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STUDIES IN FLUORINATED 1,3-DIKETONES AND RELATED COMPOUNDS, PART XVI: MIXED LIGAND COMPLEXES OF RUTHENIUM WITH FLUORINATED 1,3-DIKETONES

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SUMMARY

Spectral data of some new ruthenium(II) complexes with 1,5-cyclooctadiene (COD) and fluorinated 1,3-diketones reveal marked effects on the geometry of these complexes on incorporation of fluorine in the 1,3-diketone skeleton. As the degree of fluorination in these diketonates increases, the presence of an additional isomer is observed.

INTRODUCTION

The chemistry of ruthenium complexes with COD has been extensively pursued [1-4] due to their possible applications as catalysts in organic synthesis [1,2] and the probability of diverse structural behaviours [3,4]. There is however limited information on (COD) Ru mixed ligand complexes with chelating ligands [5] and no detailed study has been made on structural possibilities in such systems. In the present communication, synthesis and detailed spectral study of some (COD)Ru bis(fluorinated 1,3-diketonates) are reported and the observed data correlated to the substitution and orientation effects in the complexes.

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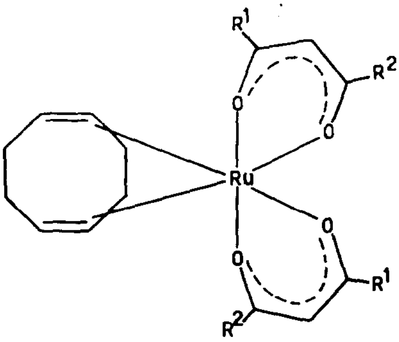
RESULTS AND DISCUSSION

Spectral studies of the (COD)Ru (fluoro-1,3-diketonate) complexes investigated give evidence for the O,O'-coordination and chelation of the 1,3-diketone anions (Fig. 1). The ir (Table 1) spectra show no bands in the region 1650-1700 cm^{-1} and thus the probability of a C-bonded 1,3-diketone anion [6] and a bridging ligand, as reported for the carboxylate anion [3], is ruled out. Besides, the formation of a hydride structure [4] is not considered as no ν Ru-H band is observed around 1990 cm^{-1}. The proposed mode of coordination is also supported by the nmr spectral data. The disappearance of the nolic proton signal in the coordinated 1,3-diketone anion and the low field shift of the methine signal are consistent with the pseudo aromatic nature of the chelate ring [6].



	R^1	R^2
(a)	CH_3	$p\text{-}FC_6H_4$
(b)	CF_3	C_6H_5
(c)	C_2F_5	$p\text{-}FC_6H_4$

Fig. 1. Spectral representation.

In the ir spectra of the complexes, the C $\overset{---}{-}$ O band is observed around 1600-1630 cm^{-1} and the band in the region 1560-1480 cm^{-1} has been assigned to the C $\overset{---}{-}$ C vibration

TABLE 1

IR spectral data of (COD)Ru $\left[R^1C(O)CHC(O)R^2\right]_2$ complexes (KBr; cm^{-1})

Compound	1,3-diketone anion		COD	Other bands
	$\mathrm{C}\overset{---}{\text{—}}\mathrm{O}$	$\mathrm{C}\overset{---}{\text{—}}\mathrm{C}$	$\mathrm{C}\overset{---}{\text{—}}\mathrm{C}$	
(a)	1590vs 1565vs	1515sh 1495vs	1420s 1250s	2960br, 1390s, 1290vs, 1170vs, 1140vs, 1070sh, 1020m, 940s, 800m, 750vs, 710m, 680s, 650s
(b)	1600vs 1570vs	1520sh 1495vs	1410s 1210s	2950br, 1385vs, 1290m, 1260m, 1155s, 1095s, 1015m, 850m, 800s, 760s, 680sh, 610s
(c)	1600vs 1570vs	1525vs 1520sh	1410vs 1210s	2950br, 1390vs, 1300vs, 1280m, 1155s, 1095m, 1010s, 845s, 800sh, 760s, 680sh, 610s

(abbreviations : vs = very strong, s = strong, sh = shoulder, m = medium, br = broad).

coupled slightly with C-H bending mode. The shifts observed for these bands with change in alkyl substituents are as reported [6]. The ν C-O and ν C-C bands show positive shifts. The C-F bands are observed in the region 1150-1100 cm^{-1}. The bands observed in the region 1430-1410 cm^{-1} have been assigned to the C $\overset{\cdots}{=}$ C vibration of the coordinated COD coupled with other vibrations [7].

