Journal of Organometallic Chemistry, 56 (1973) 339–343

INFRARED SPECTROSCOPIC EVIDENCE FOR DIHYDRIDOTRICARBONYL(TRIPHENYLPHOSPHINE)RUTHENIUM

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(Received November 27th, 1972)

SUMMARY

The reactions of $Ru(CO)_4PPh_3$ and $Ru(CO)_5$ under pressures of hydrogen have been studied using a high-pressure spectrophotometric cell. Infrared spectral evidence has been obtained for the formation of $H_2Ru(CO)_3PPh_3$ in reversible equilibrium with $Ru(CO)_4PPh_3$ and hydrogen. Reaction of $Ru(CO)_5$ with hydrogen at low temperatures affords $H_2Ru(CO)_4$ as the initial product; above 20° decomposition occurs resulting in the formation of polynuclear products.

INTRODUCTION

The thermally stable series of dihydrides $H_2Os(CO)_4$[1], $H_2Os(CO)_3PPh_3$[2], and $H_2Os(CO)_2(PPh_3)_2$[2] has been prepared by the reaction of molecular hydrogen under pressure with the species $Os(CO)_{5-n}(PPh_3)_n$, where $n=0$, 1 and 2 respectively. Of the ruthenium analogues, in contrast, only $H_2Ru(CO)_2(PPh_3)_2$[2] has been isolated by this route. Attempts to prepare $H_2Ru(CO)_3PPh_3$ by the reaction of $Ru(CO)_4PPh_3$ with H_2 (120 atm pressure and 130°) were unsuccessful, probably because of the decomposition of $Ru(CO)_4PPh_3$ under the reaction conditions[2], and evidence for the formation of the extremely thermally unstable product $H_2Ru(CO)_4$[3] has been obtained by an alternative route, that of acidification of $[Ru(CO)_4]^{2-}$ at very low temperatures. From the reaction of this dihydride with triphenylphosphine only $H_2Ru(CO)_2(PPh_3)_2$ was isolated[3].

Because of the apparent instability under ambient conditions of the ruthenium carbonyl hydrides $H_2Ru(CO)_4$ and $H_2Ru(CO)_3PPh_3$, which may also be of interest catalytically[4], we have studied the reaction of $Ru(CO)_5$ and $Ru(CO)_4PPh_3$ with hydrogen in a high-pressure infrared spectrophotometric cell[5] in order to determine if either of these species may be stabilised under pressure. In this way we have obtained infrared spectral evidence which is consistent with the formation of $H_2Ru(CO)_3PPh_3$ in reversible equilibrium with $Ru(CO)_4PPh_3$ and hydrogen at high pressures and temperatures. Similarly, evidence for the initial formation of $H_2Ru(CO)_4$ from the reaction of $Ru(CO)_5$ with hydrogen at low temperatures has been obtained. Details are described herein.

RESULTS AND DISCUSSION

Reaction of $Ru(CO)_4PPh_3$ with hydrogen

When a heptane solution of $Ru(CO)_4PPh_3$ is pressurised to 500 atm with hydrogen, spectral changes are observed as the temperature is increased (see Fig. 1).

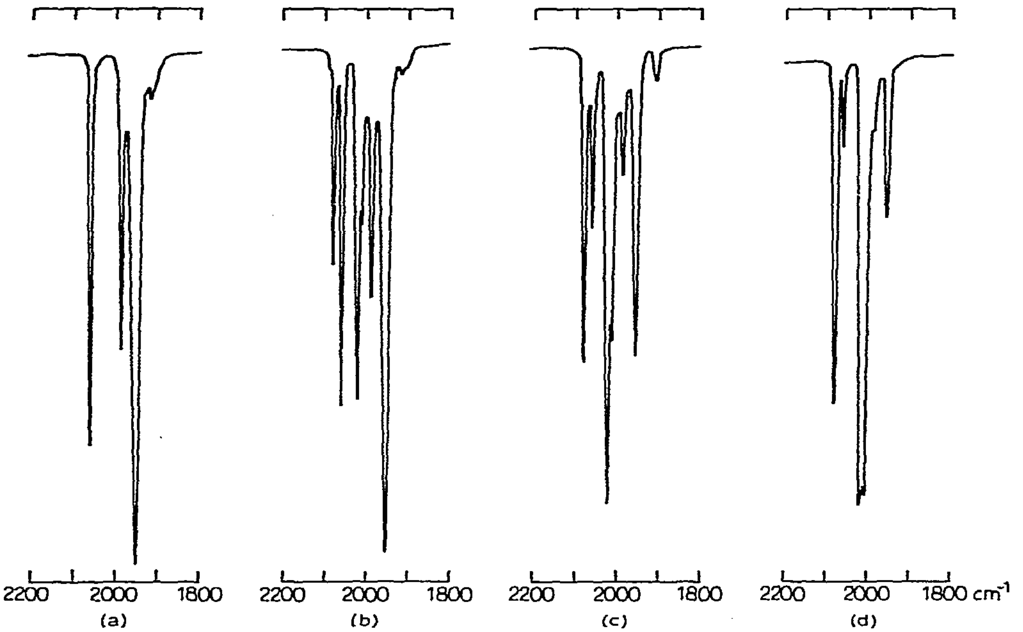

Fig. 1. Reaction of $Ru(CO)_4PPh_3$ with hydrogen and deuterium: (a) 510 atm hydrogen at 20°; (b) 530 atm hydrogen at 60°; (c) 550 atm hydrogen at 100°; (d) 370 atm deuterium at 90°.

