

PREPARATION AND REACTIONS OF TETRAHYDRIDOTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(IV)*

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(Received October 4th, 1972)

SUMMARY

The reduction of $\text{RuCl}_2(\text{PPh}_3)_3$ by sodium borohydride produces $\text{RuH}_4(\text{PPh}_3)_3$. Small molecules react with this complex in several ways. They add with replacement of hydrogen (N_2 , CO, NO); they are reduced (C_2H_4) or they insert into a metal-hydride bond (CS_2). Chemical evidence for the presence of a dithioformato ligand is discussed.

INTRODUCTION

In a preliminary communication¹, we reported the preparation of $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$ by treating molecular nitrogen with a ruthenium hydride, $\text{RuH}_2(\text{PPh}_3)_3$. The method of preparation of the hydride involved the addition of triethylamine under hydrogen. The by-product Et_3NHCl proves difficult to separate without some decomposition of the very reactive hydride. In this work, we describe a better method of preparation for the pure hydride. Its characterization shows it should now be considered as the tetrahydride $\text{RuH}_4(\text{PPh}_3)_3$, reported earlier by Knoth^{2,3}. The tetrahydride reacts under very mild conditions with a variety of molecules. In particular, we describe the insertion reactions with CS_2 into the metal-hydrogen bonds.

RESULTS AND DISCUSSION

The tetrahydride is prepared easily and in good yield from $\text{RuCl}_2(\text{PPh}_3)_3$ ⁴ and sodium borohydride in a benzene/methanol solution. When pure, it is white but remaining traces of solvent give the solid a reddish tinge. It is very air-sensitive, decomposing, within minutes, to a dark green solid. It is, however, stable indefinitely under argon. Its IR spectrum, in addition to phosphine bands, contains a single broad hydride absorption at 1950 cm^{-1} as reported by Knoth³ as well as a hydride deformation band at 805 cm^{-1} . The corresponding bands in the deuteride $\text{RuD}_4(\text{PPh}_3)_3$ are found at 1400 and 580 cm^{-1} ($\nu(\text{Ru-H})/\nu(\text{Ru-D})$, $\delta(\text{Ru-H})/\delta(\text{Ru-D}) = 1.39$). The complex is soluble, with decomposition, in halogenated solvents and slightly soluble

* This paper is based on the dissertation submitted by L. Sadavoy to the Graduate School, University of Toronto, in partial fulfillment of the requirements for the M.Sc. degree, October 1972.

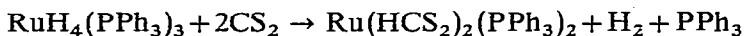
in benzene. Its ^1H NMR spectrum in benzene shows a single broad resonance at τ 17.1 ppm, the same value reported for the metal-hydride resonance in $[(p\text{-CH}_3\text{C}_6\text{-H}_4)_3\text{P}]_3\text{RuH}_4$ ³. If the preparation is carried out in the presence of a ten-fold excess of triphenylphosphine, $\text{RuH}_2(\text{PPh}_3)_4$ ⁵ is prepared. The dihydride can be converted into the tetrahydride by passing a stream of hydrogen through a benzene solution of the dihydride at room temperature. Subsequently replacing the hydrogen by argon does not reverse the process.

The solid tetrahydride has already been reported to react with N_2 , CO , NO , SO_2 and NOCl to give $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$, $\text{RuH}_2\text{CO}(\text{PPh}_3)_3$, $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$, $\text{Ru}(\text{SO}_2)_2(\text{PPh}_3)_2$, $\text{RuCl}_3\text{NO}(\text{PPh}_3)_2$ ¹. The sulphur dioxide product appears to be polymeric and its structure has not been fully established. Because it proved difficult to determine, from the physical properties of the hydride, the number of metal-hydride bands, its reactions with some of these gases were followed quantitatively. The initial results with CO ¹ could not be repeated on the pure hydride, the reaction showing no change in pressure in a closed system. In addition, the passage of purified argon over solid $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$ for extended periods caused no loss of coordinated nitrogen. To clearly establish whether the product was a di- or tetra-hydride, its reaction with CS_2 has been studied in detail.

