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Preliminary communication

Facile synthesis of new polyolefinic ruthenium(0) complexes from ruthenium(II) precursors

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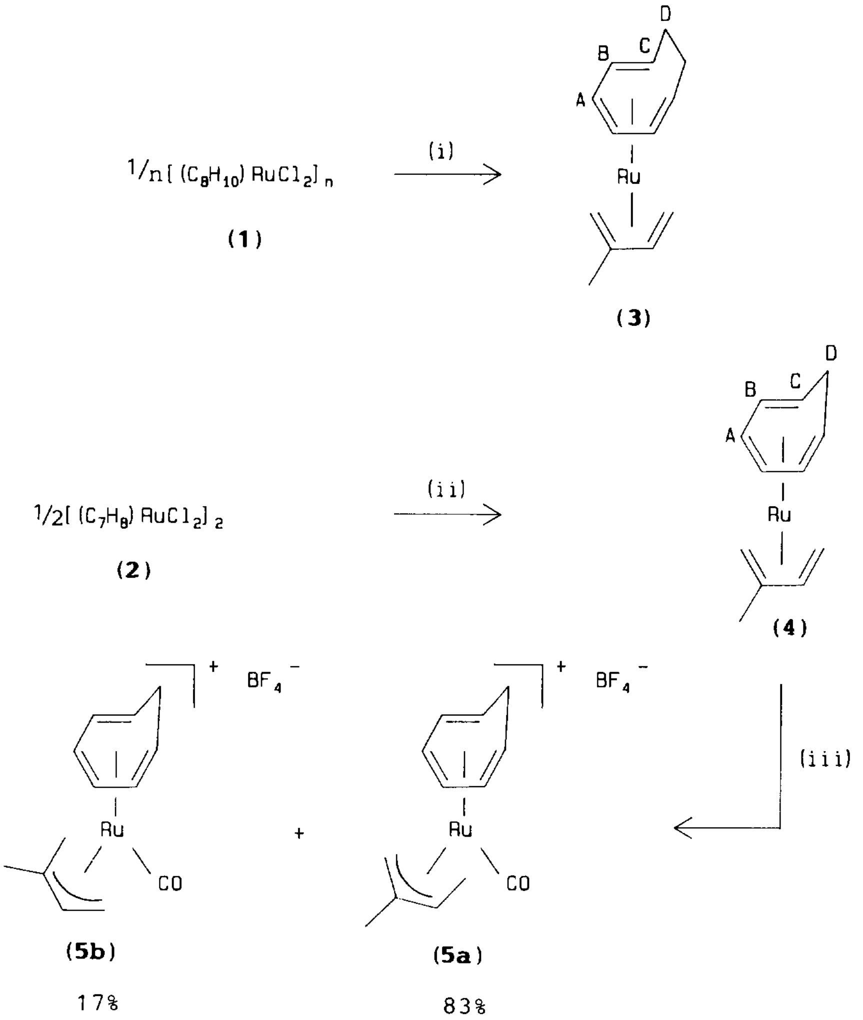
Abstract

The new ruthenium(II) complex $[(C_8H_{10})RuCl_2]_n$ (**1**) (C_8H_{10} = 1,3,5-cyclooctatriene; $n \geqslant 2$) has been obtained from the reaction of $RuCl_3 \cdot xH_2O$ with 1,3,5,7-cyclooctatetraene in refluxing ethanol. Reduction of $[(C_8H_{10})RuCl_2]_n$ and $[(C_7H_8)RuCl_2]_2$ (**2**) (C_7H_8 = 1,3,5-cycloheptatriene) by Na/Hg amalgam in the presence of isoprene (C_5H_8) gives the novel ruthenium(0) complexes $[(\eta^6\text{-}C_8H_{10})Ru(\eta^4\text{-}C_5H_8)]$ (**3**) and $[(\eta^6\text{-}C_7H_8)Ru(\eta^4\text{-}C_5H_8)]$ (**4**), respectively. $[(\eta^6\text{-}C_7H_8)Ru(\eta^4\text{-}C_5H_8)]$ reacts with CO and HBF_4 to give $[(\eta^6\text{-}C_7H_8)Ru(\eta^3\text{-}C_5H_9)(CO)][BF_4]$ (C_5H_9 = *trans*-1,2-dimethylallyl (**5a**); 1,1-dimethylallyl (**5b**)).

