

The Use of (Cyclo-octadiene)(cyclo-octatriene)ruthenium(0) as the Starting Material for the Synthesis of Mono- and Poly-nuclear Ruthenium Polyhydride Phosphine Complexes

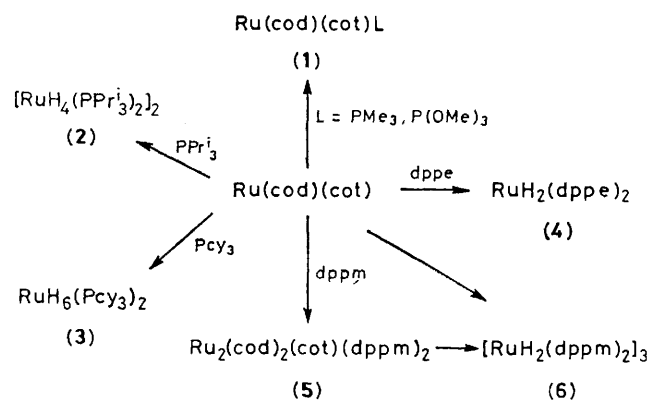
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Ru(cod)(cot) (cod = 1-2:5-6- η -cyclo-octadiene; cot = 1-2:3-4:5-6- η -cyclo-octatriene) has been shown to be an efficient starting material for the synthesis of a number of ruthenium(0) and ruthenium hydride phosphine complexes; with monophosphines Ru(cod)(cot)L [L = P(OMe)₃, PMe₃], the dinuclear complex (RuH₄L₂)₂ (L = PPrⁱ₃, PBu^t₃), and the hexahydride complex RuH₆L₂ (L = Pcy₃, cy = cyclohexyl) have been obtained whereas with diphosphines, the ruthenium(0) dinuclear complex Ru₂(cod)₂(cot)(dppm)₂ (dppm = Ph₂PCH₂PPh₂), the hydrido trinuclear complex [RuH₂(dppm)₂]₃, and RuH₂(dppe)₂ (dppe = Ph₂PCH₂CH₂PPh₂) are produced.

Although ligand-free nickel¹ or platinum² compounds are well known and have been used to produce a variety of mono- and poly-nuclear complexes (*e.g.* some very interesting hydride phosphine platinum clusters have been produced recently^{3,4}) no such reactions have been reported for ruthenium com-

plexes. Ru(cod)(cot) (cod = 1-2:5-6- η -cyclo-octadiene; cot = 1-2:3-4:5-6- η -cyclo-octatriene), recently prepared in high yield by Pertici *et al.*,⁵ seemed a valuable starting material for mononuclear and polynuclear ruthenium polyhydrides. Also, this derivative could lead to polynuclear diphosphine com-



Scheme 1. Reactions of Ru(cod)(cot) with various phosphines and diphosphines under hydrogen.

plexes; so far only mononuclear complexes have been obtained.⁶ We report here the reactions† of Ru(cod)(cot) with a number of mono- and di-phosphines under hydrogen (Scheme 1).

Ru(cod)(cot) reacts with the phosphines L = P(Me)₃ or P(OMe)₃ to give, quantitatively, the ruthenium(0) complex Ru(cod)(cot)L (1) by a simple substitution of an olefinic group; the free double bond is observed at 1630 cm⁻¹ in the i.r. spectra.⁷

With the more bulky phosphine L = PPr₃ a red diamagnetic compound is formed at 40 °C which was found by analysis to be [RuH₄L₂]₂ (2) (yield ca. 60%). Terminal (2000 cm⁻¹ sharp, m) and bridging (1550 cm⁻¹ br., m) hydrides are detected by i.r. spectroscopy. The high-field ¹H n.m.r. spectrum consists of a broad singlet at room temperature at δ -12.8 (integration ratio 4H:2PPr₃) which is split into three broad peaks at -80 °C [δ -10.6(2), -11.8(1), and -21.2(1)].

The ³¹P n.m.r. also consists of a singlet at room temperature (δ 88.5 p.p.m.‡), split into four peaks at -80 °C [δ 95.1 br.; 91.0, *J*_{HP} 21 Hz; 85.6, d, *J*_{HP} 21 Hz; and 81.2 p.p.m. br. (intensity 1:1:1:1)]. These data and a comparison with Ru₂H₈(PPh₃)₄⁸ suggest an analogous structure with a double metal-metal bond and four bridging hydrides. This indicates that the tetrahydrido bridged complexes of ruthenium (only Re₂H₈L₄ was known before our work⁹) can be obtained easily and show a similarity to rhenium complexes. With PBut₃, the complex Ru₂H₈L₄, obtained in low yield (ca. 30%) after crystallization in hexane at -78 °C, is more fluxional and shows a quintet in the ¹H n.m.r. spectrum for the hydrides at δ -14.7 (*J*_{PH} ca. 17 Hz) as for Re₂H₈L₄.

If Pcy₃ (cy = cyclohexyl) is allowed to react with Ru(cod)(cot) a white solid, which can be recrystallized from toluene, is precipitated in high yield. Two very strong terminal ν_{Ru-H} signals are observed at 1927 and 1890 cm⁻¹ in the i.r. spectrum but no bridging signal. The complex is fluxional at all temperatures showing only a singlet in its high field ¹H n.m.r. spectrum (δ -7.7) and ³¹P n.m.r. spectrum (δ 79.2 p.p.m.). Analytical

† All the reactions described have been carried out in hexane at room temperature with two equiv. of the phosphine under hydrogen except where stated otherwise. All the complexes have been obtained in crystalline form by crystallization from hexane [(1) and (2)] or toluene-hexane [(3), (4), (5b), and (6)], and characterized by analytical and spectroscopic means [i.r., ¹H n.m.r. (250 MHz), and {¹H} ³¹P n.m.r. spectroscopy (101.2 MHz on a Bruker WM 250)]. The solvents used for recording the spectra are C₆D₆ or C₇D₈.

