

Preliminary Communication

The photochemical generation and some exploratory reactions of the novel di-hydrido tri-ruthenium cluster ($\text{H}_2\text{Ru}_3(\text{CO})_{10}$)

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Abstract

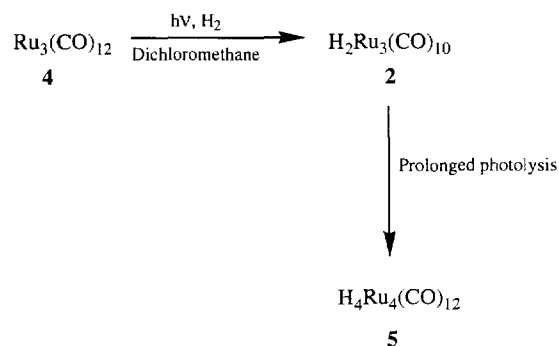
The title compound, $\text{H}_2\text{Ru}_3(\text{CO})_{10}$ **2**, is synthesised by the photolysis of $\text{Ru}_3(\text{CO})_{12}$ **4** under an atmosphere of di-hydrogen, and has been shown by IR and NMR to be structurally analogous to $\text{H}_2\text{Os}_3(\text{CO})_{10}$ **1**. The reaction of **2** with triphenylphosphine and phenylacetylene leads to the formation of the simple adducts $\text{H}_2\text{Ru}_3(\text{CO})_{10}\text{PPh}_3$ **6** and $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{Ph})$ **7**, respectively. The reaction of **2** with cyclohexa-1,3-diene at room temperature results in the formation of the mononuclear complex $\text{Ru}(\text{CO})_3(\text{C}_6\text{H}_8)$ **9**. © 1997 Elsevier Science S.A.

One of the most versatile tri-osmium clusters known is the di-hydrido species $\text{H}_2\text{Os}_3(\text{CO})_{10}$ **1** due to its ability to form simple adducts. This reagent has found applications both as a starting material for a wide variety of target clusters and in the catalytic isomerisation and hydrogenation of alkenes at room temperature without the need for dissociation to create coordination sites (for a general introduction to the chemistry of **1** see ref. [1]). To date, it has not been possible to prepare the ruthenium analogue $\text{H}_2\text{Ru}_3(\text{CO})_{10}$ **2** using thermolytic, pyrolytic or ligand substitution techniques and hence the potential of this reagent has not been explored.

Studies in this laboratory have focused on the generation of novel ruthenium mononuclear and cluster compounds by photochemistry. This methodology involves the formation and recombination of reactive fragments and has led to synthetic routes to a variety of novel tri-ruthenium clusters including the *tris*-acetonitrile compound $\text{Ru}_3(\text{CO})_9(\text{MeCN})_3$ **3** and a variety of catalytically active bis-phosphine complexes [2]. Here we report, as an extension to this work, the preparation of **2**.

The deep orange di-hydrido tri-ruthenium cluster $\text{H}_2\text{Ru}_3(\text{CO})_{10}$ **2** is prepared in high yield by broad band UV irradiation of a dichloromethane solution of

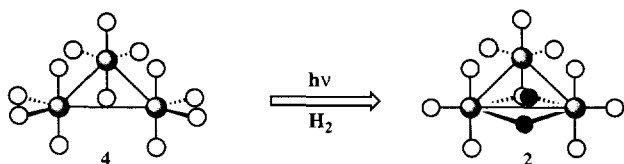
$\text{Ru}_3(\text{CO})_{12}$ **4** under an atmosphere of hydrogen and has been characterised by IR and ¹H-NMR spectroscopy



(Scheme 1).¹ The photochemical reaction is thought to occur via the formation of an 'Ru(CO)₃' intermediate generated by initial photofragmentation of **4** followed by dissociation of CO. Continued irradiation of the dichloromethane solution of **2** under hydrogen leads to the generation of the tetranuclear hydrido cluster $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ **5** in somewhat reduced yield based on initial $\text{Ru}_3(\text{CO})_{12}$ **4**. The stability of **2** is solvent dependent, evaporation to dryness leading to **5** and **4** amongst other products.

