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Preliminary communication

ALLYLDIALKYL COMPLEXES OF RUTHENIUM(IV): PREPARATION AND REDUCTIVE C–C BOND FORMATION FOLLOWED BY C–H BOND ACTIVATION

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Summary

New η^3-allyldimethyl complexes $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)(CH_3)_2$, where R = H or CH_3, are prepared from $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)Br_2$ by alkylation with trimethylaluminium. The Ru^{IV} dimethyl complex is thermally converted to the Ru^{II} 1-methylallyl compound, $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}CH_2CHCHCH_3)L$, where L = CO or $t\text{-}C_4H_9NC$, with evolution of methane. Kinetic and deuteration studies on the reductive process are also discussed.

Ruthenium alkyl compounds, such as $Ru(\eta^5\text{-}C_5R_5)(R)L_2$ [1,2], $Ru(\eta^6\text{-}C_6R_6)(R)(X)L$ [3], $Ru(R)_2L_4$ or $Ru(R)(X)L_4$ [4] have been prepared from the corresponding halogeno precursors by alkylation with alkyl-lithium, -magnesium, or -mercury reagents. In contrast to the abundance of the Ru^{II} alkyl complexes, only a few alkyl complexes have been known to form derivatives in higher oxidation states. In this context, the authors now report for the first time, the preparation and substantial thermal stability of $Ru(CH_3)(I)(1\text{-}3:6\text{-}7:10\text{-}12\text{-}\eta\text{-}C_{12}H_{18})$ [5] and $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)(CH_3)Br$ [6], both of which are in the Ru^{IV} oxidation state. We have also found that such ruthenium(IV) alkylallyl complexes induced facile reductive elimination by forming a C–C bond between the allyl and methyl ligands giving 1-butene and the more stable Ru^{II} compounds [5,6]. We report here the preparation and the reductive reaction of allyldimethyl Ru^{IV} complexes.

When ether or hexane suspensions of (previously reported) $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)Br_2$ (**1a**, R = H) [7] or (**1b**, $R = CH_3$) [8], were treated with 4 equiv. of trimethylaluminium (1 *N* hexane solution) at $-5 \sim 0°C$ for 1 h, the corresponding Ru^{IV} allyldimethyl complexes, $Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)(CH_3)_2$ (**2a**, R = H) or (**2b**, $R = CH_3$), were isolated as colorless crystals, after hydrolytic work up at $-40°C$ followed by ether extraction and chromatographic purification (alumina; pentane), in 90 ~ 93% yields. It is notable that **2a** and **2b** are stable at ambient temperature and to hydrolysis which is in contrast to $Ru(CH_3)_2(1\text{-}3:6\text{-}7:10\text{-}12\text{-}\eta\text{-}C_{12}H_{18})$,

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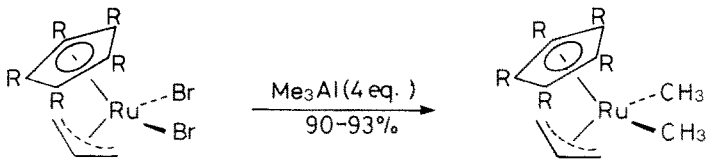


1a: R=H
1b: R=CH_3

2a: R=H
2b: R=CH_3

SCHEME 1.

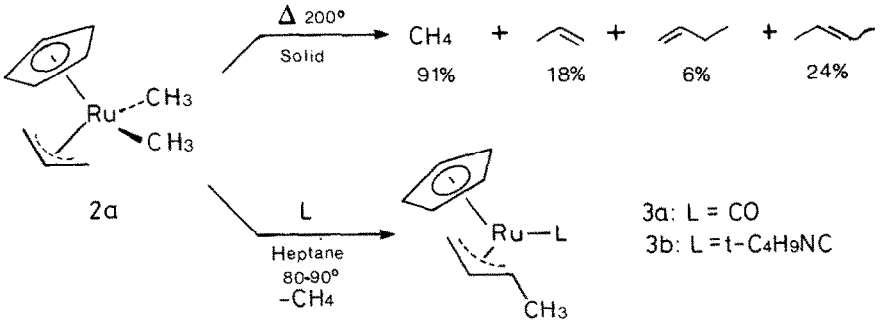
which decomposed below 0°C [5], although two methyl groups are located in a *cis* configuration in the former: **2a**; m.p. 119–120°C (dec); Anal. Found: C, 50.00; H, 7.00. $C_{10}H_{16}Ru$ calc: C, 50.62; H. 6.79%. ^1H NMR ($CDCl_3$), δ 0.21 (s, 6H, CH_3), 2.19 (d, 2H, J 9.0 Hz, *anti* proton of the allyl), 2.27 (d, 2H, J 5.6 Hz, *syn*), 2.75 (m, 1H, central allyl), 4.83 (s, 5H, C_5H_5) ppm: **2b**; m.p. 144–145°C (dec); Anal. Found: C, 58.64; H, 8.62. $C_{15}H_{26}Ru$ calc: C, 58.60; H, 8.52%. ^1H NMR ($CDCl_3$), δ −0.52 (s, 6H, CH_3Ru), 1.00 (d, 2H, J 9.0 Hz, *anti*), 1.59 (s, 15H, CH_3 attached to the ring), 2.22 (d, 2H, J' 5.8 Hz, *syn*), 2.70 (m, 1H, central allyl) ppm.

