Preparative Applications of Metal Vapours obtained by Evaporation of Metal Powders from Coated Filaments: a New Preparation of Dibenzeneruthenium and Observation of its Limiting N.M.R. Spectrum

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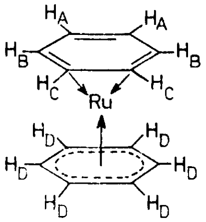
Summary Ruthenium vapour, conveniently prepared by resistive heating of tungsten filaments coated with a mixture of ruthenium powder and epoxy resin, yields stable $(Me_2NPF_2)_5Ru$ and thermally unstable $(C_6H_6)_2Ru$ on condensation with Me_2NPF_2 and benzene respectively; the ^1H n.m.r. spectrum of $(C_6H_6)_2Ru$ is consistent with a 1—4-η : 1—6-η formulation.

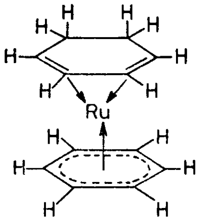
WE have studied some chemistry of ruthenium atoms using the following simple technique for evaporation of the powdered metal. A paint was formed from ruthenium powder, 10—15% by weight of freshly mixed, slow-curing 'Araldite' epoxy cement, and xylene. This paint was applied in two coats to 15 cm lengths of 1 mm tungsten wire; each coat was cured in an oven at 120—140 °C for 10 min. The filaments can be heated to evaporate the ruthenium in a typical metal vapour reactor equipped for resistive heating;[1] the work described here was performed in a 30 l stainless steel reactor.[2] After first carbonizing the epoxy cement by slow heating *in vacuo* to red heat, ruthenium was evaporated from the filaments at about 2400 °C using an electrical input of 60 A at 10 V. Filaments coated with about 0·15 g of ruthenium yielded 0·06—0·1 g of ruthenium vapour in 15—30 min. Preliminary experiments suggest that other powdered platinum metals can be conveniently evaporated in this way.

As a test of this method the ruthenium vapour from one such filament was cocondensed with an excess of (*ca.* 5 ml) of Me_2NPF_2 diluted with 25 ml of pentane. Isolation of product from the reactor by conventional methods followed by crystallization from warm hexane gave cream $[Me_2NPF_2]_5$-Ru, identified by elemental analyses (C, H, N) and the presence of intense ions $[Me_2NPF_2]_nRu^+$ (n = 5, 4, 3, 2) in its mass spectrum. The ruthenium complex $[Me_2NPF_2]_5Ru$, like its recently reported iron analogue,[3] appears to be relatively air-stable.

The cocondensation of ruthenium vapour with benzene is of particular interest because of the information it gives relative to the nature of dibenzeneruthenium, which Fischer and Elschenbroich[4] first claimed to have observed as a thermally unstable orange-yellow solid from the reduction of $[(C_6H_6)_2Ru](PF_6)_2$ with sodium in liquid ammonia. We have now found that cocondensation of ruthenium vapour with benzene followed by addition of n-hexane gives a thermally unstable orange solution which upon evaporation gives orange crystals decomposing below 0 °C to give a brown solid. The n.m.r. spectrum ($CFCl_3$ solution) arising from the orange crystals exhibits resonances at τ 4·22 (2H), 4·84 (6H), 5·10 (2H), and 7·11 (2H) assigned to H_A, H_D, H_C and H_B, respectively, in the 1—4-η : 1—6-η-structure (I) analogous to the well established structure[5] for the far more stable hexamethylbenzene analogue $(Me_6C_6)_2Ru$. A major basis for this assignment is the similarity of the positions of the proton resonances in $(C_6H_6)_2Ru$ to those of analogous protons in the reported spectrum (C_6H_6 solution) of $C_6H_6RuC_6H_8$ (II).[6]



(I)



(II)

The ^1H n.m.r. spectrum of $(C_6H_6)_2Ru$ indicates that the molecule is not fluxional under conditions where it is stable. This contradicts the impression from the early work of Fischer and Elschenbroich[4] who apparently only identified the strong singlet resonance from the six equivalent hexahaptobenzene protons which suggested that $(C_6H_6)_2Ru$ exhibited only one proton resonance.

We have found that ruthenium atoms also form complexes with ethylene, cyclo-octa-1,5-diene, cyclopentadiene, and indene, but isolation of pure, characterisable products has proved difficult. The metallocenes $(C_5H_5)_2Ru$[7] and $(C_9H_7)_2Ru$[8] are formed, among other products, from cyclopentadiene and indene respectively. The product from cyclo-octa-1,5-diene and ruthenium atoms is a yellow air-sensitive liquid, thermally stable at room temperature, which exhibits an intense ion $(C_8H_{12})_2Ru^+$ in its mass spectrum and a very complex ^1H n.m.r. spectrum suggesting a mixture of products involving extensive rearrangements. This behaviour contrasts with the reaction of iron vapour with cyclo-octa-1,5-diene[9] which gives brown crystalline $(1,5\text{-}C_8H_{12})_2Fe$ decomposing above -20 °C.

An unusual feature of these ruthenium vapour experiments is the apparent absence of bulk ruthenium metal among the reaction products.

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