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Preliminary communication

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

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Summary

The trihydrides (η^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 (η^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 (η^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 (η^5-C_5H_5)$RuH_3(PPh_3)$ was prepared by Davies [3]. Recently, Arliguie and Chaudret reported the preparation of trihydridoruthenium(IV) complexes, (η^5-C_5Me_5)$RuH_3(PR_3)$, by treatment of (η^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 (η^5-C_5Me_5)$RuCl_2(PR_3)$ with $NaBH_4$ in ethanol.

Here we report the preparation of trihydridoruthenium(IV) complexes, (η^5-C_5Me_5)$RuH_3(PR_3)$ (**2**), and the intermediary ruthenium(II) tetrahydroborate complexes, (η^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, (η^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,

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TABLE 1

SELECTED SPECTRAL DATA OF (η^5-C_5Me_5)$RuH_3(PR_3)$ (**2**)

	PR_3	Yield(%)	^{1}H NMR[a]		IR[d]
			C_5Me_5[b]	Ru–H[c]	ν(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 ^{1}H NMR spectra of **2a–2f** for the three hydride ligands.

Complex **2f** was alternatively prepared by the reaction of (η^5-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, (η^5-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 and ^{1}H 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 ^{1}H 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.

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

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 (η^5-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).

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

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).

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

References

1 For example, R.H. Crabtree, J.M. Mihelcic, and J.M. Ouirk, J. Am. Chem. Soc., 101 (1979) 7738; R.H. Crabtree, M.F. Mellea, J.M. Mihelcic, and J.M. Quirk, ibid., 104 (1982) 107; D. Baudry, M. Ephritikhine, and H. Felkin, J. Chem. Soc., Chem. Commun., (1980) 1243; A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 104 (1982) 352; M.J. Wax, J.M. Stryker, J.M. Buchanan, C.A. Kovac, and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 1121; R.A. Periana and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 7272; J.M. Buchanan, J.M. Stryker, and R.G. Bergman, J. Am. Chem. Soc., 108 (1986) 1537; W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 104 (1982) 4240; 106 (1984) 1650; R.H. Crabtree, Chem. Rev., 85 (1985) 245 and ref. cited therein.

2 For example, R.H. Morris and Shiralian, J. Organomet. Chem., 260 (1984) C47; B. Chaudret, ibid., 268 (1984) C33; B. Chaudret and R. Poilblanc, Organometallics, 4 (1985) 1722.

3 S.G. Davies, S.D. Moon, and S.L. Simpson, J. Chem. Soc. Chem., Chem. Commun., (1983) 1278; G.J. Baird, S.G. Davies, S.D. Moon, and S.J. Simpson, and R.H. Jones, J. Chem. Soc. Dalton Trans., (1985) 1479.

4 T. Arliguie and B. Chaudret, J. Chem. Soc., Chem. Commun., (1986) 985.

5 H. Suzuki, D.H. Lee, N. Oshima, S. Narasaka, Z. Xi, and Y. Moro-oka, manuscript in preparation.

6 N. Oshima, H. Suzuki, Y. Moro-oka, H. Nagashima, and K. Itoh, J. Organomet. Chem., 314 (1986) C46