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Short Communication

Haloalkyl complexes of the transition metals
IX. The synthesis and properties of $[CpRu(CO)_2\{(CH_2)_nX\}]$ ($n=3$, X=Cl, Br, I; $n=4$, 5, X=Br, I)

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Abstract

The complexes $[CpRu(CO)_2\{(CH_2)_nX\}]$ ($n=3$, X=Cl, Br, I; $n=4$, 5, X=Br, I; Cp=η^5-C_5H_5) have been prepared and fully characterised by elemental analyses, IR, ^1H NMR, ^{13}C NMR and mass spectroscopy. Some properties of these new compounds are discussed.

Introduction

Whilst halomethyl complexes of the type $[L_yMCH_2X]$ (L_yM= a transition metal and its associated ligands, X= a halogen) are now well known [1], transition metal complexes with longer haloalkyl chains $[L_yM\{(CH_2)_nX\}]$ ($n>1$) are less common, although some, notably those of Pt [2, 3], Mo, W [4, 5] and Fe [6, 7] have been studied. These ω-haloalkyl complexes have been shown to be precursors for homo- and heterodinuclear complexes [3, 7–9], cyclic carbene complexes [4, 5, 7, 10] and some, where $n=3$, have been shown to have good organic synthetic utility as cyclopropane precursors [11, 12]. We now report on the synthesis and properties of the ruthenium complexes $[CpRu(CO)_2\{(CH_2)_nX\}]$ ($n=3$, X=Cl, Br, I; $n=4$, 5, X=Br, I).

Experimental

General experimental details were as reported previously [6]. $[CpRu(CO)_2]_2$ was prepared by a literature method [13].

Preparation of $[CpRu(CO)_2\{(CH_2)_3Cl\}]$

$Na[CpRu(CO)_2]$ (2 mmol) in THF (13 ml) was added over 6 min to a stirred solution of $Cl(CH_2)_3Cl$ (2.5 mmol) at −78 °C. The solution was allowed to attain room temperature and stirred for 2.25 h. The solvent was removed under reduced pressure; the brown residue was extracted with hexane, filtered, concentrated under reduced pressure and transferred to an alumina column. A colourless band was eluted with hexane, concentrated and then cooled to −78 °C under N_2. Colourless needles of $[CpRu(CO)_2\{(CH_2)_3Cl\}]$ separated. The mother liquor was syringed off and the product dried under reduced pressure. The product melted to an oil on warming to room temperature.

Preparation of $[CpRu(CO)_2\{(CH_2)_nBr\}]$ ($n=3$–5)

$Na[CpRu(CO)_2]$ (1.3 mmol) in THF (8 ml) was added over 5 min to a stirred solution of $Br(CH_2)_nBr$ ($n=3$–5) (1.5 mmol) at −78 °C. The solution was stirred for 20 min at −78 °C after which time the solvent was removed under reduced pressure. The work-up was identical to the procedure described above.

Preparation of $[CpRu(CO)_2\{(CH_2)_nI\}]$ ($n=3$–5)

NaI (2 mmol) was added to a solution of $[CpRu(CO)_2\{(CH_2)_nBr\}]$ ($n=3$–5) (1 mmol) in acetone (4 ml). The mixture was stirred at room temperature for 13 h. The reaction can be monitored using ^1H NMR spectroscopy, by observing the disappearance of the triplet due to CH_2Br. The solvent was then removed under reduced pressure. The work-up was identical to the procedure described above.

Results and discussion

The complexes $[CpRu(CO)_2\{(CH_2)_nX\}]$ (X=Cl, $n=3$; X=Br, $n=3$–5) were prepared by reacting $Na[CpRu(CO)_2]$ with $X(CH_2)_nX$ at −78 °C, eqn. (1).

$$Na[CpRu(CO)_2] + X(CH_2)_nX \xrightarrow[\text{THF}]{-78\ ^\circ C} [CpRu(CO)_2\{(CH_2)_nX\}] + NaX \quad (1)$$

($n=3$, X=Cl, Br; $n=4$, 5, X=Br)