Interest in polyolefinic ruthenium(0) complexes arises from their potential catalytic applications [1–3] and their use as synthetic precursors [3–9]. The great majority of these complexes contain cyclic olefins, and are of the type $[(\eta^6\text{-olefin})Ru(\eta^4\text{-olefin})]$. Typically, the η^6-bonded olefin is 1,3,5-cyclooctatriene (C_8H_{10}), 1,3,5-cycloheptatriene (C_7H_8), or 1,3,5,7-cyclooctatetraene (C_8H_8), while the η^4-bonded olefin is usually 1,5-cyclooctadiene (C_8H_{12}) or norbornadiene (NBD). The main routes to these compounds are, (i) zinc reduction of $RuCl_3 \cdot xH_2O$ in the presence of suitable cyclic dienes [10]; (ii) Grignard reduction of the chloro-bridged complexes $[(\text{olefin})RuCl_2]_n$ (olefin = C_8H_{12}, C_7H_8, NBD) in the presence of cyclic dienes and trienes [11]; and (iii) the reduction of $[(\text{diene})RuCl_2]_n$ (diene = C_8H_{12}, NBD) by $K_2(C_8H_8)$ [12]. More recently, metal vapour synthesis has been employed to generate other ruthenium(0) species [13].

As noted previously [10,14], the development of convenient synthetic routes to new polyolefinic ruthenium(0) complexes has been retarded by the lack of suitable starting materials. In this paper the preparation of a new ruthenium(II) starting material as well as the synthesis of new ruthenium(0) complexes containing η^6-bonded cyclic trienes and η^4-bonded isoprene is reported. The coordinated isoprene is shown to react with H^+.

When C_8H_8 and $RuCl_3 \cdot xH_2O$ (3 : 1 molar excess) are refluxed in ethanol for 3 days, the orange insoluble material $[(C_8H_{10})RuCl_2]_n$ ($n \geqslant 2$) (**1**) is obtained, and not $[(C_8H_8)RuCl_2]_n$ as previously reported [15]. The reaction proceeds only in the presence of atmospheric oxygen, and the yield of **1** is typically 70–80 % [16 *]. Since



Scheme 1. Reaction conditions: (i) and (ii) Na/Hg amalgam, 2 equiv. isoprene, THF, 6 h, room temperature; (iii) CO, HBF_4, Et_2O, $-78\,^\circ C$.

the C_8H_8 is hydrogenated to form C_8H_{10}, it appears that the olefin is intimately involved in the reduction of the $RuCl_3 \cdot xH_2O$. Like those in $[(C_7H_8)RuCl_2]_2$ (**2**) [11b,17], the chloro-bridges in **1** are readily cleaved by neutral monodentate ligands (L) to yield soluble monomeric complexes of the type $[(\eta^6\text{-}C_8H_{10})Ru(Cl)_2(L)]$ [18*].

Stirring a suspension of **1** or **2** in a solution of THF and isoprene (C_5H_8; 2 molar equivalents) over Na/Hg amalgam for 6 hours at ambient temperature gives the complexes $[(\eta^6\text{-}C_8H_{10})Ru(\eta^4\text{-}C_5H_8)]$ (**3**) and $[(\eta^6\text{-}C_7H_8)Ru(\eta^4\text{-}C_5H_8)]$ (**4**), respectively (Scheme 1). Due to the light, and extreme air sensitivity of these complexes, the reactions must be carried out under dinitrogen by standard Schlenk techniques, and the isolated products shielded from light. After work up and extraction with

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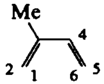
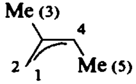
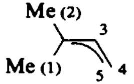
* Reference number with asterisk indicates a note in the list of references.

