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**Preliminary communication**

# Preparation of novel aluminohydride complexes of ruthenium(II)

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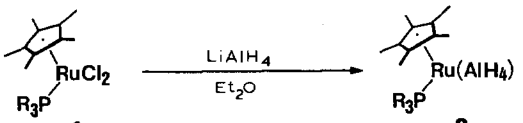
## Abstract

Treatment of $(\eta^5\text{-}C_5Me_5)RuCl_2(PR_3)$ (**1**) with $LiAlH_4$ in diethyl ether gives the ruthenium(II) tetrahydroaluminate complexes, $(\eta^5\text{-}C_5Me_5)Ru(AlH_4)(PR_3)$ (**2**) ($R_3 = Me_3$, $Et_3$, ${}^iPr_3$, $Ph_2Me$, $Ph_3$), which can be quantitatively converted to the trihydridoruthenium(IV) complexes $(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)$ (**4**), via protonolysis either by reaction with ethanol or by filtration through alumina. Low-temperature $^1H$ NMR studies suggest the fluxionality of complexes **2** in solution at ambient temperature.

One of the most general methods for preparation of transition metal hydride complexes is the reaction of a transition metal halide with hydridic agents such as $NaBH_4$, $LiAlH_4$, or $LiBHEt_3$. In some cases, however, complexes containing $BH_4^-$ or $AlH_4^-$ entities are obtained instead of simple hydrides. Although a number of transition metal borohydride complexes have been synthesized and their structures determined [1], only a few examples of transition metal aluminohydride complexes are known [2]. Recently we reported the synthesis of ruthenium(II) tetrahydroborates, $(\eta^5\text{-}C_5Me_5)Ru(BH_4)(PR_3)$ (**3**) ($R_3 = Me_3$, $Et_3$, ${}^iPr_3$, $Cy_3$, $MePh_2$, and $Ph_3$), starting from ruthenium(III) dichlorides, $(\eta^5\text{-}C_5Me_5)RuCl_2(PR_3)$ (**1**), and $NaBH_4$ [3]. Here we describe the preparation of a series of novel aluminohydride complexes of ruthenium(II).

The aluminohydride complexes **2a**–**2e** are synthesized from the corresponding dichlororuthenium(III) complexes, $(\eta^5\text{-}C_5Me_5)RuCl_2(PR_3)$ (**1**) [4], by treatment with excess $LiAlH_4$ in diethyl ether (eq. 1).



**1** **2** (1)

Table 1

Yields and selected spectral data of ($\eta^5$-$C_5Me_5$)Ru($AlH_4$)($PR_3$) (**2**)

| | $PR_3$ | Yield (%) | $^1H$ NMR (ppm) [a] | | | IR [d] ($cm^{-1}$) $\nu(RuH_2AlH_2)$ |
|---|---|---|---|---|---|---|
| | | | $C_5Me_5$ [b] | Ru–H–Al [c] | Al–H | |
| **2a** | $PMe_3$ | 78 | 1.98 (1.4) | −13.55 (26.5) | 4.52 | 1830, 1794 |
| **2b** | $PEt_3$ | 91 | 1.96 (1.2) | −13.74 (24.6) | 4.55 | 1845, 1748, 1718 |
| **2c** | $P^iPr_3$ | 87 | 1.96 (1.1) | −13.87 (24.6) | 4.47 | 1875, 1745 |
| **2d** | $PPh_2Me$ | 82 | 1.76 (1.4) | −13.22 (25.3) | 4.35 | 1856, 1749, 1737 |
| **2e** | $PPh_3$ | 80 | 1.73 (1.3) | −13.01 (24.8) | 3.57, 4.45 | 1895, 1845, 1744 |

[a] Relative to $SiMe_4$ at 100 MHz and 30 °C in $C_6D_6$. [b] $^4J$(PH) (Hz) in parentheses. [c] $^2J$(PH) (Hz) in parentheses. [d] In KBr.