The reaction is similar to that used for the preparation of $[CpFe(CO)_2\{(CH_2)_nX\}]$ [6, 7] except that a significantly lower temperature is needed to prevent the formation of $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ than is needed in the case for the iron analogues. The [CpRu-

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$(CO)_2\{(CH_2)_nX\}]$ (X = Cl, Br) complexes were obtained as colourless oils in good to moderate yields. Like their iron analogues, the $[CpRu(CO)_2\{(CH_2)_nBr\}]$ complexes react with NaI to form $[CpRu(CO)_2\{(CH_2)_nI\}]$, eqn. (2) ($n$ = 3–5).

$$[CpRu(CO)_2\{(CH_2)_nBr\}] + NaI \longrightarrow [CpRu(CO)_2\{(CH_2)_nI\}] + NaBr \qquad (2)$$

The complex $[CpRu(CO)_2\{(CH_2)_3I\}]$ was isolated as a colourless, low melting solid, whilst $[CpRu(CO)_2\{(CH_2)_nI\}]$ (n = 4, 5) were obtained as colourless oils. The $[CpRu(CO)_2\{(CH_2)_nX\}]$ complexes appear to be significantly more stable to air and light than are their iron analogues and they may thus be useful precursors for other functionalised ruthenium alkyl compounds. The iodoalkyl complex $[CpRu(CO)_2\{(CH_2)_3I\}]$ has since been briefly reported, but as a yellow solid [10]. Our experience has shown that a yellow colour indicates the presence of trace quantities of $[CpRu(CO)_2]_2$. The complex $[CpRu(CO)_2\{(CH_2)_3Cl\}]$ also reacts with NaI to form $[CpRu(CO)_2\{(CH_2)_3I\}]$; however, a large excess of NaI (*c.* 100 fold) and long reaction times (2–3 days) are needed to obtain even moderate yields. The data for the ruthenium haloalkyl complexes are reported in Tables 1 and 2.

As with the iron haloalkyl complexes, the IR ν(CO) bands of the ruthenium complexes show a very slight trend towards lower wave numbers as the carbon chain lengthens from n = 3 to 5. Little change is observed on changing X from Cl to Br to I.

Assignments of the ^1H and ^{13}C NMR spectra of these complexes were made using COSY and HETCOR experiments. The ^1H NMR data is shown in Table 1. The chemical shift of the Cp peaks is not affected by either n or X. In contrast both n and X affect the shifts of the CH_2X peaks. Thus these peaks are shifted 0.1–0.2 ppm upfield as X changes from Cl to Br to I, reflecting the electronegativity differences of the halogens. As n changes from 3 to 4, the CH_2X triplets move downfield by 0.1 ppm, presumably reflecting a decrease in the influence of the ruthenium group.

The ^{13}C NMR data are shown in Table 2. The CO peaks of the complexes move to a marginally lower field as n changes from 3 to 5. The nature of the halogen does not appear to affect the position of the CO or Cp peaks. The effect of the halogen on the δ value of the CH_2 carbon α to ruthenium is very apparent for n = 3 but diminishes with increasing n. The peak due to the α-carbon is shifted upfield for complexes with smaller values of n. This is contrary to what one would expect from consideration of the inductive effect of the halogens. Of particular interest are the compounds where n = 3, for which the peak of the CH_2 carbon α to ruthenium is at a higher field for X = Br than for X = I. These observations could possibly be explained in terms of a weak bonding interaction between the halogen and the ruthenium. The interaction between ruthenium and X is also shown by the 1–2 ppm downfield shift of the peaks of the carbons α to X for n = 3, relative to the corresponding peaks for compounds with n = 4 or 5. Thus as n increases, the distance between X and Ru increases, and the effect of their interaction decreases. This is as observed for their iron analogues [6]. Such an interaction is also indicated by the mass spectral data. Apart from spectroscopic evidence [6], kinetic [3], thermal [14] and synthetic [11] evidence

