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Communication

# Dimerisation and reactivity of $HC{\equiv}CC{\equiv}CFc$ at ruthenium centres

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ABSTRACT

In contrast to the simple diynyl complexes formed in reactions between $HC{\equiv}CC{\equiv}CFc$ and $MCl(dppe)Cp^*$; (M = Fe, Ru), an analogous reaction with $RuCl(PPh_3)_2Cp^*$; in the presence of $KPF_6$ and dbu resulted in dimerisation of the diyne at the Ru centre to afford a mixture of $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(L)CH{=}CC{=}CHFc\}(PPh_3)Cp^*]PF_6$ (L = dbu **1**, $PPh_3$ **2**). Similar reactions with $RuCl(PR_3)_2L$ gave $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(dbu)CH{=}CC{=}CHFc\}(PR_3)L]PF_6$ (L = Cp, R = Ph **3**, *m*-tol **4**; L = $\eta^5\text{-}C_9H_7$, R = Ph **5**). The reaction between **3** and $I_2$, followed by crystallization of the paramagnetic product from MeOH, afforded the dicationic $[Ru\{C(C{\equiv}CFc)C(dbu)CH{=}C(OMe)C(OMe){=}CHFc\}(PPh_3)Cp](I_3)_2$ **6**. The molecular structures of $\mathbf{2}\cdot 2CH_2Cl_2$ and **6**.S (S = $2CH_2Cl_2$, $C_6H_6$) were determined by single-crystal XRD studies.

## 1. Introduction

As a continuation of our studies of Group 8 complexes containing di- and poly-ynyl ligands [2], we earlier described the synthesis and some reactions of the complexes $Ru(C{\equiv}CC{\equiv}CFc)(dppx)Cp$ (x = m, e) [1]. The syntheses followed precedent by reacting $FcC{\equiv}CC{\equiv}CSiMe_3$ with $RuCl(dppx)Cp$ in the presence of $KPF_6$ in thf/dbu (dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene) to give these complexes in 28 and 57% yields, respectively. During these studies, there was no evidence for the formation of any other product. However, when a ruthenium precursor containing a more labile monodentate phosphine ligand, namely $RuCl(PPh_3)_2Cp^*$, reacted with $FcC{\equiv}CC{\equiv}CH$, the reaction took a different course, resulting in the formal dimerisation of the diyne and subsequent reaction with nucleophiles present in the reaction mixture. Similar products were obtained with $P(m\text{-}tol)_3$ or $\eta^5$-indenyl and Cp ligands. These studies are described below.

## 2. Results

The reaction between $FcC{\equiv}CC{\equiv}CH$ and $RuCl(PPh_3)_2Cp^*$ was carried out in refluxing thf in the presence of $KPF_6$ (to encourage dissociation of the chloride) and dbu (as base) to afford a mixture of two complexes, which could be separated by preparative t.l.c. to give $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(X)CH{=}CC{=}CHFc\}(PPh_3)Cp^*]PF_6$ [X = dbu **1** (78%), $PPh_3$ **2** (14%)] (Scheme 1) as red and purple solids, respectively. Spectroscopic properties of **1** and **2** included weak $\nu(C{\equiv}C)$ and $\nu(C{=}C{=}C)$ bands at 2155 and 1778 (for **1**) and 2129 and 1881, 1782 $cm^{-1}$ (for **2**). For **1**, resonances for the $Ru(PPh_3)Cp^*$ moiety were found at $\delta_H$ 1.33, $\delta_C$ 9.21, 98.41 (Ru–Cp*) and $\delta_P$ 51.5, with singlets for the Fe–Cp group at $\delta_H$ 1.39, ca 4.3, $\delta_C$ 70.61, 70.75. Several signals between $\delta_H$ 1.42 and 3.70 and $\delta_C$ 20.85 and 72.04 were assigned to the dbu fragment. For **2**, signals at $\delta_H$ 1.36 and 4.07, 4.60 (2 × Fe–Cp), $\delta_C$ 6.76, 101.42 (Ru–Cp*) and two singlets at $\delta_P$ 0.95, 25.8 (2 × $PPh_3$) were present; the spectra were simplified by the absence of the dbu resonances in this case. In the electrospray mass spectrum (ES-MS), molecular cations were found at *m*/*z* 1119 (**1**) and 1229 (**2**). The molecular structure of **2** was determined from a single-crystal XRD study (see below).