The alkylation of **1a** or **1b** with an excess of methyllithium also took place in 50 ~ 80% yields. Although the dichloro precursors could be similarly employed in the alkylation with trimethylaluminium, their methylation with methyllithium gave much lower yields together with uncharacterizable by-products.

When **2a** was heated at 200°C in the solid state under reduced pressure in a sealed tube, gaseous products (yields were estimated from amount of **2a** charged) composed of methane (91%), propene (18%), 1-butene (6%), and a mixture of 2-butenes (24%) were obtained. The above distribution is quite different from that of Ru(η^5-C_5H_5)(η^3-C_3H_5)(CH_3)(Cl), which selectively gave 1-butene (> 90%) [6]. It is important to note that methane was formed in nearly quantitative yield. This suggests that one of the methyl ligands in **2a** is lost as methane by abstraction of the hydrogen atom.

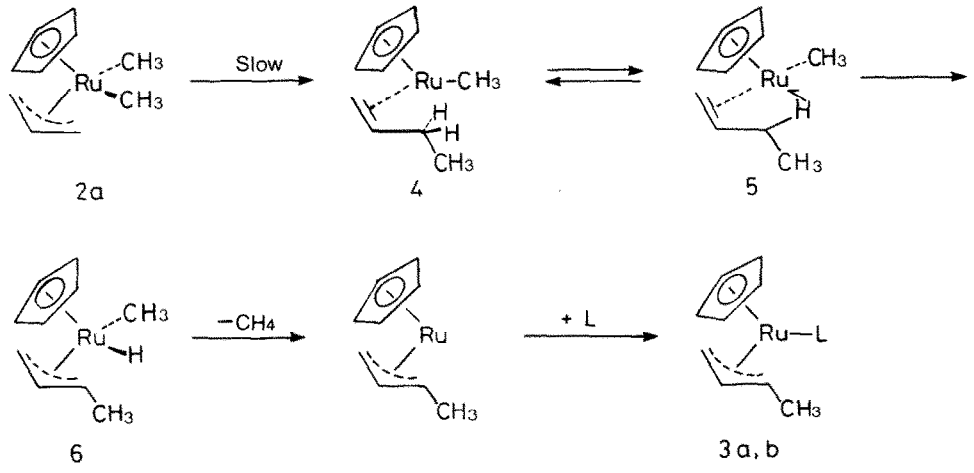
When the pyrolysis was performed in a heptane solution in the presence of carbon monoxide (1 atm) under moderate conditions at 90°C for 3 h, the ruthenium(II) 1-methylallyl carbonyl complex, Ru(η^5-C_5H_5)(η^3-CH_2CHCH-CH_3)(CO), **3a**, was obtained in 94% yield with evolution of methane: **3a**; Anal. Found: C, 48.36; H, 4.96. $C_{10}H_{12}ORu$ calc: C, 48.19; H, 4.85%. ^1H NMR ($CDCl_3$), δ 1.00 (d, 1H, J 10.4 Hz, *anti* at C(1)), 1.63 (d, 3H, J 6.1 Hz, CH_3), 1.8–2.3 (m, 1H, *anti* at C(3)), 2.67 (dd, 1H, J' 7.0 and 1.8 Hz, *syn*), 3.7–4.1 (m, 1H, H at C(2)), 4.96 (s, 5H, C_5H_5) ppm. IR (Nujol), ν(CO) 1930 cm^{-1}.

