A Novel Hexamethylbenzenerhodium Chloride Complex

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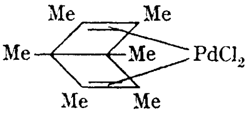
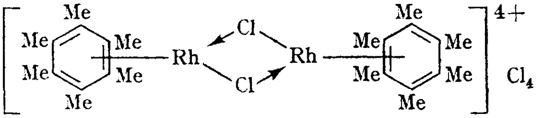
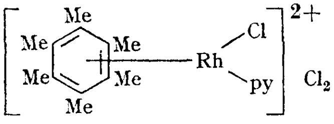
THE preparations of several transition-metal complexes of bicyclo[2,2,0]hexa-2,5-diene derivatives have been described recently.[1,2] As part of a general study of the reactions of such derivatives we have independently obtained the unstable, yellow compound, dichloro(hexamethylbicyclo-[2,2,0]hexa-2,5-diene)palladium (I) by a method similar to that described recently,[2] and confirm the reported data. The isolation of a novel arene–rhodium complex from hexamethylbicyclo-[2,2,0]hexa-2,5-diene is now described.


(I)


(II)


(III)

When hexamethylbicyclo[2,2,0]hexa-2,5-diene is stirred with $RhCl_3,3H_2O$ in aqueous methanol at 60°, an orange-brown solid is produced (43%). The ^1H n.m.r. spectrum in $CDCl_3$ shows only one band (τ 8·40) indicating the equivalence of the methyl protons; the band is shifted upfield from that observed for hexamethylbenzene (τ 7·85). Its u.v. spectrum in water shows the characteristic absorptions [λ_{max} 204—205, 223—224, and 377—380 mμ (ϵ 9750; 19,500; 4180)] of an aromatic compound, and the i.r. spectrum differs considerably from that of the hexamethylbicyclo-[2,2,0]hexa-2,5-dienepalladium complex referred to above, and resembles more those of hexamethylbenzene and the previously reported[3] arene complexes $[(C_6Me_6)_2Rh^{II}]X_2$ (X = $PtCl_6^-$ or PF_6^-) and $[(C_6Me_6)_2Rh^{I}]^+PF_6^-$. Elemental analysis for C, H, and Rh, molecular weight (750, 830 by osmometry in different solvents), and equivalent conductance measurements are fully consistent with a molecular formula $[(Me_6C_6RhCl)_2]^{4+}Cl_4$ (II) [*M*, 743], and an ionic chlorine determination has confirmed the presence of two Cl^- ions per Rh atom. The compound (II) reacts with sodium iodide in water replacing the four Cl^- ions to give black crystals which analyse (C, H, Rh) correctly for the corresponding tetraiodide, and have a ^1H n.m.r. spectrum (singlet, τ 8·10 in CH_2Cl_2) and i.r. spectrum very similar to those of compound (II). Sodium tetraphenylborate in water at 20° appears to replace only two Cl^- ions in compound (II) as evidenced by elemental analysis (C, H) on the brown solid product (61% yield) and its ^1H n.m.r. spectrum in CH_2Cl_2 which shows a complex multiplet centred at τ 2·8 (phenyl) and a singlet at τ 8·42 (methyl) in the approximate ratio of 18 : 20. Compound (II) reacts readily with pyridine in $CHCl_3$ at room temperature to give an orange-yellow solid (66% yield) having an elemental analysis (C, H, N, Rh, Cl^-) consistent with a molecular formula $[Me_6C_6RhClpy]^{2+}Cl_2$ (III), and a ^1H n.m.r. spectrum in CH_2Cl_2 showing multiplet bands at τ 3·35, 2·95 and 1·80 for pyridine and a singlet at τ 8·55 for the methyl protons with an overall intensity ratio ^1H (pyridine) : ^1H (methyl) of approximately 5 : 17 in good agreement with the assigned structure (*cf.* ratio 5 : 18).

Attempts to prepare compound (II) by heating hexamethylbenzene and $RhCl_3,3H_2O$ in aqueous methanol under reflux for 2 days gave only recovered starting materials. This suggests that the formation of compound (II) from hexamethylbicyclo[2,2,0]hexa-2,5-diene occurs by the intermediate formation of a hexamethylbicyclo[2,2,0]-hexa-2,5-dienerhodium chloride complex, with subsequent rearrangement of the ligand.

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