

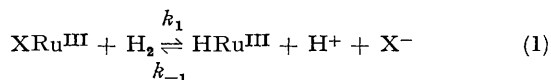
Base-promoted Reactions of Dihydrogen with Ruthenium(III) Tertiary-phosphine and -arsine Complexes

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Summary Reaction of H_2 with the ruthenium(III) complexes RuX_3L_2 ($X = Cl$ or Br ; $L = PPh_3$ or $AsPh_3$) can yield the five-co-ordinate dimeric ruthenium(II) hydride complexes $[HRuXL_2]_2$; the reactions proceed generally *via* intermediate $HRuX_2L_2$ and RuX_2L_2 species, and evidence is presented for the existence of $[HRuBr_2(AsPh_3)_2]$, the first reported ruthenium(III) hydride.

THE D_2 - H_2O exchange catalysed by chlororuthenate(III) species in HCl solutions gives good evidence for a ruthenium(III) hydride intermediate *via* an overall equilibrium shown in reaction (1).¹ No visible reaction occurred

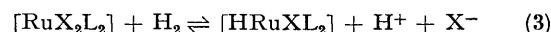


during the exchange process (*i.e.*, $k_{-1} > k_1$), but over a very long period slow reduction to ruthenium(II) was apparent, and reaction (2) was invoked.²



We have now found more direct evidence for reactions (1) and (2) by studying the H_2 reaction with ruthenium(III)

bis(tertiary-phosphine and -arsine) complexes, and also report a simple procedure for the production of the catalytically important ruthenium(II) hydridobisphosphine (or arsine) species,³ *via* reactions (1)–(3).



The complexes⁴ $[RuX_3L_2] \cdot MeOH$ ($X = Cl$ or Br ; $L = PPh_3$ or $AsPh_3$) are unreactive toward 1 atm H_2 in toluene. However, in the presence of an added base [we have used 1,8-bis(dimethylamino)naphthalene, 'proton sponge'] and/or a polar aprotic solvent such as *NN*-dimethylacetamide (DMA), reactions such as (1)–(3) are promoted.² In the presence of 'proton sponge,' the overall stoichiometry of reaction (4) is observed in both toluene and DMA. The



hydrides have been isolated as $[HRuBr(PPh_3)_2]_2$, $[HRuCl(PPh_3)_2]_2 \cdot 2DMA$, and $[HRuX(AsPh_3)_2]_2 \cdot 2DMA$, which have been fully characterised by elemental analysis, molecular weight data, and *i.r.* ($Ru-H$, 2040–2100 cm^{-1}), and *n.m.r.* ($Ru-H$, τ 22.5–23.7) spectroscopy. The DMA is unco-ordinated (*i.r.*, 1650 cm^{-1}),⁵ and the hydrides are all

halide-bridged five-co-ordinate complexes; their solutions are extremely sensitive toward, for example, O₂ and CO (2CO are absorbed per Ru), and addition of 1 mole of PPh₃ to the bisphosphine species (λ_{\max} 500 nm) gives solutions containing the well-characterized [HRuX(PPh₃)₃] complexes³ (λ_{\max} 525 nm).

The observed reactions of 1 atm H₂ with the [RuX₃L₂] complexes in DMA in the absence of 'proton sponge' depend very much on X and L, and the temperature. At 25 °C, [RuBr₃(AsPh₃)₂] absorbs 1 mole H₂ reversibly to form [HRuBr₂(AsPh₃)₂] according to reaction (1), while at 80 °C, reaction (2) becomes important and the overall stoichiometry of reaction (5) is observed; reaction (5) corresponds to reactions (1) plus (2). At intermediate temperatures, an



initial H₂ absorption towards a 1:1 stoichiometry is followed by evolution towards the final 0.5:1 stoichiometry as the reverse of reaction (1) occurs to accommodate reaction (2). This reaction (2), which can be studied separately by mixing solutions of [RuBr₃(AsPh₃)₂] and [HRuBr₂(AsPh₃)₂], presents the first opportunity for direct investigation of the second stage of the mechanism of H₂-reduction of a transition metal complex; this stage

is invariably fast following a rate-determining formation of the hydride. It is difficult to isolate analytically pure [HRuBr₂(AsPh₃)₂] because of reaction (2) and the reverse of reaction (1), but an i.r. band at 2020 cm⁻¹ is attributed to the hydride; solutions of the hydride show a very different visible spectrum (λ_{\max} 575 nm) to that of [HRuBr(AsPh₃)₂] (λ_{\max} 535 nm).

At 25 °C in DMA, [RuCl₃(PPh₃)₂] and [RuCl₃(AsPh₃)₂] react according to the stoichiometry of reaction (5), with no direct evidence for the HRu^{III} intermediate, while [RuBr₃(PPh₃)₂] reacts to give [HRuBr(PPh₃)₂] according to reaction (4) with no evidence for any intermediate stoichiometries exemplified by reactions (1)–(3). Solutions containing [RuBr₂(AsPh₃)₂] or [RuCl₂(PPh₃)₂] react with a further mole of H₂ only in the presence of 'proton sponge' to give the Ru^{II} hydrides according to reaction (3).

Solutions of [HRuXL₂] react with HX according to the reverse of reaction (3); this equilibrium, analogous to the related platinum(II) systems,⁶ presumably involves the ruthenium(IV) dihydride intermediate [H₂RuX₂L₂].

We thank the N.R.C. for financial support and Johnson Matthey and Co. Ltd., for a loan of ruthenium.

(Received, 20th July 1976; Com. 819.)

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