The deuterated analogue of **2a**, Ru(η^5-C_5H_5)(η^3-C_3H_5)(CD_3)$_2$, prepared from **1a** with CD_3Li in 60% yield, gave Ru(η^5-C_5H_5)(η^3-$CH_2CHCHCD_3$)(CO) in 83% yield upon pyrolysis at 90°C for 5 h under carbon monoxide (1 atm). The selective coupling of one of the CD_3 ligands in **2a** to the allyl moiety is evident, because the *anti* proton signal at δ 2.17 ppm became a doublet (J 9.5 Hz), in the deuterated product. Furthermore, this experiment suggests that the hydrogen atom present at the allyl terminal carbon atom in the starting material (**2a**) is lost in the Ru^{II} product (**3a**). Consequently, the selective formation of methane during thermolysis is explained in terms of the activation of the allylic C–H bond by one of the methyl



SCHEME 2.

ligands. Together with the previous finding [6], the reductive elimination of 1-butene from the monomethyl compound, $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_3)X$, the first step of the reaction of **2a** to **3a** is the formation of a C–C bond between one of the methyl groups and the allyl ligand to give a Ru^{II} alkyl-alkene intermediate, $Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-1-butene})(CH_3)$ (**4**), which is coordinatively unsaturated. This unsaturation of **4** may be filled by an agostic C–H---Ru interaction with the closest allylic C–H bond of the 1-butene ligand (**5**), and this interaction facilitates oxidative addition, yielding a hydrido-1-methylallylmethyl Ru^{IV} intermediate (**6**), which immediately eliminates methane. There have been precedents on the Ru^{II} agostic interaction [9], on the allylic C–H bond activation [10], as well as on the substantial stability of Ru^{IV} alkylallyl complexes [5,6]. Therefore the most likely mechanism for the conversion of **2a** to **3a** and methane is shown in Scheme 3. When **2a** was heated at 80°C in heptane for 20 h in the presence of t-C_4H_9NC, $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCHCH_3)$(t-$C_4H_9NC$) (**3b**) was isolated in 95% yield: **3b**, Anal. Found: C, 55.20; H, 7.09. $C_{14}H_{21}NRu$ calc: C, 55.25; H, 6.95%. ^1H NMR ($CDCl_3$), δ 0.63 (dd, 1H, J 9.5 and 1.4 Hz, *anti* proton at C(1)), 0.95 (d, 1H, J' 6.4 Hz), 1.33 (s, 9H,



SCHEME 3.

CH_3 of t-C_4H_9NC), 2.54 (dd, 1H, J'' 6.6 and 1.4 Hz, *syn*), 1.65 (m, 3H, CH_3 of the allyl), 3.5–4.0 (m, 1H, central allyl), 4.74 (s, 5H, C_5H_5) ppm.

Kinetic studies on the reduction of Ru^{IV} to Ru^{II} were made in the case of the reaction of **2a** in the presence of t-C_4H_9NC to generate **3b** by measuring the decrease of the methyl or cyclopentadienyl proton signals with ^1H NMR spectroscopy in C_6D_6. It was found that the rate followed first-order kinetics and did not depend on the concentration of the added isocyanide ligand for a relatively wide range of the ligand concentration; **2a**/t-$C_4H_9NC = 1.0 \sim 5.0$; at 80°C, $k_1 = 2.1 \times 10^{-4}$ s^{-1}. Based on the rate constants measured between 67 and 110°C, the following kinetic parameters are estimated; **2a**; E_a 23.9 kcal/mol; $\Delta S^{\star}$ −7.2 cal/mol K (300 K); **2b**; E_a 19.4 kcal/mol, $\Delta S^{\star}$ −25.2 cal/mol K (300 K). The independence of the ligand concentration for the thermolysis of **2a** or **2b**, as well as the kinetic parameters, and the fact that the initial rate of the decomposition of **2a** in the absence of the added ligand is approximately identical to the rate when the ligand is present, suggest that the rate determining step of the reductive process is the reductive elimination step, **2** → **4**, in which the 1-butene ligand is formed.

During the course of the above kinetic investigations, we found that the cyclopentadienyl proton signal rapidly induced the H-D exchange with the solvent (C_6D_6) when the thermolysis was performed in the absence of the added neutral ligand. At 80°C the signal at δ 4.38 ppm virtually disappeared within 2 h, and the allyldimethyl complex isolated (58% chemical yield) showed 94% deuteration only at the cyclopentadienyl protons after 30 h. At the same time, an insoluble violet complex was formed, its structure however could not be characterized.

$$Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_3)_2 + C_6D_6 \underset{80\,^\circ C}{\rightleftharpoons} Ru(\eta^5\text{-}C_5D_5)(\eta^3\text{-}C_3H_5)(CH_3)_2 + C_6H_6$$

At the present stage, the mechanism of this particular H-D exchange is not clear; however, it is possible that the coordinatively unsaturated $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCH\text{-}CH_3)$ formed by the reductive elimination of methane may induce catalytic activation of the C–D bond of the solvent in the abence of the added ligand, followed by the H-D exchange with **2a** present in the system. Detailed studies are proceeding.

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