¹ Spectroscopic data for **2**: IR (hexane) $\nu(\text{CO})$ 2112(w), 2077(s), 2067(s), 2030(vs), 2012(s), 1997(m), 1972(w) cm^{-1} ; ¹H-NMR (CDCl_3); δ -13.6(s). Yield: ~60%

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Scheme 1. The synthesis of $\text{H}_2\text{Ru}_3(\text{CO})_{10}$ **2**.

Compound **2** is formally 'electron deficient', there being two electrons less than would be expected for a 48-electron closed shell configuration. This is structurally rationalised, as in the case of **1**, either in terms of a formal ruthenium–ruthenium double bond or, more correctly, in terms of multicentre delocalised bonds [3]. For that reason, the preparation of **2** is interesting not only from a synthetic viewpoint but also because it is one of the few examples of a ruthenium cluster containing a di-hydride bridged metal–metal bond. It has been shown crystallographically that di-hydride bridging of a Ru–Ru bond leads to shortening of the bond length [4]. This is in contrast to conventional mono-hydride bridged ruthenium clusters such as **5**, where the hydride interacts with an antibonding metal orbital forming either a 3-centre, 2-electron or 4-centre, 2-electron bond. This results in a decrease in bond order of the metal–metal bond thus increasing the bond length. It must be noted, however, that this effect may be masked by other structural features, such as carbonyl bridging of the same M–M edge.

A consideration of the spectral data for **2** confirms the structural similarity between this and the osmium analogue, **1**, for which the molecular structure has been obtained by X-ray crystallography [5]. The $^1\text{H-NMR}$ of **2** shows a single resonance at -13.6 ppm indicative of chemically equivalent hydrides bridging one of the Ru–Ru bonds, the hydride signal being observed at -11.7 ppm in **1**. This signal is shifted down-field compared to that in a cluster such as **5** where only single Ru–Ru bonds are present, characteristic of the increased bond order of the di-hydride bridged metal–metal bond in **2**.

Due to the unsaturated nature of **2**, the cluster is prone to simple nucleophilic attack. In general, nucleophilic attack occurs as the second order component of substitution reactions and there are few examples, such as **2**, where simple addition occurs. It is this ability of **2** to add a variety of two-electron donors to form simple substitution products at ambient temperature that makes it such a useful starting material. This is in contrast to the case of many clusters where reaction with nucleophiles at elevated temperatures can lead to modification of the geometry or nuclearity of the parent system, allowing for the preparation of a variety of cluster adducts often unrelated to the starting material.

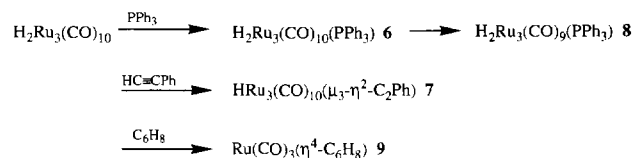
In an attempt to illustrate the reaction chemistry of **2**, a number of exploratory reactions have been performed. Addition of triphenylphosphine and phenylacetylene to

a dichloromethane solution of **2** at room temperature leads to the formation of $\text{H}_2\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)$ **6** and $\text{HRu}_3(\text{CO})_{10}(\mu_3-\eta^2-\text{C}_2\text{Ph})$ **7**, respectively. These complexes have been characterised by comparison of IR and $^1\text{H-NMR}$ spectroscopic data ² with the corresponding osmium analogues formed by reaction of **1** with these reagents [6,7]. It is interesting to note that reaction of **2** with phenylacetylene leads only to the acetylide derivative **7** as compared to the case of **1** where, in addition to $\text{HOs}_3(\text{CO})_{10}(\mu_3-\eta^2-\text{C}_2\text{Ph})$, the vinyl cluster $\text{HOs}_3(\mu_2-\sigma,\pi-\text{HC}_2\text{HPh})(\text{CO})_{10}$ is formed [7].