Carbon disulphide is being used increasingly as a reactive ligand, several types of product being found. It can coordinate through a $\text{C}=\text{S}$ π -bond, structurally similar to complexed allene, or it can lose a sulphur to form a thiocarbonyl¹⁶. It can also take part in various insertion reactions¹⁷. Albano *et al.*⁸ have determined the crystal structure of (dithioformato)bis(triphenylphosphine)dicarbonylrhenium formed by treating carbon disulphide with $\text{ReH}(\text{PPh}_3)_2(\text{CO})_2$. The thio acid occupies two coordination sites through equivalent sulphurs.

Carbon disulphide reacts instantly with both $\text{RuH}_4(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ to form a deep red solution from which a dark red crystalline product can be obtained. The complex is air-stable, analysing for $\text{Ru}(\text{HCS}_2)_2(\text{PPh}_3)_2$ and is monomeric in benzene solution (mol wt. found 830, calcd. 790, osmometry). If the reactions are carried out in a closed evacuated system, the tetrahydride liberates 0.9 moles of hydrogen. No gas is liberated by the dihydride.

The reactions are therefore:



The ^1H NMR and IR spectra contain no bands assignable to metal hydride. The IR spectrum does contain three new sets of bands which can be assigned to the asymmetric, symmetric and bending modes of the coordinated thioformates. These are found at 1220, 1215; 915, 908 and 784, 775 cm^{-1} .

The NMR spectrum contains a doublet due to the two acidic protons at δ 11.5 ppm (J 1.5 cps) from internal TMS, and of relative intensity 1/15 to the phenyl protons. The splitting is field independent and must arise therefore from long range ^{31}P -H coupling. The presence of a doublet suggests that the two dithioformate groups are *cis* to one another (see Fig. 1). These reactions clearly establish the starting material to be a tetrahydride.

Nitriles also react directly with the tetrahydride, in a similar manner to N_2 and CO . Both acetonitrile and benzonitrile react rapidly at room temperature on the solid

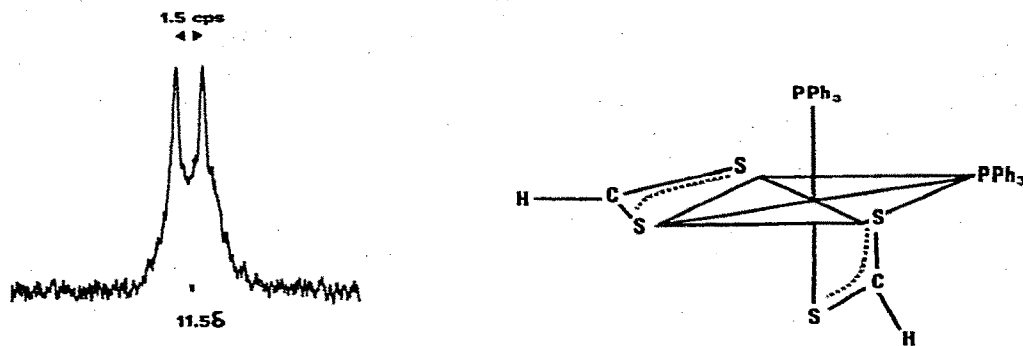


Fig. 1. ^1H NMR spectrum and proposed structure of $\text{Ru}(\text{HCS}_2)_2(\text{PPh}_3)_2$.

hydride or in benzene solution to form light green $\text{RuH}_2(\text{CH}_3\text{CN})(\text{PPh}_3)_3$ and orange-brown $\text{RuH}_2(\text{C}_6\text{H}_5\text{CN})(\text{PPh}_3)_3$, both air-sensitive. Knoth³ has already shown the coordinated nitrogen in $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$ can be replaced by benzonitrile. In systems that coordinate both dinitrogen and nitriles, it has been found that $\nu(\text{CN})$ is lowered on complexation⁹. This was found for the benzonitrile complex but only slightly so for the acetonitrile. In the free ligand $\nu(\text{CN})$ occurs at 2255 cm^{-1} and in the complex at 2250 cm^{-1} .