Table 1

^{1}H NMR data for the new complexes [a]

Complex [b]	Triene [c,d]	Other [d]
		
3	5.67 (pseudo t, 1H, J(H(A)–H(A′,B)) 7.09, H(A)), 5.38 (pseudo t, 1H, J(H(A′)–H(A,B′) 7.04, H(A′)), 5.30 (pseudo t, 1H, J(H(B)–H(A,C) 7.80, H(B)), 4.96 (pseudo t, 1H, J(H(B′)–H(A′,C′)) 7.66, H(B′)), 4.47 (m, 2H, H(C and C′)), 1.91 (m, 2H, H(D$_{endo}$ and D′$_{endo}$)), 0.78 (m, 2H, H(D$_{exo}$ and D′$_{exo}$))	4.35 (pseudo t, 1H, J(H(4)–H(6,5)) 6.92, H(4)), 1.71 (s, 3H, Me), 1.59 (br.s, 1H, H(2)), 1.39 (dd, 1H, J(H(5)–H(4)) 6.12, J(H(5)–H(6)) 1.62, H(5)), 0.08 (br.s, 1H, H(1)), −0.096 (dd, 1H, J(H(6)–H(4)) 7.74, J(H(6) – H(5)) 1.62, H(6))
4	5.83 (t, 1H, J(H(A)–H(A′,B)) 6.66, H(A)), 5.63 (t, 1H, J(H(A′)–H(A,B′) 6.68, H(A′)), 4.89 (pseudo t, 1H, J(H(B)–H(A,C)) 6.79, H(B)), 4.73 (pseudo t, 1H, J(H(B′)–H(A′,C′)) 6.75, H(B′)), 3.25 (td, 1H, J(H(C)–H(B,D$_{endo}$)) 8.12, J(H(C)–H(D$_{exo}$))3.38, H(C)), 3.16 (td, 1H, J(H(C′)–H(B′,D$_{endo}$)) 8.10, J(H(C′)–H(D$_{exo}$)) 3.40, H(C′)), 2.91 (dt, 1H, J(H(D$_{endo}$)–H(D$_{exo}$))13.78, J(H(D$_{endo}$)–H(C,C′)) 8.72, H(D$_{endo}$)), 1.95 (dt, 1H, J(H(D$_{exo}$)–H(D$_{endo}$)) 13.55, J(H(D$_{exo}$)–H(C,C′)) 3.35, H(D$_{exo}$))	4.34 (pseudo t, 1H, J(H(4)–H(5,6)) 6.84, H(4)), 1.75 (br.s, 1H, H(2)), 1.68 (s, 3H, Me), 1.53 (dd, 1H, J(H(5)–H(4)) 5.99, J(H(5)–H(6)) 1.90, H(5)), 0.03 (br.s, 1H, H(1)), −0.17 (dd, 1H, J(H(6)–H(4)) 7.69, J(H(6)–H(5)) 1.90, H(6))
		
5a [e]	6.49 (m, 1H, H(A)), 6.37 (m, 1H, H(A′)), 6.29 (m, 2H, H(B and B′)), 4.51 (td, 1H, J(H(C))–H(B,D$_{endo}$)) 8.10, J(H(C)–H(D$_{exo}$)) 4.29, H(C)), 4.43 (td, 1H, J(H(C′)–H(B′,D$_{endo}$)) 8.12, J(H(C′)–H(D$_{exo}$)) 4.24, H(C′)), 3.18 (dt, 1H, J(H(D$_{endo}$)–H(D$_{exo}$)) 13.89, J(H(D$_{endo}$)–H(C,C′)) 8.81, H(D$_{endo}$)), 2.04 (dt, 1H, J(H(D$_{exo}$)–H(D$_{endo}$)) 13.89, J(H(D$_{exo}$)–H(C,C′)) 4.14, H(D$_{exo}$))	4.34 (br.q, 1H, J(H(4)–Me(5)) 6.72, H(4)), 3.62 (pseudo t, 1H, J(H(2)–H(1.4)) 1.70, H(2)), 2.41 (dd, 1H, J(H(1)–H(2)) 2.04, J(H(1)–H(4)) 0.58, H(1)), 1.91 (s, 3H, Me(3)), 1.25 (d, 3H, J(Me(5)–H(4)) 6.72, Me(5))
		