In contrast to the osmium analogue, **6** is unstable with respect to further reaction. It is proposed that initially decarbonylation occurs to yield $\text{H}_2\text{Ru}_3(\text{CO})_9(\text{PPh}_3)$ **8** then, over the period of approximately 2 h, a number of mononuclear and cluster products are, these being uncharacterised at present ³.

Reaction of **2** with cyclohexa-1,3-diene leads to the formation of the mononuclear complex $\text{Ru}(\text{CO})_3(\eta^4-\text{C}_6\text{H}_8)$ **9**. ⁴ In contrast, the dienyne cluster $\text{HOs}_3(\text{CO})_9(\mu_3-\sigma:\eta^2:\eta^2-\text{C}_6\text{H}_7)$ is formed on reaction of cyclohexa-1,3-diene with **1** [8]. This is a clear example of the difference in metal–metal bond strengths in ruthenium and osmium cluster compounds. In addition, this reflects the fact that, although **1** and **2** may be proposed as structurally analogous, the kinetics of reaction of the two clusters is clearly different.

The reaction chemistry of **2** is summarised in Scheme 2.



These exploratory reactions mark only the start of a large area of work that can be undertaken to fully harness the synthetic potential of $\text{H}_2\text{Ru}_3(\text{CO})_{10}$ **2** as a starting material, and work is currently underway to investigate the catalytic properties of **2** for the hydrogenation of unsaturated hydrocarbons.

² Spectroscopic data for **6**: IR (hexane) $\nu(\text{CO})$ 2105(w), 2065(s), 2060(vs), 2024(vs), 2016(s), 1989(m), 1973(w) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3); δ 7.6(m, 5H), -17.8 (s, br 2H). Yield: $\sim 80\%$ by IR. Spectroscopic data for **7**: IR (hexane) $\nu(\text{CO})$ 2102(w), 2060(vs), 2054(vs), 2029(vs), 2013(s), 2000(m), 1985(w) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3); δ 7.75(m, 1H), 7.4(m, 5H), 5.2(d, 1H), -17.7 (s, br 2H). Yield: $\sim 70\%$ by IR.

³ Spectroscopic data for **8**: IR (hexane) $\nu(\text{CO})$ 2098(m), 2070(s), 2055(vs), 2020(vs), 2004(m), 1992(w) cm^{-1} . Yield: $\sim 50\%$ by IR.

⁴ Spectroscopic data for **9**: IR (hexane) $\nu(\text{CO})$ 2057(s), 1984(vs), 1962(s) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3); δ 5.44(dd), 3.42(m), 1.78(s). MS (-FAB) m/z 264(obs.), 265(calc.). Yield 75%.

References

- [1] (a) R.D. Adams, J.P. Selegue, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon, UK, 1982, p. 968; (b) K. Burgess, *Polyhedron*, 3 (1984) 1175.
- [2] A.J. Edwards, N.E. Leadbeater, J. Lewis, P.R. Rathby, *J. Organomet. Chem.* 513 (1995) 15.
- [3] P.R. Raithby, in: B.F.G. Johnson (Ed.), *Transition Metal Clusters*, Wiley, UK, 1980, p. 28.
- [4] H. Nagashima, T. Fukahori, K. Aoki, K. Itoh, *J. Am. Chem. Soc.* 115 (1993) 10430.
- [5] A.G. Orpen, A.V. Rivera, E.G. Bryan, D. Pippard, G.M. Sheldrick, *J. Chem. Soc. Chem. Commun.* (1978) 723.
- [6] A.J. Deeming, S. Hasso, *J. Organomet. Chem.* 114 (1976) 313.
- [7] A.J. Deeming, S. Hasso, M. Underhill, *J. Chem. Soc. Dalton Trans.* (1975) 1615.
- [8] M.P. Gomez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby, A.H. Wright, *J. Chem. Soc. Chem. Commun.* (1985) 1682.