Thus new absorptions appear at 2080, 2021 and 2010 cm^{-1} with a concomitant decrease in the intensity of the bands at 2061, 1987 and 1955 cm^{-1} corresponding to the starting $Ru(CO)_4PPh_3$. Optimum conversion to the new species occurs at 100° when the new absorption at 2080 cm^{-1} is slightly more intense than that at 1955 cm^{-1}, the strongest band in the spectrum of the starting $Ru(CO)_4PPh_3$. If at this stage the reaction solution is allowed to cool to room temperature then the equilibrium is reversed in favour of $Ru(CO)_4PPh_3$; complete conversion to the latter occurs on releasing the excess hydrogen pressure. If the temperature of the high pressure system is increased above 120° then irreversible reactions take place with the appearance of several additional bands which probably correspond with the formation of polynuclear compounds.

When the reaction is repeated at lower initial hydrogen pressures, *e.g.* 400, 300 and 200 atm, similar spectral changes are observed but the new peaks are proportionally weaker in intensity. This pressure dependence implies that the species giving rise to the new absorptions is being formed by reaction of $Ru(CO)_4PPh_3$ with molecular hydrogen. In addition no spectral changes are observed when heptane solutions of $Ru(CO)_4PPh_3$ are treated with pressures of nitrogen (or carbon monoxide) under similar reaction conditions.

TABLE 1

ν(CO) STRETCHING FREQUENCIES IN HEPTANE

$Ru(CO)_4PPh_3$	$Ru(CO)_4PPh_3+H_2$ (550 *atm*, 100°)	$Ru(CO)_4PPh_3+D_2$ (370 *atm*, 90°)	$H_2Os(CO)_3PPh_3$ (*ref.* 1)
	2089 vw(sh)	2090 vw(sh)	
	2080 s	2080 s	2079 vs
2061 s	2061 m	2061 mw	
	2021 vs	2016 vs	2027 vs
	2010 s(sh)	2007 vs	2018 vs
1987 ms	1987 mw	1987 w	
1955 vs	1955 s	1955 m	1959 w
1919 vw			1922 w
	1908 w		

The new absorptions appearing in the spectra are of similar frequencies to those of the dihydridoosmium complex $H_2Os(CO)_3PPh_3$ (see Table 1), a stable compound which has been prepared by both the reaction of $H_2Os(CO)_4$ with PPh_3[1] and from the reaction of hydrogen with $Os(CO)_4PPh_3$[2]. It seems likely therefore that the ruthenium analogue, $H_2Ru(CO)_3PPh_3$, has been stabilised under the high pressures of hydrogen used.

In contrast to the osmium system we have observed only one band, at 1908 cm^{-1}, which is readily assignable to a metal–hydrogen stretching vibration. Comparison with the infrared spectra of the complexes $H_2Os(CO)_3PPh_3$, $H_2Os(CO)_2(PPh_3)_2$ and $H_2Ru(CO)_2(PPh_3)_2$ suggests that, for a similar structure to the tricarbonylosmium derivative, $H_2Ru(CO)_3PPh_3$ should exhibit two ν(M–H) vibrations at ca. 1910 and 1870 cm^{-1}. The observation of only one band, together with differences in relative intensities of the doublet ν(CO) absorption [compared with the spectrum of $H_2Os(CO)_3PPh_3$], suggests that $H_2Ru(CO)_3PPh_3$ may exist under high pressure and temperature conditions in a different isomeric form from that established for *fac*-$H_2Os(CO)_3PPh_3$.

Treatment of $Ru(CO)_4PPh_3$ with deuterium [see Fig. 1 (d)] confirms the assignment of the ruthenium–hydrogen stretching frequency at 1908 cm^{-1}; no peak is observed in this position under pressures and temperatures similar to those described above. For similar reaction conditions however, the equilibrium

$$Ru(CO)_4PPh_3+X_2 \rightleftarrows X_2Ru(CO)_3PPh_3+CO$$

is displaced further to the right when X=D than when X=H.

Another change which is noted on deuteration is that the ν(CO) absorptions at 2021 and 2010 cm^{-1} in the dihydride both shift to slightly lower wavenumbers and change in relative intensities giving a doublet at 2016 and 2007 cm^{-1}. Much larger shifts were observed on deuteration of $H_2Os(CO)_3PPh_3$ and these were explained in terms of removal of a resonance interaction between ν(Os–H) and ν(CO) on substitution of hydrogen by deuterium[1]. Such mixing is expected to be much weaker with first and second row transition metal derivatives[6] and possibly this is the first example of such an effect with a second row transition element. Another possible explanation for the band shifts is that reaction with deuterium favours the formation of a different isomer of $X_2Ru(CO)_3PPh_3$ than that observed for $X=H$.

