Reduction of Tris(triphenylphosphine)dichlororuthenium(II) in Acetonitrile: Reformulation of the Nature of the Product; Detection of the First Paramagnetic d^8 Complex†

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Summary The complex alleged to have the stoicheiometry $Ru(MeCN)_2(PPh_3)_4$ and to contain a π-bonded acetonitrile, produced by electrochemical reduction of $RuCl_2(PPh_3)_n$ (n = 3 or 4) in presence of acetonitrile, has been shown to be the hydrido *ortho*-metallated phosphine species $RuH(MeCN)(C_6H_4PPh_2)(PPh_3)_2$; in the reduction of $RuCl_2(PPh_3)_3$ in tetrahydrofuran–MeCN a red transient intermediate, believed on the basis of e.s.r. studies to be a d^8 ruthenium(0) species, is formed.

Since several putative complexes of ruthenium(0) were shown to be otherwise,[1,2] another prime candidate for reformulation is $Ru(MeCN)_2(PPh_3)_4$.[3] This complex, alleged to contain a π-bonded acetonitrile on the basis of i.r. spectra was obtained by electrochemical reduction of $RuCl_2(PPh_3)_4$ in MeCN.

The reduction of $RuCl_2(PPh_3)_n$ (n = 3 or 4) by sodium or magnesium amalgam in tetrahydrofuran (THF) containing *ca.* 10% MeCN gives a yellow complex evidently identical with that reported.[3] Thus all similar are the melting point, quoted i.r. frequencies, solubilities, and the reaction[4] with propene to give $RuH(C_3H_5)(MeCN)(PPh_3)_2$.

However, additional peaks in the i.r. spectrum at 1550 and 1410 cm^{-1} suggest[1] an *ortho*-metallated phenyl ring. The quoted[3] absorption at 1910 cm^{-1} is clearly due to the presence of a Ru–H bond, not π-MeCN, and this is proved by ^1H n.m.r. study in THF–MeCN in which the compound is soluble and stable; there is a doublet of doublets of doublets at δ −11·8. The ^{31}P n.m.r. spectrum (three doublets of doublets) confirms that the three phosphorus atoms non-

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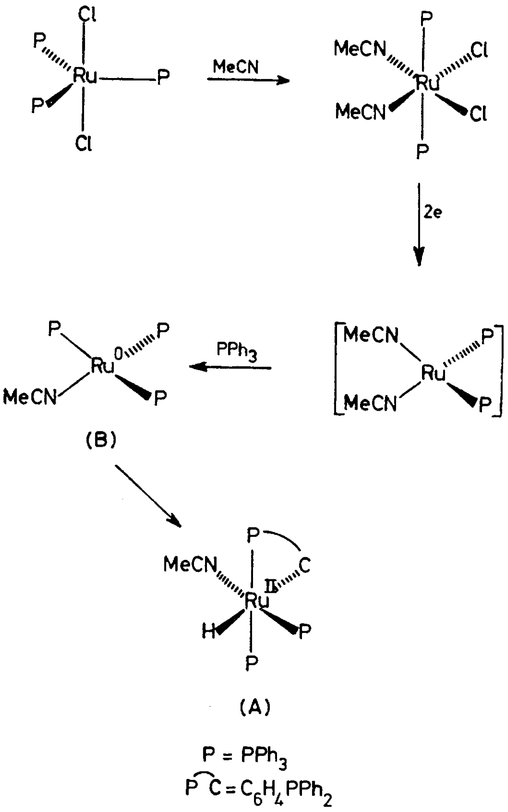
† No reprints available.



Scheme

equivalent and meridional as in (A) (Scheme). The compound is thus RuH(MeCN)($C_6H_4PPh_2$)(PPh_3)$_2$ and all the reactions reported for 'Ru(MeCN)$_2$(PPh_3)$_4$' may easily be accommodated on this basis.

Most interesting however, is that in the reduction of $RuCl_2(PPh_3)_3$ in THF–MeCN a transient red intermediate is formed. This has a half-life of *ca.* 1 min at 25 °C but is reasonably stable at low temperatures. Electron paramagnetic resonance study of solutions frozen when red, and after re-warming and re-reduction allows the identification of a spectrum that can be unequivocally assigned to the red species. The two, equally intense peaks can be assigned as the two central peaks of an axially symmetrical $S = 1$ spin system; the outer lines are weak and very broad suggesting marked anisotropy.

The red species is evidently a ruthenium(0), four-coordinate complex. Preliminary attempts to isolate this highly unstable species, which very readily converts into (A), suggest that it is Ru(MeCN)(PPh_3)$_3$ (B). This appears to be the first paramagnetic d^8 complex of an element in the second or third row transitional series. It may be noted that, although having a distorted tetrahedral structure, Ru(styrene)$_2$(PPh_3)$_2$ is diamagnetic.[2]

The mechanism of reduction of $RuCl_2(PPh_3)_n$ ($n = 3$ or 4) in the presence of MeCN is shown in the Scheme; the complex $RuCl_2(MeCN)_2(PPh_3)_2$ is known.[5]

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