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

By Brian R. James,* Alexander D. Rattray, and Daniel K. W. Wang
(*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada* V6T 1W5)

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

$$XRu^{III} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRu^{III} + H^+ + X^- \quad (1)$$

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]

$$HRu^{III} + XRu^{III} \rightarrow 2Ru^{II} + H^+ + X^- \quad (2)$$

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).

$$[RuX_2L_2] + H_2 \rightleftharpoons [HRuXL_2] + H^+ + X^- \quad (3)$$

The complexes[4] $[RuX_3L_2]\cdot MeOH$ (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 stoicheiometry of reaction (4) is observed in both toluene and DMA. The

$$[RuX_3L_2] + 1{\cdot}5\ H_2 \rightarrow [HRuXL_2] + 2HX \quad (4)$$

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, O_2 and CO (2CO are absorbed per Ru), and addition of 1 mole of PPh_3 to the bisphosphine species (λ_{max} 500 nm) gives solutions containing the well-characterized $[HRuX(PPh_3)_3]$ complexes[3] (λ_{max} 525 nm).

The observed reactions of 1 atm H_2 with the $[RuX_3L_2]$ complexes in DMA in the absence of 'proton sponge' depend very much on X and L, and the temperature. At 25 °C, $[RuBr_3(AsPh_3)_2]$ absorbs 1 mole H_2 *reversibly* to form $[HRuBr_2(AsPh_3)_2]$ according to reaction (1), while at 80 °C, reaction (2) becomes important and the overall stoicheiometry of reaction (5) is observed; reaction (5) corresponds to reactions (1) plus (2). At intermediate temperatures, an initial H_2 absorption towards a 1:1 stoicheiometry is followed by evolution towards the final 0·5:1 stoicheiometry as the reverse of reaction (1) occurs to accommodate reaction (2). This reaction (2), which can be studied separately by mixing solutions of $[RuBr_3(AsPh_3)_2]$ and $[HRuBr_2(AsPh_3)_2]$, presents the first opportunity for direct investigation of the second stage of the mechanism of H_2-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 $[HRuBr_2(AsPh_3)_2]$ 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 $[HRuBr(AsPh_3)_2]$ (λ_{max} 535 nm).

$$2[RuBr_3(AsPh_3)_2] + H_2 \rightarrow 2[RuBr_2(AsPh_3)_2] + 2HBr \quad (5)$$

At 25 °C in DMA, $[RuCl_3(PPh_3)_2]$ and $[RuCl_3(AsPh_3)_2]$ react according to the stoicheiometry of reaction (5), with no direct evidence for the HRu^{III} intermediate, while $[RuBr_3(PPh_3)_2]$ reacts to give $[HRuBr(PPh_3)_2]$ according to reaction (4) with no evidence for any intermediate stoicheiometries exemplified by reactions (1)—(3). Solutions containing $[RuBr_2(AsPh_3)_2]$ or $[RuCl_2(PPh_3)_2]$ react with a further mole of H_2 only in the presence of 'proton sponge' to give the Ru^{II} hydrides according to reaction (3).

Solutions of $[HRuXL_2]$ 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 $[H_2RuX_2L_2]$.

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

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

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