In a recent communication¹⁰, $\text{RuH}_2(\text{PPh}_3)_4$ has been shown to react with ethylene in benzene to give $\text{Ru}(\text{C}_2\text{H}_4)(\text{PPh}_3)_3$. We have treated the solid tetrahydride with ethylene (0.5 atm) at room temperature but no identifiable product could be isolated. The IR spectrum of the solid changes on the addition of gas giving a complex hydride pattern in the 1950 cm^{-1} region although no band assignable to coordinated ethylene was observed. The mass spectrum of the residual gases shows the presence of ethane. The starting material could be regenerated if the system was then flushed with hydrogen. Wilkinson and coworkers¹¹ have shown that a variety of rhodium and ruthenium complexes act as hydrogenation catalysts particularly towards terminal olefins. Examples are $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, $\text{RhCl}(\text{PPh}_3)_3$, $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$. The ease of hydrogenation increases in the order given suggesting that the tetrahydride may be an active hydrogenating agent. None of these complexes hydrogenate ethylene, although $\text{RhCl}(\text{PPh}_3)_3$ forms a stable complex $\text{RhCl}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ ¹² which may account for its inactivity. The tetrahydride was found to convert ethylene to ethane but the reaction does not take place rapidly. If a 1/1 mixture of ethylene and hydrogen (6.0 mmoles) is introduced over solid $\text{RuH}_4(\text{PPh}_3)_3$ (0.1 mmoles) at room temperature, 1.0 mmoles C_2H_6 are produced over a period of one week. The IR spectrum of the solid is always that of the tetrahydride. In benzene, the tetrahydride reacts with a variety of compounds containing double bonds. For example, the product from styrene shows $\nu(\text{Ru-H})$ at 2040 and 2035 (sh) cm^{-1} and a weak coordinated $\nu(\text{C=C})$ at 1495 cm^{-1} . Work on these systems is continuing.

EXPERIMENTAL

Infrared spectra were recorded as Nujol mulls on a Beckman IR-12 spectrometer on KBr plates between $4000\text{--}500\text{ cm}^{-1}$ and on polyethylene plates between $500\text{--}200\text{ cm}^{-1}$. NMR spectra were measured on either a Varian HA 100 or T-60

spectrometer. Mass spectra were measured on an AEI-MS10c2 mass spectrometer. All the compounds were found to be diamagnetic (Gouy). Solvents were of purified grade and before use were saturated with the appropriate gas. Analyses were by A. B. Gygli, Toronto and Dornis and Kolbe, W. Germany.

Tetrahydridotris(triphenylphosphine)ruthenium(IV), RuH₄(PPh₃)₃

RuCl₂(PPh₃)₃ (1.0 g) was dissolved in hydrogen-saturated benzene (60 ml) and methanol (100 ml). Solid NaBH₄ was added until the originally deep red solution had changed to light orange. Rapid stirring of this for a few minutes produced the white product. This was collected, washed several times with degassed methanol and stored, all under argon. Yield 0.7 g, 75%. (Found: C, 73.0; H, 5.69. C₅₄H₄₉P₃Ru calcd.: C, 72.7; H, 5.50%.)

The complex can also be prepared in benzene using (C₂H₅)₃N as base but removal of the initial precipitate of (C₂H₅)₃NHCl gives some decomposition in solution and impure products. LiAlH₄ in tetrahydrofuran gives carbonyl containing products.

The corresponding tetradeuteride RuD₄(PPh₃)₃ was prepared using NaBD₄ and a CH₃OD/benzene mixture.

Dihydridotetrakis(triphenylphosphine)ruthenium(II), RuH₂(PPh₃)₄

RuCl₂(PPh₃)₃ (1.0 g) was dissolved in a hydrogen-saturated solution of benzene (60 ml)/methanol (100 ml) containing triphenylphosphine (6 g) and NaBH₄ added as before. The solution was stirred for 1 h at room temperature during which time the initial precipitate of RuH₄(PPh₃)₃ changed to yellow RuH₂(PPh₃)₄. The product was washed with methanol, air-dried and stored under argon. Yield 1.0 g, 85%. (Found: C, 74.8; H, 5.34. C₇₂H₆₂P₄Ru calcd.: C, 75.1; H, 5.42%.)

The IR spectrum includes a single sharp medium metal-hydride stretch at 2080 cm⁻¹ (lit.⁵ 2080 cm⁻¹) and a hydride deformation at 820 cm⁻¹.

