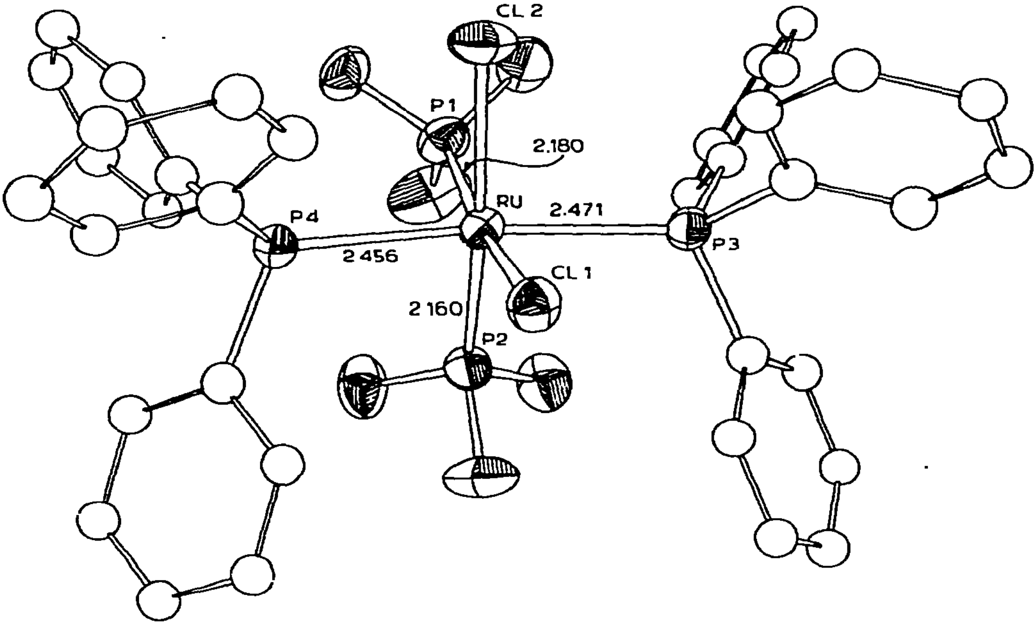

Fig. 1. Molecular structure of the complex $RuCl_2(PF_3)_2(PPh_3)_2$.

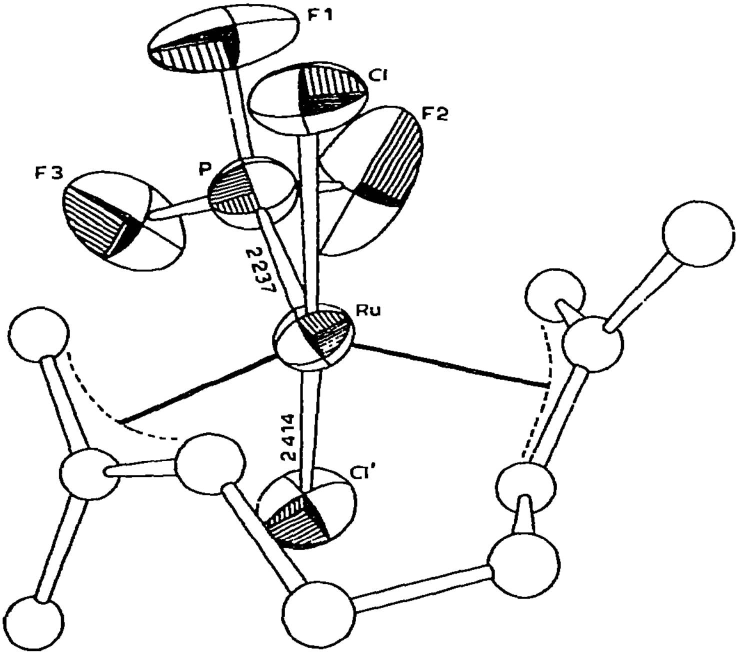

Fig. 2. Molecular structure of the complex $RuCl_2(PF_3)(C_{10}H_{16})$.

tions are occupied by the chlorine atoms. The organic moiety which consists of a linear tail to tail dimer of isoprene occupies two of the equatorial sites and the third position is occupied by PF_3. The trifluorophosphine molecule is totally disordered about a two-fold rotation axis along the metal--phosphorus bond.

The ruthenium—PF_3 bond distance in II is found to be 2.237(3) Å which, although significantly longer than the mean of the Ru—PF_3 distances found in I, is nevertheless at the short end of the range of Ru—P distances (2.2-2.4 Å) in other phosphineruthenium complexes [8-18].

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