TABLE 1. Data for the $[CpRu(CO)_2\{(CH_2)_nX\}]$ complexes

n	X	Yield (%)	m.p. (°C)	IR ν(CO)^a (cm^{-1})	^1H NMR^b (δ)					
					Cp	CH_2X	α-CH_2	β-CH_2	γ-CH_2	δ-CH_2
3	Cl	38	oil	2021vs, 1963vs	5.20s	3.39t ^3J = 7.0	1.56m	1.94m		
	Br	67	oil	2022vs, 1965vs	5.24s	3.30t ^3J = 7.2	1.60m	2.06qu ^3J = 7.8		
	I	75	37–39	2022vs, 1962vs	5.25s	3.10t ^3J = 7.4	1.58m	2.04m		
4	Br	54	oil	2020vs, 1961vs	5.24s	3.43t ^3J = 6.8	1.64m	1.64m	1.85m	
	I	88	21–22	2020vs, 1960vs	5.24s	3.21t ^3J = 7.0	1.76m	1.76m	1.82m	
5	Br	68	oil	2019vs, 1960vs	5.21s	3.38t ^3J = 6.9	1.60m	1.60m	1.42m	1.85qu ^3J = 7.1
	I	80	oil	2019vs, 1960vs	5.22s	3.17t ^3J = 6.9	1.56m	1.56m	1.37m	1.83qu ^3J = 7.2

[a] In hexane. [b] In $CDCl_3$ relative to TMS, J values in Hz, α-CH_2 refers to those protons on the carbon α to ruthenium etc.; t = triplet, qu = quintet.

TABLE 2. Further data for the $[CpRu(CO)_2\{(CH_2)_nX\}]$ complexes

n	X	^{13}C NMR[a]							Elemental analysis[b]	Molecular ion[c]
		CO	Cp	CH_2X	α-CH_2	β-CH_2	γ-CH_2	δ-CH_2		
3	Cl	201.9	88.5	47.6	−8.6	42.2			C: 40.20(39.98) H: 4.00(3.66)	300
	Br	201.8	88.4	36.2	−7.4	42.2			C: 35.10(34.80) H: 3.40(3.20)	348
	I	201.8	88.4	10.1	−4.5	43.5			C: 30.90(30.69) H: 2.80(2.81)	392
4	Br	202.1	88.5	33.8	−5.3	37.7	37.4		C: 37.60(36.90) H: 3.50(3.60)	362
	I	202.1	88.5	7.4	−5.6	40.1	38.0		C: 32.90(32.61) H:3.10(3.23)	406
5	Br	202.3	88.5	34.2	−4.1	38.7	33.1	32.5	C: 39.30(38.72) H: 3.90(4.06)	376
	I	202.3	88.5	7.6	−4.1	38.5	35.5	33.3	C: 35.20(34.38) H: 3.75(3.61)	420

[a] In $CDCl_3$, relative to TMS; α-CH_2 refers to those protons on the carbon α to ruthenium etc. [b] Calculated values in parentheses. [c] Refers to most abundant isotope peak in the molecular ion pattern of the mass spectrum.

for such an interaction is available for other halopropyl transition metal complexes. Also apparent are the large chemical shift differences (*c.* 11 ppm) between the carbon α to Cl and Br, respectively, and Br and I (*c.* 26 ppm), respectively, reflecting the different electron withdrawing characters of the halogens.

The low resolution mass spectra of these ruthenium complexes have been recorded. Although no high resolution or metastable data were obtained, the spectra indicate that the ruthenium haloalkyl complexes behave identically to their iron analogues under electron impact mass spectral conditions [6]. Notably, the fragments $[CpRu(CO)_2X]$ and $[CpRu(CO)X]$ have significant relative intensities only for the complexes where $n=3$, implying that the Ru–X bond is formed much more easily in these complexes. The observed relative intensities also imply that the Ru–I bond is more readily formed than the Ru–Br bond, lending further support to the explanation of the deshielding effect seen in the ^{13}C NMR data discussed earlier.

Preliminary studies have shown that these $[CpRu(CO)_2\{(CH_2)_nI\}]$ complexes are good precursors to ruthenium-containing heterobimetallic complexes of the type $[Cp(CO)_2Ru(CH_2)_nM(CO)_3Cp]$ (M = Mo or W) [15]. Further work on the reactions of these $[CpRu(CO)_2\{(CH_2)_nX\}]$ complexes is in progress and will be reported in a forthcoming paper [16].

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