Reaction of RuH₂(PPh₃)₄ with H₂

RuH₂(PPh₃)₄ (0.3 g) was dissolved in 30 ml of benzene saturated with hydrogen. Addition of 50 ml of hydrogen saturated methanol or hexane gave an immediate precipitate of white RuH₄(PPh₃)₃ (0.2 g). When the experiment was repeated using argon as saturating gas, the starting material was recovered.

Reactions of the tetrahydride with N₂, CO, NOCl, NO

(i) *RuH₂(N₂)(PPh₃)₃*

RuH₄(PPh₃)₃ (0.2 g) was placed in a flask under argon and nitrogen passed over the solid for 4 h. The crude product can be dissolved in benzene and reprecipitated with hexane, all under an N₂ atmosphere. The product is stored under N₂. Yield 0.15 g, 70%. (Found: C, 68.5; H, 5.40; N, 2.6. C₅₄H₄₇N₂P₃Ru calcd.: C, 70.9; H, 5.17; N, 3.03%.)

The IR spectrum has a strong sharp absorption at 2147 cm⁻¹ (ν(N=N)) as well as hydride bands at 1960 and 1938 cm⁻¹. The IR spectrum for the deuteride RuD₂N₂(PPh₃)₃ has only one band attributable to ν(Ru-D) at 1400 cm⁻¹, and a hydride deformation band at 580 cm⁻¹.

(ii) $RuH_2(CO)(PPh_3)_3$

The carbonyl complex was prepared similarly to the dinitrogen complex. Alternatively, $RuH_2(PPh_3)_4$ (0.2 g) was dissolved in benzene (15 ml) and CO bubbled through the solution. Within 5 min the yellow colour of the solution disappeared. The gas flow was stopped after 15 min. Addition of methanol (30 ml) precipitated white $RuH_2CO(PPh_3)_3$. The complex was recrystallized as white needles from benzene. Yield 0.16 g, 80%. (Found: C, 72.7; H, 5.39. $C_{55}H_{47}OP_3Ru$ calcd.: C, 72.0; H, 5.16%.)

Its IR spectrum shows $\nu(Ru-H)$ at 1965 and 1905 cm^{-1} and $\delta(Ru-H)$ at 780 and 768 cm^{-1} . The carbonyl band is at 1942 cm^{-1} (lit.¹¹ 1960, 1900 and 1940 cm^{-1}). The deuteride shows $\nu(Ru-D)$ at 1415 and 1458 cm^{-1} . The deformation bands are expected to be under the phosphine bands in the 500 cm^{-1} region.

(iii) $RuCl_3NO(PPh_3)_2$

The red-brown product is formed immediately on passing NOCl over solid tetrahydride (0.2 g). The complex is sparingly soluble in methanol or benzene. It is recrystallized from benzene (100 ml) on the addition of light petroleum (50 ml) as golden crystals. Yield 0.15 g, 80%. (Found: C, 56.7; H, 3.97; N, 2.10; Cl, 14.0. $C_{36}H_{30}NOCl_3P_2Ru$ calcd.: C, 57.0; H, 3.99; N, 2.16; Cl, 13.0%.)

Its IR spectrum has one very sharp NO stretch at 1877 cm^{-1} . In addition, a doublet at 600 and 590 cm^{-1} may arise from $\delta(N-O)$. Apart from triphenylphosphine absorptions, only one other band, at 335 cm^{-1} of medium intensity, is seen ($\nu(Ru-Cl)$). The complex appears identical to that prepared by treating PPh_3 with $RuNOCl_3$ ¹³ ($\nu(N-O)$ 1877 cm^{-1}).

(iv) $Ru(NO)_2(PPh_3)_2$

A similar reaction occurs if NO is passed over the solid tetrahydride (0.2 g). The crude product is dissolved in degassed benzene (20 ml) and degassed hexane (30 ml) added. There is an immediate flocculent brown precipitate of by-products. This mixture was decanted through glass wool and from the resulting clear solution the black red crystals of the product precipitated. They can be kept in air but solutions are extremely air-sensitive. Yield 0.13 g, 80%. (Found: C, 63.3; H, 4.31; N, 4.18. $C_{30}H_{30}N_2O_2P_2Ru$ calcd.: C, 63.1; H, 4.41; N, 4.09%.)

Its IR spectrum shows two nitrosyl bands at 1630 and 1670 cm^{-1} , both broad and strong, a medium intensity band at 655 cm^{-1} and a doublet at 576 and 561 cm^{-1} , assigned to $\delta(N-O)$.

