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Preliminary communication

**CYCLOTRIMERIZATION OF ACETYLENIC COMPOUNDS WITH  
 (BENZENE)(1,3-CYCLOHEXADIENE)RUTHENIUM(0): PREPARATION  
 OF BIS-ARENE DERIVATIVES OF RUTHENIUM HAVING DIFFERENT  
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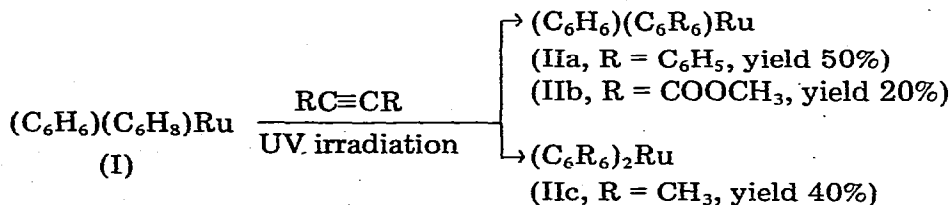
Summary

The reaction between (benzene)(1,3-cyclohexadiene)ruthenium(0) and acetylenes  $RC\equiv CR$  under UV irradiation yields complexes of the formula  $(C_6R_6)_2Ru$  or  $(C_6H_6)(C_6R_6)Ru$ , depending on the acetylene used.

It is well known that acetylenes can be cyclooligomerized in the presence of transition metal compounds. In many cases the cyclooligomerization products are formed as  $\eta$ -complexes with the transition metal: several arene and cyclobutadiene complexes have been produced in this way [1].

We now report the formation of some bis-areneruthenium(0) complexes via the cyclotrimerization of acetylenic compounds by (benzene)(1,3-cyclohexadiene)ruthenium(0). Depending on the acetylenic compound used, the reaction can yield, bis-arene derivatives having two different arene molecules coordinated to the same ruthenium atom.

Treatment of  $(C_6H_6)(C_6H_8)Ru$  (I) with an excess of an acetylenic compound (molar ratio 1/10) in n-hexane at 40°C for 1–2 days, under UV irradiation gave the bis-arene complexes II. No catalytic trimerization of the acetylenic compound was observed. UV irradiation appeared necessary for the reactions.



Complexes II are orange-red diamagnetic compounds, which were characterized by elemental analysis, IR,  $^1\text{H}$  NMR and mass spectra. IIa and IIb are the first examples of bis-areneruthenium(0) complexes having two different arenes coordinated to the same Ru atom; IIc is the well-known bis(hexamethylbenzene)ruthenium(0) [2].

The  $^1\text{H}$  NMR spectra of IIa and IIb at  $35^\circ\text{C}$  show a single peak due to the benzene protons (Table 1) which indicates that in these complexes the

TABLE 1  
NMR DATA FOR RU(BENZENE)(ARENE) COMPLEXES<sup>a</sup>

| Compound  | Benzene resonances | Arene resonances          |
|---|--------------------|---------------------------|
| $\text{Ru}(\text{C}_6\text{H}_6)[\text{C}_6(\text{C}_6\text{H}_5)_6]^b$ | 4.90(s)            | from 2.50 to 3.40         |
| $\text{Ru}(\text{C}_6\text{H}_6)[\text{C}_6(\text{COOCH}_3)_6]^c$       | 4.37(s)            | 6.20(s), 6.37(s), 6.42(s) |

<sup>a</sup>Proton chemical shifts ( $\tau$ , ppm) measured at MHz relative to internal TMS. <sup>b</sup>In  $\text{CDCl}_3$  at ca.  $35^\circ\text{C}$ . <sup>c</sup>In  $\text{CD}_3\text{COCD}_3$  at ca.  $35^\circ\text{C}$ .

benzene ring is  $\eta^6$ -bonded to the ruthenium atom. From the spectra it appears that the substituted benzene is  $\eta^4$ -bonded in both complexes. In the case of IIa this has been confirmed by determination of the molecular structure by single crystal X-ray examination [3].

The reaction of I with phenylacetylene and 2-butyne-1,4-diol under UV irradiation was also examined. From phenylacetylene a product of the formula  $\text{Ru}[\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)_3]_2$  was obtained, which was difficult to purify, presumably because several isomers were present. From butyne-1,4-diol an insoluble product was obtained, which could not be purified and which was tentatively assigned the formula  $\text{Ru}(\text{C}_6\text{H}_6)[\text{C}_6(\text{CH}_2\text{OH})_6]$  on the basis of elemental analysis. The reaction of I with acetylene was also examined, no pure product was isolated.

No reaction was observed between I and several substituted benzenes under UV irradiation at temperatures up to ca.  $100^\circ\text{C}$ .

The reaction of I with an acetylene  $\text{RC}\equiv\text{CR}$ , under UV irradiation first yields the complex  $(\text{C}_6\text{H}_6)(\text{C}_6\text{R}_6)\text{Ru}$ , which, depending on the acetylenic compound used, can further react to give  $(\text{C}_6\text{R}_6)_2\text{Ru}$ . Since I can be easily obtained [4], the reaction offers a convenient route to new bis-arene derivatives of ruthenium(0).

### Acknowledgement

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### References

- 1 L.P. Yur'eva, Russ. Chem. Rev. 43 (1974) 48 and references therein.
- 2 E.O. Fischer and C. Elschenbroich, Chem. Ber., 103 (1970) 162.
- 3 A. Immirzi (Istituto di Chimica delle Macromolecole, Via A. Corti 12, Milano, Italy) unpublished results.
- 4 P. Pertici, G. Vitulli and L. Porri, Chem. Commun., (1975) 846.