

Preliminary communication

ARENE-OLEFIN COMPLEXES OF ZEROVALENT IRON AND RUTHENIUM

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Summary

Convenient syntheses of arene-olefin complexes of iron(0) and ruthenium(0), e.g. $M(\eta^6\text{-C}_6\text{Me}_6)(\eta^4\text{-diene})$ ($M = \text{Fe, Ru}$, diene = 1,3-cyclohexadiene or 1,5-cyclooctadiene), $\text{Fe}(\eta^6\text{-C}_6\text{Me}_6)(\eta^4\text{-C}_7\text{H}_8)$ ($\text{C}_7\text{H}_8 = 1,3,5\text{-cycloheptatriene}$) and $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{C}_2\text{H}_4)_2$ are given, and some protonation reactions are described.

Arene-olefin complexes of zerovalent iron and ruthenium are of interest as potential catalysts for olefin oligomerization and for comparison with the well-known tricarbonyl diene complexes of these elements, but few convenient synthetic routes are available. The 1,3-cyclohexadiene complexes $M(\text{C}_6\text{H}_6)(\text{C}_6\text{H}_8)$ ($M = \text{Fe, Ru, Os}$) [1—3] and the *tetra*hpto-hexamethylbenzene complex $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\eta^4\text{-C}_6\text{Me}_6)$ [4] have been known for some time and, more recently, the 1,5-cyclooctadiene complex $\text{Ru}(\text{C}_6\text{H}_6)(\text{C}_8\text{H}_{12})$ has been isolated in poor yield from the reaction of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$ with the diene in the presence of isopropyl-Grignard reagent [5]. Other complexes of the type $\text{Ru}(\text{arene})(\text{C}_8\text{H}_{12})$ are formed by displacement of 1,3,5-cyclooctatriene from $\text{Ru}(1,3,5\text{-C}_8\text{H}_{10})(\text{C}_8\text{H}_{12})$ [6], which is itself readily accessible from the reaction of “ $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ” with 1,5-cyclooctadiene and zinc dust in ethanol [7].

We have shown [8] that *tetra*hpto-cyclooctatetraene complexes $\text{Ru}(\text{arene})\text{-}(1\text{-}4\text{-}\eta\text{-C}_8\text{H}_8)$ are readily prepared by reaction of cyclooctatetraene dianion with the readily available $[\text{RuCl}_2(\text{arene})]_2$ complexes (arene = benzene, mesitylene or hexamethylbenzene) [9—11], and we now report that the latter react with 1,5-cyclooctadiene or 1,3-cyclohexadiene in the presence of ethanol and either base (Na_2CO_3) or zinc dust to give yellow, air-sensitive complexes $\text{Ru}(\text{arene})\text{-}(\text{diene})$ in yields of ca. 60%. The 1,3-cyclohexadiene complex $\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_6\text{H}_8)^*$ is also isolated from the same reaction using 1,4-cyclohexadiene. The reaction between $[\text{RuCl}_2(\text{C}_6\text{Me}_6)]_2$, cycloheptatriene and sodium carbonate does not give

*Except where stated otherwise, satisfactory elemental analyses and spectroscopic data have been obtained for all new compounds described herein.

the zerovalent complex $\text{Ru}(\text{C}_6\text{Me}_6)(1-4-\eta\text{-C}_7\text{H}_8)$ but its protonation product $[\text{Ru}(\text{C}_6\text{Me}_6)(1-5-\eta\text{-C}_7\text{H}_9)]^+$, isolated as its PF_6^- or BF_4^- salt. These reactions reveal the close analogy between $[\text{RuCl}_2(\text{arene})]_2$ and the isoelectronic pentamethylcyclopentadienylrhodium(III) complex $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)]_2$ [12-14]. Reaction between $[\text{RuCl}_2(\text{C}_6\text{Me}_6)]_2$, aqueous ethanolic Na_2CO_3 and ethylene gives the tan, air-sensitive ruthenium(0) bis(ethylene) complex $\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_2\text{H}_4)_2$ ($^1\text{H NMR}$, C_6D_6 , 32°C : δ (ppm) 1.70 (s, 18H, C_6Me_6), 1.48 (m, 4H, C_2H_4), 1.04 (m, 4H, C_2H_4)) in ca. 40% yield. Although the ethylene resonances are broadened considerably at 116°C in $\text{C}_6\text{F}_5\text{Br}$, complete coalescence is not observed, indicating a higher barrier to ethylene rotation than in the analogous isoelectronic rhodium(I) complexes $\text{Rh}(\text{C}_5\text{R}_5)(\text{C}_2\text{H}_4)_2$ ($\text{R} = \text{H}, \text{CH}_3$) [12, 15].