Dihydrido(acetonitrile)tris(triphenylphosphine)ruthenium(II), $RuH_2(CH_3CN)(PPh_3)_3$

$RuH_4(PPh_3)_3$ (0.2 g) was suspended in degassed benzene (20 ml) and acetonitrile (2 ml) added. On stirring for 5 min the solution became clear green. Addition of degassed hexane (50 ml) produced, on standing, a light green powder. This was washed with hexane and air-dried. The product must be stored under argon. Yield 0.6 g, 30%. (Found: C, 71.5; H, 5.20; N, 1.61; P, 10.1. $C_{56}H_{50}NP_3Ru$ calcd.: C, 72.2; H, 5.41; N, 1.50; P, 10.0%.)

Its IR spectrum contains a medium band, $\nu(CN)$ at 2250 cm^{-1} and hydride bands at 1918 and 1895 cm^{-1} . The deformation bands are hidden under the phosphine absorptions.

Dihydro(benzonitrile)tris(triphenylphosphine)ruthenium(II), RuH₂(C₆H₅CN)(PPh₃)₃

A similar reaction with benzonitrile gives an immediate clear orange solution. Addition of degassed hexane gave an orange powder. The product must be stored under argon. Yield 0.1 g 50%. (Found: C, 73.9; H, 5.12; N, 1.54. C₆₁H₅₂NP₃Ru calcd.: C, 73.8; H, 5.28; N, 1.41%.)

Its IR spectrum has $\nu(\text{CN})$ at 2200 cm⁻¹ (lit.³ 2208 cm⁻¹) and $\nu(\text{Ru-H})$ at 1935 and 1891 cm⁻¹.

Bis(dithioformato)bis(triphenylphosphine)ruthenium(II), Ru(HCS₂)₂(PPh₃)₂

RuH₄(PPh₃)₃ (0.2 g) was added to CS₂ (10 ml) under argon. After the brisk effervescence had stopped, the dark red solution was pumped dry. The crude product was dissolved in chloroform (10 ml) and reprecipitated slowly by adding methanol (30 ml). The deep orange-red crystals were washed with methanol and air-dried. Yield 0.16 g, 90%. (Found: C, 58.6; H, 3.97; P, 8.10; S, 16.5. C₃₈H₃₂P₂S₄Ru calcd.: C, 58.5; H, 4.11; P, 7.96; S, 16.4%.)

Alternatively, RuH₂(PPh₃)₄ (0.25 g) can be used. After 30 minutes, excess CS₂ is removed.

ACKNOWLEDGEMENT

Grateful acknowledgement is made to the National Research Council of Canada for support of this research and to the Province of Ontario for a grant to one of us (L.S.). We should also like to thank Mr. Garfield Purdon for mass spectral measurements.

REFERENCES

- 1 T. I. Eliades, R. O. Harris and M. C. Zia, *Chem. Commun.*, (1970) 1709.
- 2 W. H. Knoth, *J. Amer. Chem. Soc.*, 90 (1968) 7172.
- 3 W. H. Knoth, *J. Amer. Chem. Soc.*, 94 (1972) 104.
- 4 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 28 (1966) 945.
- 5 T. Ito, S. Kitazume, A. Yamamoto and S. Ikeda, *J. Amer. Chem. Soc.*, 92 (1970) 3011.
- 6 M. P. Yagupsky and G. Wilkinson, *J. Chem. Soc., A*, (1968) 2813.
- 7 J. A. Evans, M. J. Hacker, R. D. W. Kemmit, D. R. Russell and J. Stocko, *Chem. Commun.*, (1972) 72.
- 8 V. A. Albano, P. L. Bellor and G. Ciani, *J. Organometal. Chem.*, 31 (1971) 75.
- 9 R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 9 (1970) 227.
- 10 S. Komiya, A. Yamamoto and S. Ikeda, *J. Organometal. Chem.*, 42 (1972) C65.
- 11 P. S. Hallman, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc., A*, (1968) 3143.
- 12 J. A. Osborne, F. H. Jardine, J. E. Young and G. Wilkinson, *J. Chem. Soc., A*, (1966) 1711.
- 13 M. B. Fairy and R. J. Irving, *J. Chem. Soc., A*, (1966) 475.