*Journal of Organometallic Chemistry*, 317 (1986) C45–C47
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

**Preliminary communication**

# TRIHYDRIDORUTHENIUM(IV) COMPLEXES: PREPARATION AND PHOTO-INDUCED H/D EXCHANGE REACTION

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(Received August 5th, 1986)

## Summary

The trihydrides ($\eta^5$-$C_5Me_5$)$RuH_3(PR_3)$($PR_3$ = $PMe_3$, $PEt_3$, $Pipr_3$, $PCy_3$, $PPh_2Me$, and $PPh_3$) (**2**) are formed in the reaction of paramagnetic ($\eta^5$-$C_5Me_5$)$RuCl_2(PR_3)$ (**1**) with $NaBH_4$ in ethanol. The reaction of **1** with $NaBH_4$ in THF yields intermediary tetrahydroborate complexes ($\eta^5$-$C_5Me_5$)$Ru(PR_3)(BH_4)$ (**3**), which are converted to the trihydrides **2** by treatment with ethanol. Irradiation of **2c** and **2f** in $C_6D_6$ solution with UV light causes H/D exchange reaction among the solvent, hydride ligands, and the coordinated phosphine.

The chemistry of middle and late transition metal polyhydride complexes has recently received much attention owing to the potential use of these complexes as precursors of the active catalysts for the H/D exchange reaction and the C–H bond activation [1]. Since the early 1970s polyhydridoruthenium complexes have been known, and in recent years, some of them have been shown to catalyze the H/D exchange reaction with deuterated solvents [2]. In 1983, thermally stable neutral trihydride ($\eta^5$-$C_5H_5$)$RuH_3(PPh_3)$ was prepared by Davies [3]. Recently, Arliguie and Chaudret reported the preparation of trihydridoruthenium(IV) complexes, ($\eta^5$-$C_5Me_5$)$RuH_3(PR_3)$, by treatment of ($\eta^5$-$C_5Me_5$)$RuCl_2(PR_3)$ with $LiBHEt_3$ in tetrahydrofuran [4]. We have independently established a preparative method for trihydridoruthenium(IV) complexes with a variety of phosphine ligands involving the reaction of ($\eta^5$-$C_5Me_5$)$RuCl_2(PR_3)$ with $NaBH_4$ in ethanol.

Here we report the preparation of trihydridoruthenium(IV) complexes, ($\eta^5$-$C_5Me_5$)$RuH_3(PR_3)$ (**2**), and the intermediary ruthenium(II) tetrahydroborate complexes, ($\eta^5$-$C_5Me_5$)$Ru(PR_3)(BH_4)$ (**3**). The H/D exchange reaction catalyzed by the ruthenium trihydrides under UV irradiation is also described.

The trihydridoruthenium(IV) complexes **2a–2f** are directly synthesized from the corresponding paramagnetic dichlororuthenium(III) complexes, ($\eta^5$-$C_5Me_5$)$RuCl_2$-$(PR_3)$ (**1a–1f**) [5], by treatment with excess $NaBH_4$ in ethanol at ambient temperature for 5 h (eq. 1). After removal of ethanol from the reaction mixture in vacuo,

0022-328X/86/$03.50 

TABLE 1
SELECTED SPECTRAL DATA OF $(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)$ (2)

| | $PR_3$ | Yield(%) | $^1H$ NMR [a] | | IR [d] |
|---|---|---|---|---|---|
| | | | $C_5Me_5$ [b] | Ru–H [c] | $\nu$(Ru–H) |
| **2a** | $PMe_3$ | 92 | 1.94(1.2) | −10.61(21.7) | 1960 [e] |
| **2b** | $PEt_3$ | 94 | 1.99(1.3) | −10.88(20.8) | 1976, 1966 |
| **2c** | $P^iPr_3$ | 85 | 2.01(1.3) | −11.05(22.0) | 1999, 1986 |
| **2d** | $PCy_3$ | 65 | 2.07(1.3) | −11.01(22.0) | 1991 [e] |
| **2e** | $PPh_2Me$ | 58 | 1.84(1.3) | −9.98(20.5) | 1965 [e] |
| **2f** | $PPh_3$ | 85 | 1.84(1.3) | −9.72(20.5) | 1975, 1960 (1975, 1960) [e] |

[a] Shifts are in ppm, relative to $SiMe_4$ at 100 MHz and 30°C in $C_6D_6$. [b] Number in parentheses is $^4J$(PH), in Hz. [c] Number in parentheses is $^2J$(PH), in Hz. [d] Measured in $C_6H_6$. [e] Measured in KBr.

trihydride complexes **2a–2f** were extracted with n-pentane. Recrystallization from n-pentane or diethyl ether afforded analytically pure trihydride complexes, **2a–2f**. Trihydrides **2a–2f** were characterized by use of standard analytical and spectroscopic methods. The yields and the selected spectroscopic data of **2a–2f** are listed in Table 1.

$$\underset{\mathbf{1}}{(\eta^5\text{-}C_5Me_5)RuCl_2(PR_3)} \xrightarrow{NaBH_4,\ EtOH} \underset{\mathbf{2}}{(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)} \qquad (1)$$

The IR spectra of the trihydrides reveal sharp absorption bands due to the stretching vibration of the Ru–H bond in the region of 1960–1990 $cm^{-1}$. In addition, equivalent resonance peaks are observed around $\delta - 10 \sim -11$ as doublets ($J$ ca. 20 Hz) in the $^1H$ NMR spectra of **2a–2f** for the three hydride ligands.

