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Arenecarbonylcarbide ruthenium clusters (π-arene)$Ru_6C(CO)_{14}$ with functional substituents in arene ring

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Abstract

A number of arenecarbonylcarbide clusters of ruthenium of the type (arene)$Ru_6C(CO)_{14}$ have been obtained, including those with functional substituents in arene ring.

Introduction

Properties of π-arene ruthenium clusters of the type (η^6-arene)$Ru_6C(CO)_{14}$ (I) practically have not been studied. All the known compounds of this type were obtained only on the examples of benzene and some of its alkyl derivatives upon heating of $Ru_3(CO)_{12}$ in excess of the corresponding arene [1]. In order to study the properties of these compounds it was necessary to have a series of such complexes containing not only benzene and its homologues but also arenes with functional substituents.

Results and discussion

In the case of arenes with functional groups and also in the case of solid arenes it was inexpedient to use arenes as solvents. Therefore we developed a method useful for various arenes including those with functional substituents (arene = PhOMe, PhCOOEt etc., see Table 1). The reaction of arenes with $Ru_3(CO)_{12}$ was carried out in refluxing octane. (All attempts to use other solvents in this reaction were unsuccessful. In dioxane and heptane the reaction does not proceed at all, in diglyme and nonane only traces of the product are formed; mainly a decomposition takes place.)

In this reaction, as for the method described earlier [1], together with arene clusters I, the unsubstituted cluster $Ru_6C(CO)_{17}$ (II) without arene ligand was also obtained.

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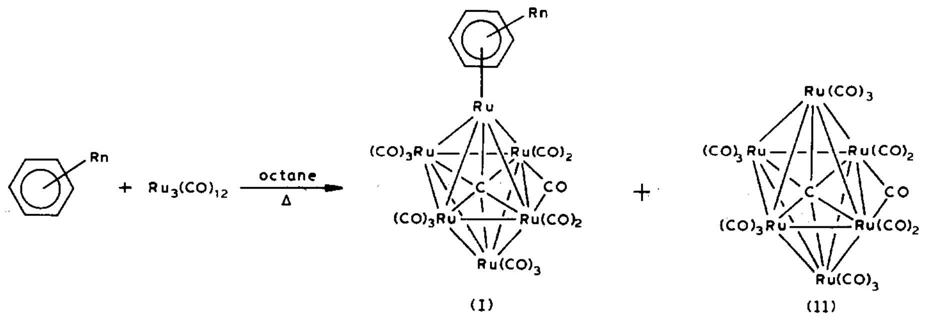

The mixture obtained was separated by chromatography on a SiO_2 column. In the case of mesitylene it was shown that the yield after refluxing in octane is not worse than on heating in pure arene. Electronic properties of substituents do not influence the yield. Thus, equal yields were obtained for the clusters with anisol and ethylbenzoate (5%). It should be noted that all attempts to obtain complexes with halogen containing arenes (PhCl, PhF, $PhCF_3$) under the same conditions lead to products without halogen. Their structures are studied now.

The structure of the prepared compounds was confirmed by IR spectra (see Table 1) and by comparison with the literature data [1]. Most of them have five bands in the metal-carbonyl region, one of which belongs to the bridging CO, the substituents in the arene having no influence on the band position. In ^1H NMR spectra in all cases the protons of the coordinated arene are situated in the region 5–6 ppm, the influence of the substituent being significant (with donor X = OCH_3 5.15–5.46 ppm, with acceptor X = COOEt 5.43–6.88 ppm).

Earlier we tried to use the unsubstituted cluster II to obtain $Me_3C_6H_3Ru_6C(CO)_{14}$ (Ic) [2]. In this way it is possible to obtain the desirable product, but with very low yield. We used some other arenes in this reaction, but in these cases, too, the arene complexes I were obtained in low yields (3–4%). These facts are in agreement with [3], showing that the cluster II does not participate actively in the formation of complexes I.

Table 1

The yields and IR and ^1H NMR data of complexes (arene)$Ru_6C(CO)_{14}$ (I)

Arene	Yield(%)	ν(C≡O)	ν(X)	δ (ppm)
PhOMe (Ia)	5	2072m, 2050m, 2018s, 1964m, 1814w	1050, 1260 (C–O–C)	5.46d(o); 5.29(wide s)(m); 5.14(wide s)(p); 3.63c(Me)
C_6Me_6 (Ib)	13	2082m, 2062s, 2014s, 1978m, 1818w	–	2.23s
$Me_3C_6H_3$ (Ic)	5–7	2072m, 2060m, 2016s, 1962m, 1808w	–	2.28s(Me); 5.37s
C_6H_6 (Id)	6–9	2072s, 2064m,sh, 2024s,1978m, 1810w	–	5.56s
PhCOOEt (Ie)	5	2074s, 2028s, 1982m, 1814m	1728	6.28d(o); 5.77t(m); 5.43t(p); $J = 6$ Hz; 4.35q(CH_2); 1.39t(CH_3); $J = 7$ Hz

The fragmentation of some of the compounds obtained under electron impact was studied. It was found that the most classic picture is shown by the unsubstituted cluster II (only centers of groups of peaks are given, connected with the polyisotopy of ruthenium) ($[M]^+ = 1097$; $[M - CO]^+ = 1065$; $[M - 2CO]^+ = 1037$ etc.) and the mesitylene complex Ic ($[M]^+ = 1130$; $[M - CO]^+ = 1102$; $[M - 2CO]^+ = 1074$ etc.). At the same time the benzene derivative Id gives immediately after the molecular ion (1088) $[M - 3CO]^+ = 1004$ (etc.). The mass spectra of these compounds were measured at a voltage of 1.5 V, for the C_6Me_6-complex Ib it was necessary to use 10 V. Under these conditions only the following ions were found: $[M - 3Me\text{-}CO]^+ = 1095$; $[M - 3Me\text{-}2CO]^+ = 1067$ etc.

Experimental

All operations for the synthesis and isolation of the investigated compounds were carried out under argon using absolute solvents. IR spectra were recorded on a Specord 75IR (in CH_2Cl_2) and UR-20 (in KBr pellets) spectrophotometers. NMR spectra were measured on a Bruker WP-200SY spectrometer in $CDCl_3$. A VG TRIO-2 quadrupole mass spectrometer equipped with a PDP 11-250 data system was used for the mass spectrometric measurements. The samples were introduced into the mass spectrometer using the direct probe technique.

Preparation of complexes (arene)$Ru_6C(CO)_{14}$ (I)

A mixture of $Ru_3(CO)_{12}$ (0.5 g; 0.78 mmol) and the appropriate arene (1–3 ml or 1 g for C_6Me_6) in 60 ml of octane was refluxed for 14 h. After cooling the reaction mixture was chromatographed on a SiO_2 column. From the first, orange-red band, 0.06–0.23 g (15–45%) of cluster II was obtained. From the second, dark purple-brown band, the arene complex I was isolated (yields and spectral data are given in the table).

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