‡ P.p.m. to high frequency of external H₃PO₄ in D₂O.

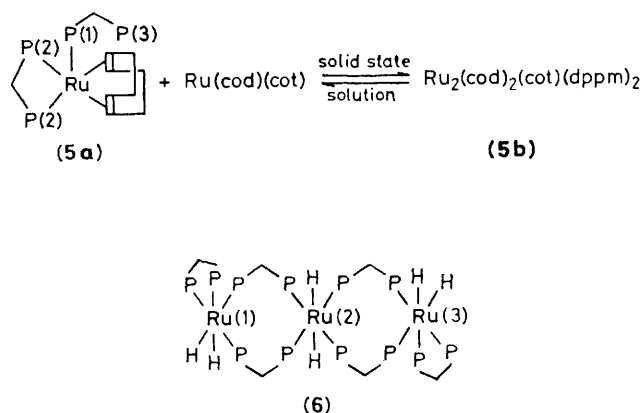


Figure 1. Proposed structure of the dppm compounds (5) and (6).

data together with a cryoscopic molecular weight determination and the white colour suggesting an 18 electron configuration¹⁰ are consistent with the monomeric structure RuH₆L₂ (3).

To the best of our knowledge this is the first hexahydride of ruthenium to be reported and this reinforces the analogy with rhenium chemistry where ReH₇L₂ has been known for some time.¹¹

Compound (3) is not very stable in solution; under vacuum or when heated it is converted quantitatively into another red fluxional compound (which can be obtained in crystalline form). This compound shows terminal and bridging ligands in its i.r. spectrum but its structure has not yet been elucidated.

With the diphosphine dppe (dppe = Ph₂PCH₂CH₂PPh₂) Ru(cod)(cot) gives RuH₂(dppe)₂ (4) quantitatively.

With dppm (dppm = Ph₂PCH₂PPh₂) the results are more interesting. In the absence of H₂, one equiv. of dppm in toluene reacts with Ru(cod)(cot) to give a yellow complex (5), quantitatively, which can be recrystallized in high yield (better than 80%) from toluene-hexane. This complex shows apparently different properties depending upon whether they are measured in solution or in the solid state. For the solid compound (5b), the only noticeable feature in the i.r. spectrum is free ν(C-C) at 1605 cm⁻¹, and the analysis is consistent with the formulation Ru₂(cod)₂(cot)(dppm)₂. However, in solution a cryoscopic molecular weight determination gives a lower result. The ³¹P n.m.r. spectrum consists of a quartet at δ 41.2 p.p.m. (P-1) and two doublets at δ -3.2 (P-2) and -19.9 p.p.m. (P-3); all having the same coupling constant (*J*_{HP} 17 Hz) (intensity 1:2:1) (see Figure 1). The chemical shift of P-3 is very close that of free dppm. P-1 could be equally coupled to P-2 on one side and P-3 on the other. These solution results lead to the structure of (5a), Ru(cod)(dppm)₂ (see Figure 1) obtained by the replacement of cot in the starting material with two molecules of dppm, one acting as a monodentate phosphine.§ The compound (5a),[¶] acting as a bulky phosphine, reacts reversibly with excess Ru(cod)(cot) by substitution of an olefinic group. By recrystallization the less soluble Ru₂(cod)₂(dppm)₂(cot) (5b) is obtained.

With one equiv. of dppm in the presence of H₂, Ru(cod)(cot) reacts to give compounds (5), (6), and unchanged Ru(cod)(cot) together with some decomposition products.

§ A relevant system with dppm co-ordinated through one phosphorous atom only has been described recently.¹²

¶ Pure (5a) was isolated from the reaction of Ru(cod)(cot) with two equiv. of dppm, in the absence of hydrogen, by recrystallisation from toluene-hexane.

When two equiv. of dppm are added to Ru(cod)(cot) in the presence of hydrogen, a yellow compound (**6**), shown to be RuH₂(dppm)₂ by analysis, is obtained quantitatively. A broad intense $\nu_{\text{Ru-H}}$ band is observed at 1830 cm⁻¹ in the i.r. spectrum. The high field ¹H n.m.r. spectrum shows two signals: a quintet at $\delta -4.7$ ($J_{\text{P-H}}$ 19.7 Hz) and a doublet of quartets at $\delta -7.4$ ($J_{\text{P-H}}$ 72.8 and $J_{\text{P-H}}$ 18.7 Hz) (intensity 1:2). The ³¹P n.m.r. shows two triplets at δ 12.9 and 0.3 p.p.m. ($J_{\text{P-P}}$ 30 Hz) and a singlet at δ 8.6 p.p.m. (integration ratio 1:1:1). Recrystallization results indicate that all these peaks belong to the same compound and heteronuclear double irradiations show that the doublet of quartet hydrides are coupled to the phosphorus giving the two triplets and that the quintet and the singlet are related. We propose a trinuclear structure (see Figure 1) where Ru-1 and Ru-3 have a *cis* dihydride environment and Ru-2 a *trans* dihydride environment. An X-ray diffraction study is necessary to confirm our hypothesis.

These preliminary results show that it is possible to synthesise ruthenium polyhydride complexes which are similar to those of rhenium. However, it has not been possible to obtain a family of compounds similar to the dppm bridged rhodium,¹³ palladium, or platinum¹⁴ complexes.

Received, 3rd August 1982; Com. 917

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