5b [e,f]	6.70 (m, 2H, H(A and A′)), 6.17 (m, 1H, H(B)), 5.65 (m, 1H, H(B′)), 4.73 (td, 1H, J(H(C)–H(B,D$_{endo}$)) 8.06, J(H(C)–H(D$_{exo}$)) 4.03, H(C)), 4.08 (td, 1H, J(H(C′)–H(B,D$_{endo}$)) 8.06, J(H(C′)–H(D$_{exo}$)) 4.03, H(C′)), 3.18 (1H, H(D$_{endo}$)), 2.04 (1H, H(D$_{exo}$))	4.62 (dd, 1H, J(H(3)–H(5)) 13.8, J(H(3)–H(4)) 7.23, H(3)), 3.44 (dd, 1H, J(H(4)–H(3)) 7.20, J(H(4)–H(5)) 2.14, H(4)), 2.14 (dd, 1H, J(H(5)–H(3)) 14.1, J(H(5)–H(4)) 2.11, H(5)), 1.76 (s, 3H, Me(2)), 1.31 (s, 3H, Me(1))

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[a] All spectra recorded at 300.13 MHz and 303 K. Chemical shift (δ) in ppm relative to SiMe$_4$ (0 ppm). [b] Recorded in acetone-d_6. [c] Atom numbering given in Scheme 1. [d] Given as: chemical shift (δ), multiplicity, relative intensity, J/Hz, assignment. [e] Recorded in CDCl$_3$. [f] Resonances of H(D$_{endo}$) and H(D$_{exo}$) obscured by the corresponding resonances of **5a**.

n-hexane, complexes **3** and **4** are obtained as orange oils of high purity (^{1}H NMR) in approximately 65–70% yield. Attempts to purify them further by column chromatography at low temperature resulted in decomposition.

The reaction of **1** or **2** with Mg(C_5H_8) [19] in THF gives the same products **3** and **4** respectively, albeit in much lower yield and of lower purity. This result suggests that in the reaction with Na/Hg amalgam, the $C_5H_8{}^{2-}$ dianion is generated *in situ*, and acts as both a reducing agent and a ligand in the formation of the ruthenium(0) complexes.

The ^{1}H NMR data (Table 1) show that the asymmetry introduced into complexes **3** and **4** by the prochiral isoprene units is reflected in the C_8H_{10} and C_7H_8 ligands by the presence of two sets of resonances for the olefinic protons of these ligands in the respective complexes. Since the H(A)–H(A′) and H(B)–H(B′) $\Delta\delta$ values are larger than the H(C)–H(C′) values, it is suggested that the Me-group of the coordinated isoprene is orientated in the same direction as the H(A,A′) protons of the cyclic trienes. Although complexes **3** and **4** almost certainly exist as racemic mixtures, it is impossible to confirm this from the NMR data since the different enantiomers of the respective complexes would give rise to identical NMR spectra.

The reaction of **4** with HBF_4 in diethyl ether at −78 °C in the presence of CO (Scheme 1) gives the cationic ruthenium(II) complexes $[(\eta^6\text{-}C_7H_8)Ru(\eta^3\text{-}C_5H_9)(CO)][BF_4]$ (C_5H_9 = *trans*-1,2-dimethylallyl (**5a**); 1,1-dimethylallyl (**5b**)). Complexes **5a** and **5b** coprecipitate from the ether solution as a beige solid in ca. 70% yield [20*]. The ^{1}H NMR data indicate that electrophilic attack by the H^+ occurs predominantly (83%) at the C-4 carbon of the coordinated isoprene to yield **5a**, while attack at the C-1 carbon leads to the minor (17%) product **5b**. These complexes are the first examples of complexes in which an allylic group is coordinated to the η^6-cycloheptatriene-ruthenium(II) moiety. The infrared spectrum of the mixture, recorded as a Nujol mull, shows a single ν(CO) absorption band at 2027 cm^{-1}.

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16 The formulation of **1** is consistent with the chemical analysis. Anal. Found C, 33.90; H, 3.62. $C_8H_{10}RuCl_2$ calc. C, 34.55; H, 3.62%. M.p. > 230° C.

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20 Chemical analysis for **5**: found C, 39.75; H, 4.22. $C_{13}H_{17}RuOBF_4$ calc. C, 41.4; H, 4.54%. M.p. of the mixture 165–167° C (dec.).