The reaction between $RuCl(PPh_3)_2Cp$ and an excess of $FcC{\equiv}CC{\equiv}CH$ was carried out in a similar manner to that described above. Conventional work-up and final purification by preparative t.l.c. and recrystallisation from acetone–dichloromethane gave maroon $[Ru\{\eta^1,\eta^2\text{-}C(C{\equiv}CFc){=}C(dbu)CH{=}CC{=}CHFc\}(PPh_3)Cp]PF_6$ **3** (Scheme 1). The $^1H$ NMR spectrum contained resonances at $\delta$ 1.43 and 3.96 (2 × Cp–Fe), together with several signals between $\delta$ 1.49–2.79 (from dbu), 3.30–4.67 ($C_5H_4$ + Ru–Cp), 6.06–6.49 (3H on $C_8$ chain), and 7.00–7.80 (Ph). It was not possible to find the resonances of the vinylic protons, which were probably masked by the aromatic proton signals. Among the plethora of signals in the $^{13}C$ NMR spectrum, those at $\delta$ 70.00, 70.07 (2 × Cp–Fe) and 91.49 (Cp–Ru) were readily assigned. The $^{31}P$ NMR spectrum contained

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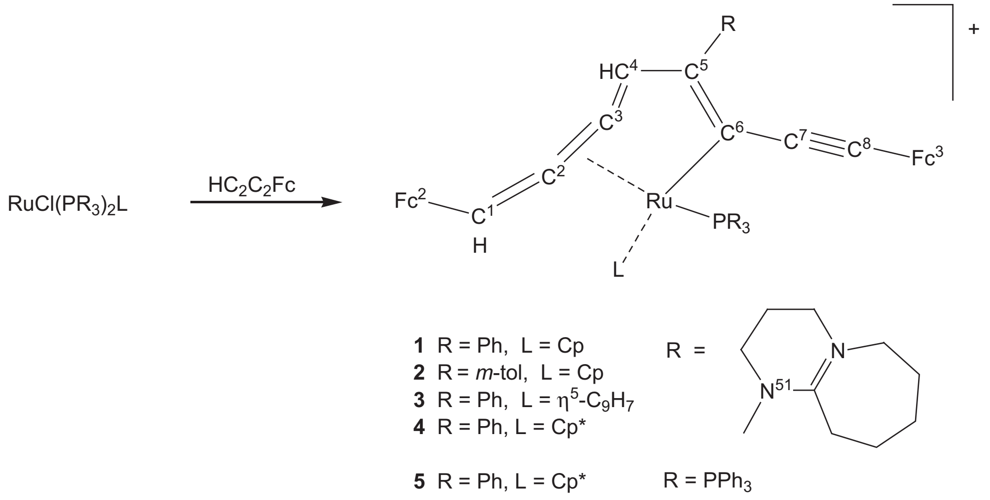
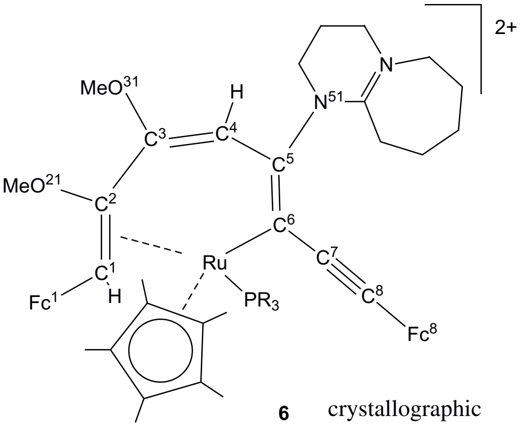


**Scheme 1.**

a singlet at $\delta$ 26.2 ($PPh_3$) and a septet at $\delta$ −142.2 ($PF_6$). The molecular cation was found at $m/z$ 1049 in the ES-MS. Similar complexes **4** (62%) and **5** (50%) were obtained from analogous reactions of FcC≡CC≡CH with RuCl{P($m$-tol)$_3$}$_2$Cp and RuCl($PPh_3$)$_2$($\eta^5$-$C_9H_7$), respectively, and were characterised by microanalysis and the usual spectroscopic methods, including ES-MS (molecular cations at $m/z$ 1091, 1099, respectively). The resonances of these complexes were quite broad, possibly due to ring flips of the dbu substituent.