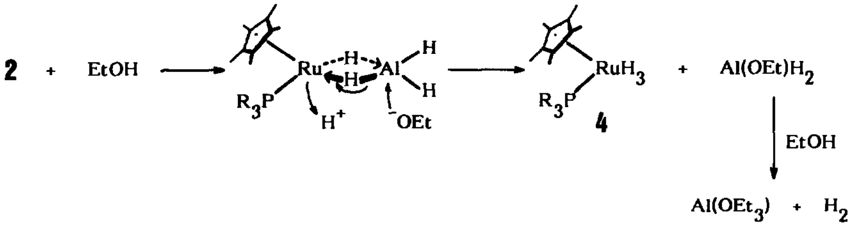
Excess $LiAlH_4$ was added to a suspension of ($\eta^5$-$C_5Me_5$)$RuCl_2$($PMe_3$) (**1a**) (0.312 g, 0.814 mmol) in diethyl ether (20 ml) at ambient temperature and the resulting mixture was stirred for 1 h to give an off-white suspension. After removal of the solvent in vacuo, extraction of the product from the residual solid with two 25 ml portions of n-pentane gave the crude tetrahydroaluminate complex, ($\eta^5$-$C_5Me_5$)Ru($AlH_4$)($PMe_3$) (**2a**), as a colorless powder. Recrystallization from the mixed solvent, diethyl ether and n-pentane, yielded analytically pure **2a** as colorless prisms (0.218 g, 78%).

The tetrahydroaluminate complexes **2b**–**2e** are highly sensitive towards air and moisture. They were characterized by $^1H$, $^{13}C$ NMR and IR spectroscopy and by microanalysis.

The yields and some spectroscopic data of **2a**–**2e** are listed in Table 1.

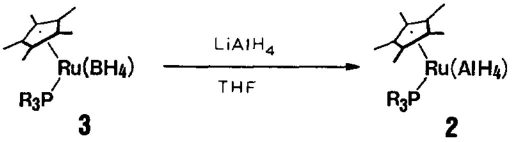
Key features in the $^1H$ NMR spectrum of **2** are the high field shifts of the bridging hydride ligands between ruthenium and aluminum at $\delta$ −13.01 ~ −13.87 ppm, and broad signals ($w_{1/2}$ ca. 75 Hz) from the terminal aluminum hydrides at $\delta$ 3.57–4.55 ppm. The broadness of the signals from the hydride ligands, especially those from terminal aluminum hydride, can be attributed to the effects of the $^{27}Al$ quadrupole moment and to the fluxionality of the complexes at ambient temperature. The fluxional behavior of **2a** in solution was confirmed by its $^1H$ NMR spectrum in toluene-$d_8$ at various temperatures. Decoalescence of the broad signal at $\delta$ 4.52 ppm is observed between 0 °C and −20 °C. Upon cooling to −60 °C, the resonance for terminal Al-H ligands splits into two broad singlets, at $\delta$ 3.86 ($w_{1/2}$ 21 Hz) and 5.35 ppm ($w_{1/2}$ 33 Hz), of equal intensity. In contrast to the terminal hydrides, the $^1H$ NMR parameters for the bridging hydrides remain almost unchanged at these temperatures. These results suggest that there is no exchange between the bridging hydrides and the terminal hydrides, and that exchange between the two terminal hydrides occurs at ambient temperature. The IR spectra of **2** revealed sharp bands between 1718–1875 $cm^{-1}$ due to the bridging and terminal hydrides.

While there are numerous examples of monomeric transition metal borohydride complexes that may have M–H–B bridges, aluminohydride complexes thus far reported are dimers with $M(\mu\text{-}H)_2AlH(\mu\text{-}H)_2M$ or $M(\mu\text{-}H)_2AlH(\mu\text{-}H)_2AlH(\mu\text{-}H)_2M$ units [2]. The molecular weight of 374 for **2a** measured cryoscopically in benzene under 1 atm argon strongly suggests that **2a** dissociates to become monomeric in solution.



Scheme 1.

An alternative method for the preparation of **2** is anion exchange of $BH_4^-$ for $AlH_4^-$. Treatment of the borohydride complexes **3** with $LiAlH_4$ in diethyl ether gives the aluminohydrides **2** in excellent yields (eq. 2).



(2)

Protonolysis of **2**, either by reaction with ethanol or filtration through an alumina column, yields the corresponding trihydridoruthenium(IV) complexes **4** quantitatively (Scheme 1).

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