In conclusion therefore the hydrogen pressure effects and the similarity of the $\nu(CO)$ frequencies to those of $H_2Os(CO)_3PPh_3$ strongly suggest the formation of $H_2Ru(CO)_3PPh_3$ in reversible equilibrium with $Ru(CO)_4PPh_3$ and hydrogen. The reversal of the equilibrium in favour of $Ru(CO)_4PPh_3$ in the absence of excess hydrogen pressure is also consistent with difficulties in isolating $H_2Ru(CO)_3PPh_3$.

Reaction of $Ru(CO)_5$ with hydrogen

A heptane solution of $Ru(CO)_5$ at −25° was pressurised to 300 atm with hydrogen and the system slowly allowed to warm to room temperature. The initial spectrum showed two bands of approximately equal intensity at 2036 and 2001 cm^{-1}, consistent with the known spectrum of $Ru(CO)_5$[7]. Additional bands at 2068, 2055 and 2052 cm^{-1} appeared and increased slowly in intensity as the temperature was allowed to rise. At 19° the new absorption at 2052 cm^{-1} was of comparable intensity with the bands due to the starting $Ru(CO)_5$. On warming above 20° additional peaks appeared giving finally a spectrum which was too complex to interpret with definition; however, $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$[4,8] and the product formulated by Stone *et al.*[3] as $H_2Ru_3(CO)_{12}$ are probably all components of the reaction mixture.

TABLE 2

$\nu(CO)$ STRETCHING FREQUENCIES

$Ru(CO)_5$ heptane	*$Ru(CO)_5+H_2$ (300 atm, 19°) heptane*	*$H_2Ru(CO)_4$ (ref. 3) vapour*	*$H_2Os(CO)_4$ (ref. 1) heptane*	*$H_2Os(CO)_4$ (ref. 1) vapour*
	2085 w	2082 mw	2141 w	2145 w
	2068 ms	2074 m	2067 m	2082 m
	2055 s(sh)	2070 s	2055 s	2075 s(sh)
	2052 s	2066 m	2048 vs	2062 vs
2036 s	2036 s			2034 w
2000 s	2001 s	2018 w	2016 w	2029 w
	1979 w	1980 w(br)		
1968 w	1967 w		1942 w	1945 w

Comparison of the solution spectrum measured at 19° with the vapour phase spectrum of $H_2Ru(CO)_4$ and both solution and vapour phase spectra of $H_2Os(CO)_4$ (see Table 2) indicates that the new bands at 2068, 2055 and 2052 cm^{-1} are consistent with the strongest bands expected in the solution spectrum of $H_2Ru(CO)_4$. It seems likely therefore that this species is formed initially in the reaction of hydrogen with $Ru(CO)_5$ at low temperatures. The thermal instability of this dihydride is further emphasised by the fact that on warming above 20°, even under 300 atm hydrogen pressure, decomposition takes place with the formation of polynuclear aggregates.

EXPERIMENTAL

Details of the high pressure spectrophotometric cell have been described previously[5]. Infrared spectra were recorded on a Perkin Elmer Model 257 spectrophotometer using X10 scale expansion and calibration with either water vapour or gaseous carbon monoxide.

Preparation of $Ru(CO)_4PPh_3$

(*a*). *From* $Ru_3(CO)_9(PPh_3)_3$. A suspension of nonacarbonyltris(triphenylphosphine)triruthenium (1.0 g) in dry heptane (70 ml) contained in a glass liner was treated with carbon monoxide (80 atm) in a small stirred autoclave at 150° for 6 h. After cooling and venting the excess pressure the pale yellow crystals of $Ru(CO)_4PPh_3$ (0.50 g) were filtered, recrystallised from benzene/hexane and dried under vacuum. (Found: C, 55.3; H, 3.1; P, 7.1. $C_{22}H_{15}O_4PRu$ calcd.: C, 55.5; H, 3.2; P, 6.6%.)

(*b*). *From* $Ru_3(CO)_{12}$ *and* PPh_3. A mixture of dodecacarbonyltriruthenium (0.41 g) and triphenylphosphine (0.53 g) in heptane (50 ml) was treated with carbon monoxide (80 atm) at 150° as above. After cooling, $Ru(CO)_4PPh_3$ (0.73 g) was filtered, recrystallised from benzene/hexane and dried under vacuum.

Preparation of $Ru(CO)_5$

Dodecacarbonyltriruthenium (0.2 g) in dry heptane (40 ml) contained in a glass liner was treated with carbon monoxide (80 atm) in a small autoclave at 150° for 3 h. The autoclave was then cooled to −80° in a dry-ice acetone bath. After venting the excess pressure 20 ml of the colourless solution of pentacarbonylruthenium were rapidly syringed into the pre-cooled high pressure infrared cell. The system was then pressurised with hydrogen (300 atm) and allowed to warm slowly to room temperature.

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