

Preliminary communication

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

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Summary

The trihydrides $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)(\text{PR}_3 = \text{PMe}_3, \text{PEt}_3, \text{Pipr}_3, \text{PCy}_3, \text{PPh}_2\text{Me}, \text{and PPh}_3)$ (**2**) are formed in the reaction of paramagnetic $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$ (**1**) with NaBH_4 in ethanol. The reaction of **1** with NaBH_4 in THF yields intermediary tetrahydroborate complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)(\text{BH}_4)$ (**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 $(\eta^5\text{-C}_5\text{H}_5)\text{RuH}_3(\text{PPh}_3)$ was prepared by Davies [3]. Recently, Arliguie and Chaudret reported the preparation of trihydridoruthenium(IV) complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$, by treatment of $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$ 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 $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$ with NaBH_4 in ethanol.

Here we report the preparation of trihydridoruthenium(IV) complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$ (**2**), and the intermediary ruthenium(II) tetrahydroborate complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)(\text{BH}_4)$ (**3**). The H/D exchange reaction catalyzed by the ruthenium trihydrides under UV irradiation is also described.

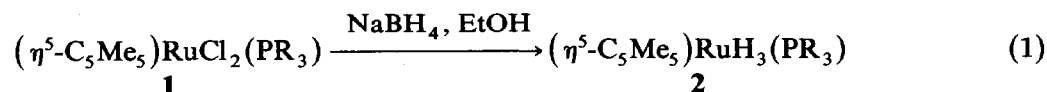
The trihydridoruthenium(IV) complexes **2a–2f** are directly synthesized from the corresponding paramagnetic dichlororuthenium(III) complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$ (**1a–1f**) [5], by treatment with excess NaBH_4 in ethanol at ambient temperature for 5 h (eq. 1). After removal of ethanol from the reaction mixture in vacuo,

TABLE 1
 SELECTED SPECTRAL DATA OF $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$ (**2**)

	PR ₃	Yield(%)	¹ H NMR ^a		IR ^d
			C ₅ Me ₅ ^b	Ru-H ^c	$\nu(\text{Ru-H})$
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 ⁱ Pr 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 ₂ Me	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 SiMe₄ at 100 MHz and 30°C in C₆D₆. ^b Number in parentheses is ⁴J(PH), in Hz. ^c Number in parentheses is ²J(PH), in Hz. ^d Measured in C₆H₆. ^e Measured in KBr.

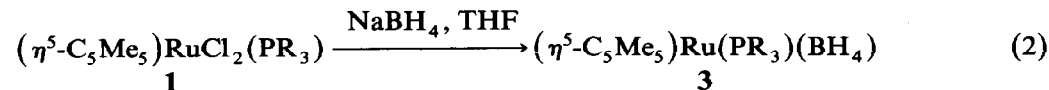
trihydride complexes **2a–2f** were extracted with n-pentane. Recrystallization from n-pentane or diethyl ether afforded analytically pure trihydride complexes, **2a–2f**. Trihydrides **2a–2f** were characterized by use of standard analytical and spectroscopic methods. The yields and the selected spectroscopic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



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 $(\eta^5\text{-C}_5\text{Me}_5)\text{RuBr}_3(\text{PPh}_3)$ with NaBH₄ in ethanol albeit in low yield [6].

In contrast to the reaction in ethanol, ruthenium(III) dichloride **1** reacted with NaBH₄ in dry tetrahydrofuran to afford the novel ruthenium tetrahydroborate complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)(\text{BH}_4)$ (**3a–3f**), as air- and moisture-sensitive orange needles (eq. 2). The key features of **3** which characterize its structure are the IR



and 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 C₆D₆ 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 ($\omega_{1/2}$ 115 ~ 180 Hz) because of quadrupole interaction with the ¹¹B nucleus.

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

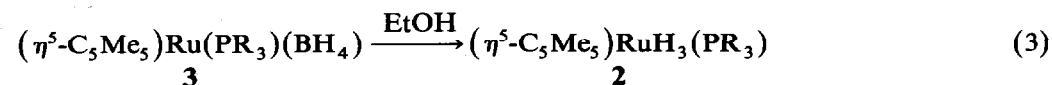
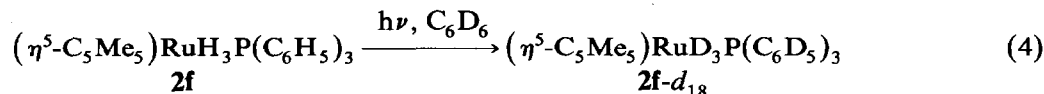


TABLE 2
SELECTED SPECTRAL DATA OF (η^5 -C₅Me₅)Ru(PR₃)(BH₄) (3)

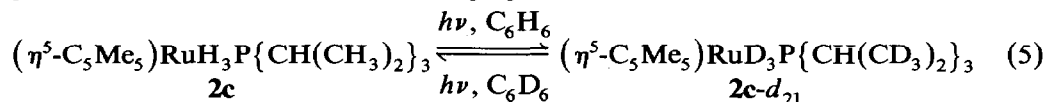
	PR ₃	Yield(%)	¹ H NMR ^a		Ir ^e ν(RuH ₂ BH ₂)
			C ₅ Me ₅ ^b	Ru-H-B ^c	
3a	PMe ₃	65	1.66(1.2)	-11.05 (-3.50, 2.14) ^d	2438, 2362, 2282
3b	PEt ₃	65	1.69(1.2)	-11.63 (-3.22, 2.10) ^d	2433, 2352, 2284
3c	p ⁱ Pr ₃	84	1.68(1.3)	-12.54	2393, 2318
3d	PCy ₃	99	1.73(1.3)	-12.36	2408, 2329
3e	PPh ₂ Me	74	1.53(1.5)	-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 SiMe₄ at 100 MHz and 30°C in C₆D₆. ^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 C₆D₆ 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 C₆D₆ in a sealed NMR sample tube (eq. 4).



The irradiation of **2c** with UV light (> 300 nm) in C₆D₆ 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 C₆H₆ at 25°C (eq. 5).



References

- For example, R.H. Crabtree, J.M. Mihelcic, and J.M. Quirk, *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.
- 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.
- 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.
- T. Arliguie and B. Chaudret, *J. Chem. Soc., Chem. Commun.*, (1986) 985.
- H. Suzuki, D.H. Lee, N. Oshima, S. Narasaka, Z. Xi, and Y. Moro-oka, manuscript in preparation.
- N. Oshima, H. Suzuki, Y. Moro-oka, H. Nagashima, and K. Itoh, *J. Organomet. Chem.*, 314 (1986) C46