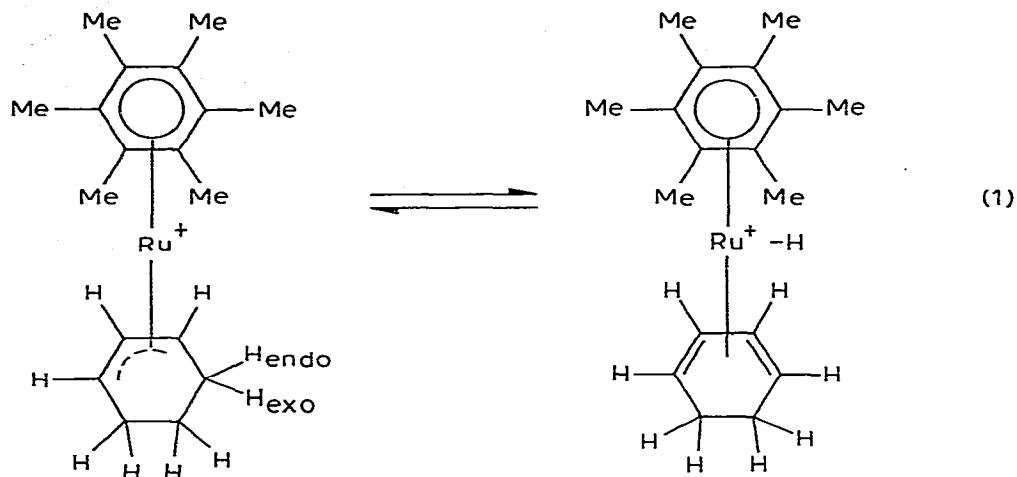
Some related iron(0) complexes have been obtained by reduction of salts of $[\text{Fe}(\text{arene})_2]^{2+}$ with cyclooctatetraene dianion $\text{C}_8\text{H}_8^{2-}$ or with sodium amalgam in tetrahydrofuran. Thus, addition of either of these reducing agents to $[\text{Fe}(\text{C}_6\text{Me}_6)_2](\text{PF}_6)_2$ gives a brown-black solution of bis(hexamethylbenzene)-iron(0), $\text{Fe}(\text{C}_6\text{Me}_6)_2$ [16]*, which on reaction with cycloheptatriene at 40°C for 16 h, gives the orange complex $\text{Fe}(\text{C}_6\text{Me}_6)(1-4-\eta\text{-C}_7\text{H}_8)$ in 51% yield. Under similar conditions both 1,3- and 1,4-cyclohexadiene give the 1,3-cyclohexadiene complex $\text{Fe}(\text{C}_6\text{Me}_6)(\text{C}_6\text{H}_8)$, and 1,5-cyclooctadiene gives a not fully characterised, thermally unstable orange-red complex which is probably $\text{Fe}(\text{C}_6\text{Me}_6)(1,5\text{-C}_8\text{H}_{12})$.

The new complexes show the expected reactivity towards electrophiles. Protonation (HBF_4 or HPF_6) at the free double bond of $\text{Fe}(\text{C}_6\text{Me}_6)(\text{C}_7\text{H}_8)$ gives the 1-5- η -cycloheptadienyl complex $[\text{Fe}(\text{C}_6\text{Me}_6)(1-5-\eta\text{-C}_7\text{H}_9)]^+$ and addition of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ gives the corresponding trityl-substituted cation $[\text{Fe}(\text{C}_6\text{Me}_6)(1-5-\eta\text{-C}_7\text{H}_8\text{CPh}_3)]^+$ without abstraction of hydride ion; similar reactions of cycloheptatrieneiron tricarbonyl are well known [18, 19]. Protonation (HPF_6) of the 1,3-cyclohexadiene complex $\text{Ru}(\text{C}_6\text{Me}_6)(\text{C}_6\text{H}_8)$ gives a salt which, in the solid state, appears to be the coordinately unsaturated, 16-electron 1-3- η -cyclohexenyl species $[\text{Ru}(\text{C}_6\text{Me}_6)(1-3-\eta\text{-C}_6\text{H}_9)]\text{PF}_6$. However, the $^1\text{H NMR}$ spectrum (CD_2Cl_2 , 32°C : δ (ppm) 2.30 (s, 18H, C_6Me_6), 2.97 (approx. q, 6H, *exo*- CH_2), -2.90 (approx. spt, 3H, *endo*- CH_2 + RuH)) indicates that *endo*-methylene hydrogen atoms migrate rapidly on the NMR time-scale between carbon and ruthenium (eq. 1).

At -80°C the signals at δ 2.97 and -2.90 ppm have almost disappeared but a limiting spectrum could not be reached. This behaviour is entirely analogous to that reported for the isoelectronic complex $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(1-3-\eta\text{-C}_6\text{H}_9)]^+$ generated by protonation of $\text{Rh}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_8)$ [20]. Addition of CO gives the coordinately saturated complex $[\text{Ru}(\text{C}_6\text{Me}_6)(1-3-\eta\text{-C}_6\text{H}_9)(\text{CO})]^+$ which exhibits the expected $^1\text{H NMR}$ spectrum for a static η^3 -allyl complex.

We are currently extending the scope of these preparative routes to other olefins and are investigating electrophilic and nucleophilic reactions of the resulting complexes.

*During the course of our work the preparation of $\text{Fe}(\text{C}_6\text{Me}_6)_2$ by sodium naphthalene reduction of $[\text{Fe}(\text{C}_6\text{Me}_6)_2](\text{PF}_6)_2$ and the reaction of $\text{Fe}(\text{C}_6\text{Me}_6)_2$ with 1,3-cyclohexadiene were reported independently [17].



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