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NOTE

SYNTHESIS OF π-ALLYLRUTHENIUM TRICARBONYL HALIDES

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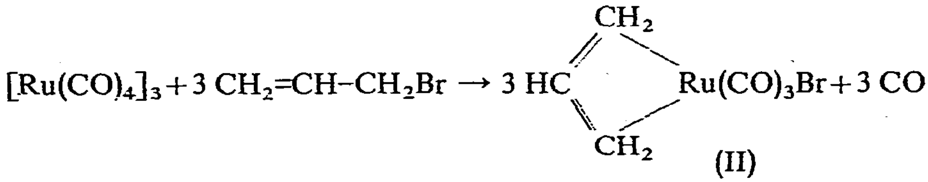
The only π-allyl derivative of ruthenium carbonyl described to date is (1-methyl-π-allyl)ruthenium tricarbonyl chloride, which was prepared by Ihrman and Coffield[1] by treating 1,3-butadieneruthenium tricarbonyl with hydrochloric acid in carbon tetrachloride or hexane. As part of our investigations on the reactivity of $[Ru(CO)_4]_3$ we have prepared some allylruthenium tricarbonyl halides and investigated their NMR and IR spectra.

From $[Ru(CO)_4]_3$ and C_3H_5Br (metal carbonyl/allyl bromide ratio 1/10), the complex π-$C_3H_5Ru(CO)_3Br$ was obtained in high yield (97%) as a yellow crystalline compound when the solution was cooled.

The amount of carbon monoxide evolved and the amount of the π-allylruthenium tricarbonyl bromide recovered suggest for this reaction the stoichiometry reported in eqn. (1).



$$[Ru(CO)_4]_3 + 3\,CH_2{=}CH{-}CH_2Br \rightarrow 3\,HC\begin{matrix}CH_2\\ \\ CH_2\end{matrix}Ru(CO)_3Br + 3\,CO \qquad (1)$$

(II)

Analogous derivatives were obtained from allyl chloride, iodide and 2-methylallyl chloride.

The yields obtained in the preparation of these compounds, their colour, melting point, the strongest CO stretching frequencies in the 2200–1800 cm^{-1} region, as well as the bands which may be assigned to the asymmetric C=C stretching in the 1450–1520 cm^{-1} region[2] of their IR spectra, are reported in Table 1.

The NMR spectra of these π-allylruthenium tricarbonyl halides (Table 2) are well resolved, and show a multiplet and two doublets having an area ratio of 1/2/2. Such a spectrum, characteristic of an AM_2X_2 system, suggests a π-allyl structure for all these compounds, iodide included, unlike the corresponding allyliron tricarbonyl iodide for which unusual features of the NMR spectra[3–5] and a molecular weight higher than the calculated one have been found[3]. The differences between the corresponding iodine derivatives of iron and ruthenium could be at least in part ascribed to the larger atomic radius of the ruthenium atom which could allow a less strained arrangement of the ligands around the central atom.

TABLE 1

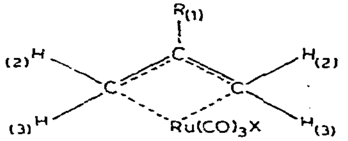
PHYSICAL PROPERTIES OF π-ALLYLRUTHENIUM TRICARBONYL HALIDES

Compound		Colour	M.p. (°C)	Yield (%)	ν(CO) (cm^{-1}) (in C_2Cl_4)	ν(C=C) (cm^{-1}) (in KBr)
$Ru(CO)_3C_3H_5Cl$	(I)	Pale-yellow	75–77	64.5	2111 vs 2060 vs 2014 vs	1462 m
$Ru(CO)_3C_3H_5Br$	(II)	Yellow	89–91	97.3	2107 vs 2057 vs 2015 vs	1467 m
$Ru(CO)_3C_3H_5I$	(III)	Orange	73–74	40.0	2102 vs 2053 vs 2016 vs	1462 m
$Ru(CO)_3C_4H_7Cl$[a]	(IV)	Pale-yellow	94–96	90.0	2110 vs 2059 vs 2011 vs	1481 m

[a] C_4H_7 = 2-methylallyl.

TABLE 2

NMR PARAMETERS OF π-ALLYLRUTHENIUM TRICARBONYL HALIDES



(R = H or CH_3)

R	X	Chemical shifts (ppm)[a]			Coupling constants (Hz)		
		$R_{(1)}$	$H_{(2)}$	$H_{(3)}$	J_{1-2}	J_{1-3}	J_{2-3}
H	Cl	5.22	4.15	2.96	8.0	12.5	0
H	Br	5.08	4.03	3.14	7.5	12.5	0
H	I	4.83	3.83	3.38	7.0	13.0	0
CH_3	Cl	2.06	3.93	2.86			

[a] From TMS at 60 Mc.

The 2/2/3 area ratio of the three singlets present in the NMR spectrum of (2-methyl-π-allyl)ruthenium tricarbonyl chloride is in agreement with what expected for a normal π-allyl structure[4].

An X-ray investigation on the structure of these compounds is in progress.

EXPERIMENTAL

Preparation of π-allylruthenium tricarbonyl bromide (II)

Triruthenium dodecacarbonyl (2.02 g) suspended in isooctane (30 ml) was treated with allyl bromide (14.3 g) and heated, with stirring, at 60–70° under nitrogen. After a few hours a yellow solution was obtained from which a new yellow solid precipitated which was filtered and dried (0.882 g). By concentration of the mother liquor and cooling to −60° more product (1.92 g) was recovered. By double crystallization

TABLE 3

ANALYTICAL DATA FOR π-ALLYLRUTHENIUM TRICARBONYL HALIDES

Compound	Found (calcd.)				
	C(%)	H(%)	Hal(%)	Ru(%)	Mol.wt.[a]
$Ru(CO)_3C_3H_5Cl$	27.87 (27.55)	1.93 (1.928)	13.9 (13.56)	38.30 (38.65)	256.1 (261.6)
$Ru(CO)_3C_3H_5Br$	23.35 (23.53)	1.69 (1.645)	26.9 (26.11)	32.42 (33.02)	323.0 (306.08)
$Ru(CO)_3C_3H_5I$	19.95 (20.41)	1.39 (1.427)	36.1 (35.94)	27.52 (28.63)	381 (353.09)
$Ru(CO)_3C_4H_7Cl$	30.1 (30.5)	2.65 (2.56)	12.9 (12.86)	36.91 (36.67)	288.2 (275.64)

[a] Determined by cryoscopy in benzene.

of the crude, from isooctane at −50°, 2.1 g of (II) was obtained as crystalline yellow product, m.p. 89–91°. The analytical data are reported in Table 3.

The same procedure was used to prepare the analogous derivatives (I), (III) and (IV).

ACKNOWLEDGEMENTS

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