Prior to crystallographic characterisation, some reactions of **3** were carried out to obtain further evidence for the structure. Among these, a reaction between **3** and diiodine in thf afforded a brown paramagnetic solid for which an acceptable microanalysis for an $I_7$ salt was obtained, but no useful structural information was forthcoming from spectroscopic data. However, recrystallisation of this complex from MeOH afforded the dicationic salt [Ru{$\eta^1,\eta^2$-C(C≡CFc)C(dbu)CH=C(OMe)C(OMe)=CHFc}($PPh_3$)Cp*]($I_3$)$_2$ **6**, as revealed by single-crystal XRD structure determinations of its $CH_2Cl_2$ and $C_6H_6$ solvates. Microanalysis and the ES-MS supported this formulation, with ions at $m/z$ 1111 ($M^+$), 849 ([M − $PPh_3$]$^+$) and 697 ([M − $PPh_3$ − dbu]$^+$).



**6** crystallographic numbering

### 2.1. Molecular structures

Fig. 1 is a plot of the cation of **2**; selected structural parameters are listed in Table 1.The usual Ru($PPh_3$)Cp* moieties [Ru–P, 2.3155 (5) Å] and Ru–C(cp) [av. 2.28(5) Å] are $\eta^1$, $\eta^2$-coordinated to the $C_8$ ligand by C(6) and C(2,3) [2.112(2), 2.136, 2.056(2) Å]. Angles P(1)–Ru–C($n$) [$n$ = 6, mid-point of C(2)–C(3)] are 90.32(5), 98.6°, and C(6)-Ru-C(2/3) are 92.3°. Along the carbon chain, the C–C separations are consistent with the structure as shown, with the C(7)–C(8) triple bond [1.215(3) Å] and the C(2)–C(3) separation [1.342(3) Å] being as expected for a coordinated C=C double bond. The Fe–C(cp) bonds for Fe(2) [av. 2.051(9) Å] and for Fe(3) [av. 2.046(7) Å] are similar.

The structure of the dication in **6** (Fig. 2, selected bond parameters in Table 1) is closely related to that of the monocation in **2**, with the exceptions of replacement of $PPh_3$ by dbu, introduction of the OMe groups on C(2) and C(3), and the coordination of C(1)–C(2)

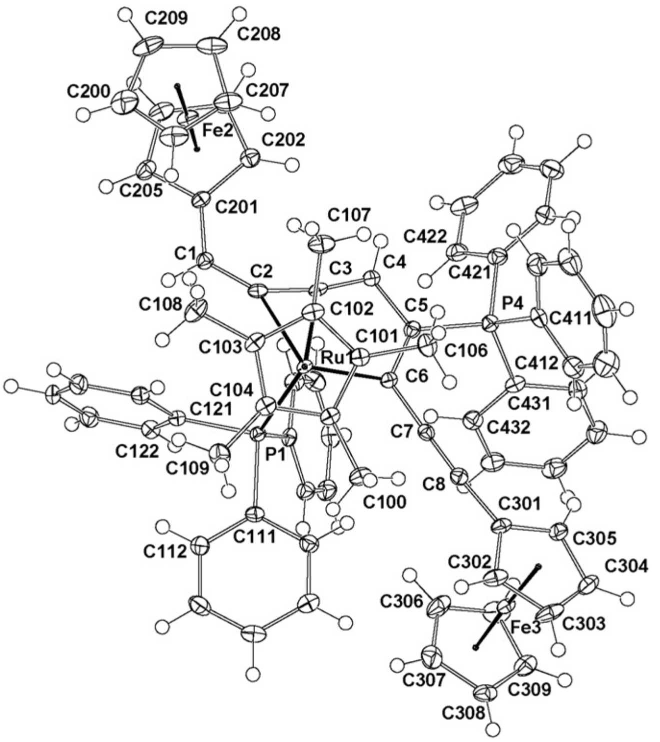


**Fig. 1.** Plot of the cation in [Ru{$\eta^1,\eta^2$-C(C≡CFc)=C(dbu)CH=CC=CHFc}($PPh_3$)Cp*] $PF_6$ **2**.