Complex **2f** was alternatively prepared by the reaction of $(\eta^5\text{-}C_5Me_5)RuBr_3(PPh_3)$ with $NaBH_4$ in ethanol albeit in low yield [6].

In contrast to the reaction in ethanol, ruthenium(III) dichloride **1** reacted with $NaBH_4$ in dry tetrahydrofuran to afford the novel ruthenium tetrahydroborate complexes, $(\eta^5\text{-}C_5Me_5)Ru(PR_3)(BH_4)$ (**3a–3f**), as air- and moisture-sensitive orange needles (eq. 2). The key features of **3** which characterize its structure are the IR

$$\underset{\mathbf{1}}{(\eta^5\text{-}C_5Me_5)RuCl_2(PR_3)} \xrightarrow{NaBH_4,\ THF} \underset{\mathbf{3}}{(\eta^5\text{-}C_5Me_5)Ru(PR_3)(BH_4)} \qquad (2)$$

and $^1H$ NMR spectra associated with the hydride ligands (Table 2). The coordination of tetrahydroborate ion via Ru–H–B bridges was established by characteristic stretching bands between 2450–2300 $cm^{-1}$. The $^1H$ NMR spectrum of **3a** measured in $C_6D_6$ at 30°C reveals magnetically equivalent bridging hydrides at $\delta - 11.05$ and two non-equivalent terminal hydrides at $\delta - 3.50$ and 2.14, respectively. The signals for hydrides are extremely broad ($w_{1/2}$ 115 ~ 180 Hz) because of quadrupole interaction with the $^{11}B$ nucleus.

Tetrahydroborate complexes **3a–3f** could quantitatively be converted to the corresponding trihydride complexes **2a–2f** by treatment with ethanol (eq. 3).

$$\underset{\mathbf{3}}{(\eta^5\text{-}C_5Me_5)Ru(PR_3)(BH_4)} \xrightarrow{EtOH} \underset{\mathbf{2}}{(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)} \qquad (3)$$

TABLE 2
SELECTED SPECTRAL DATA OF $(\eta^5\text{-}C_5Me_5)Ru(PR_3)(BH_4)$ (3)

| | $PR_3$ | Yield(%) | $^1H$ NMR [a] | | Ir [e] |
|---|---|---|---|---|---|
| | | | $C_5Me_5$ [b] | Ru–H–B [c] | $\nu(RuH_2BH_2)$ |
| **3a** | $PMe_3$ | 65 | 1.66(1.2) | −11.05 (−3.50, 2.14) [d] | 2438, 2362, 2282 |
| **3b** | $PEt_3$ | 65 | 1.69(1.2) | −11.63 (−3.22, 2.10) [d] | 2433, 2352, 2284 |
| **3c** | $P^iPr_3$ | 84 | 1.68(1.3) | −12.54 | 2393, 2318 |
| **3d** | $PCy_3$ | 99 | 1.73(1.3) | −12.36 | 2408, 2329 |
| **3e** | $PPh_2Me$ | 74 | 1.53(1.5) | −12.00 | 2387, 2292, 2223 |
| **3f** | $PPh_3$ | 97 | 1.51(1.5) | −12.05 | 2450, 2388, 2326 |

[a] Shifts are in ppm, relative to $SiMe_4$ at 100 MHz and 30°C in $C_6D_6$. [b] Number in parentheses is $^4J(PH)$, in Hz. [c] Number in parentheses is $^2J(PH)$, in Hz. [d] Terminal hydrides. [e] Measured in KBr.

While the thermal stability of the trihydride complexes **2** is remarkably high with little or no decomposition occurring over several hours at 70°C in toluene, irradiation of **2c** or **2f** in $C_6D_6$ solution with ultraviolet light (> 300 nm) causes the H/D exchange reaction. Coordinated triphenylphosphine and hydrides bound to ruthenium(IV) were deuterated by the photolysis (> 300 nm) of **2f** in $C_6D_6$ in a sealed NMR sample tube (eq. 4).

$$\underset{\mathbf{2f}}{(\eta^5\text{-}C_5Me_5)RuH_3P(C_6H_5)_3} \xrightarrow{h\nu,\ C_6D_6} \underset{\mathbf{2f}\text{-}d_{18}}{(\eta^5\text{-}C_5Me_5)RuD_3P(C_6D_5)_3} \quad (4)$$

The irradiation of **2c** with UV light (> 300 nm) in $C_6D_6$ at 25°C also caused H/D exchange among the solvent, hydride ligands, and the distal hydrogens of the coordinated triisopropylphosphine. And the trihydride **2c** was recovered by the photolysis of deuterated product in $C_6H_6$ at 25°C (eq. 5).

$$\underset{\mathbf{2c}}{(\eta^5\text{-}C_5Me_5)RuH_3P\{CH(CH_3)_2\}_3} \underset{h\nu,\ C_6D_6}{\overset{h\nu,\ C_6H_6}{\rightleftharpoons}} \underset{\mathbf{2c}\text{-}d_{21}}{(\eta^5\text{-}C_5Me_5)RuD_3P\{CH(CD_3)_2\}_3} \quad (5)$$

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