In 90 MHz spectra of the complexes, methine proton signals of the 1,3-diketone anions in the region δ 5.9-6.5 ppm showed splitting and the aryl proton multiplet was observed in the region δ 6.9-8.1 ppm. The COD methine and methylene signals were observed as multiplets in the regions δ 2.0-2.6 ppm and δ 2.0-2.6 ppm respectively. Deshielding of the methine protons of the chelate ring and COD was observed in the spectra of complexes with fluoroalkyl substituted diketones [6]. The spectrum of compound (a) [R^1 = CH_3; R^2 = p-FC_6H_4] exhibited a single methyl signal at δ 2.3 ppm and a split methine proton signal at δ 6.0 ppm. In an earlier report [5], the synthesis and ^1H nmr studies of (COD)Ru bis(benzoylacetone) have been reported and the existence of three isomers (A), (B) and (C) proposed (Fig. 2a). The <u>cis</u> isomers (A) and (B) were not distinguished and the observed -CH_3 signal attributed to either (A) or (B) while the <u>trans</u> isomer (C) was reported to exhibit two -CH_3 signals. As the spectral data obtained for the complexes under study do not correspond to the earlier reported observations, a high field ^1H nmr investigation of the complexes was carried out (Table 2).

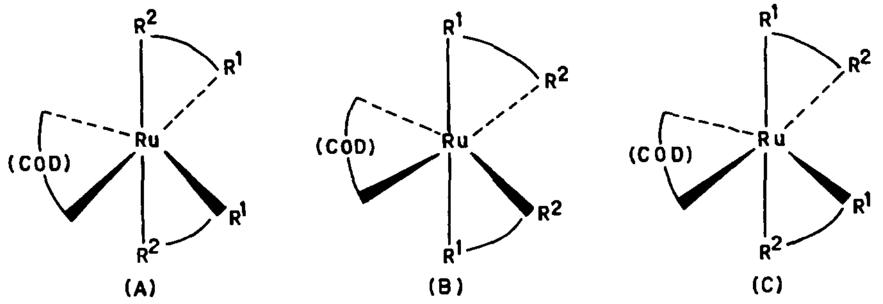
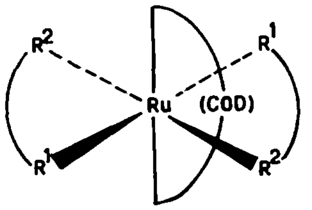


Fig. 2a. Two cis- (A, B) and a trans-isomer(s).

The high field ^{1}H nmr of the complex (a) showed only one methyl signal at δ 2.30 ppm, two methine signals at δ 5.9 ppm and δ 6.05 ppm and two sets of aryl signals for the coordinated 1,3-diketone anions. This gives evidence for the formation of two isomers in compound (a) with equivalent $-CH_3$ and non-equivalent aryl groups and rules out presence of any two isomers from the reported forms (A), (B) and (C). The above observations can be explained by considering the possibility of another trans isomer (D) (Fig. 2b) and the existence of isomers (A) and (D). The two signals observed for the =CH- proton are



(D)

Fig. 2b. Trans-isomer.

TABLE 2

High field ^1H NMR spectral data of compound (a), (b) and (c) ($CDCl_3$; δ ppm)

Compd.	Substituents in 1,3-diketone		ppm for COD protons		δ ppm for =CH protons of 1,3-diketones	δ ppm for 1,3-diketones substituent	
	R^1	R^2	=CH	$-CH_2$		R^1	R^2
(a)	$-CH_3$	$p-FC_6H_4$	4.12-4.21m 4.3 -4.4 m	2.19-2.3 m 2.41-2.51m	5.9 s, 6.05s	2.3 brs	6.95dd 7.1dbr 7.6dbr 7.98dbr
(b)	$-CF_3$	C_6H_5	4.28-4.4 m 4.46-4.72m	2.1 -2.39m 2.49-2.61m	6.45d, 6.5 d	-	7.3-7.4m 7.45-7.63m 7.71 dbr 7.80dbr 7.98dbr 8.00dbr
(c)	$-C_2F_5$	$p-FC_6H_4$	4.2 -4.4 m 4.59-4.79m	2.1 -2.32m 2.4 -2.64m	6.43s, 6.45s, 6.47s, 6.49s	-	7.01 dbr 7.06dbr 7.2 dbr 7.8 dbr 7.17dbr 7.69dbr 7.94dbr 8.1 dbr

attributed to the non-equivalent nature of the chelate rings in the proposed isomers, as it has been reported that the ring proton is very sensitive to environmental effects [8] .

The spectrum of (b) $[R^1 = CF_3$ and $R^2 = C_6H_5]$ shows methine signals of different intensity with splitting in the region δ 6.5 d and δ 6.45 d (Fig. 3) and four sets of aryl signals in the region δ 7.3 to δ 8.00 of the 1,3-diketone anion. In the spectra of (c) four sets of aryl signals and four methine signal for the 1,3-diketonate anion are observed.

The spectra for compounds (b) and (c) show the existence of all possible cis and trans isomers. Additional methine and aryl signals can be expected due to steric factors, resulting in their different orientation.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 337 spectrometer in nujol. ^{1}H nmr spectra were recorded on Jeol FX-90Q and Brucker WM-400 models in $CDCl_3$ with TMS as an internal standard and melting points were uncorrected.

Preparation of $[(COD)RuCl_2]_n$ The complex was prepared according to the method reported by Powell [5], by refluxing cyclooctadiene (2 cc) and $RuCl_3.H_2O$ (0.5 gm) in absolute ethanol on water bath for 3 hrs. A dark brown solid separates out. It is highly insoluble in common organic solvents and decomposes at temp. 250°C.

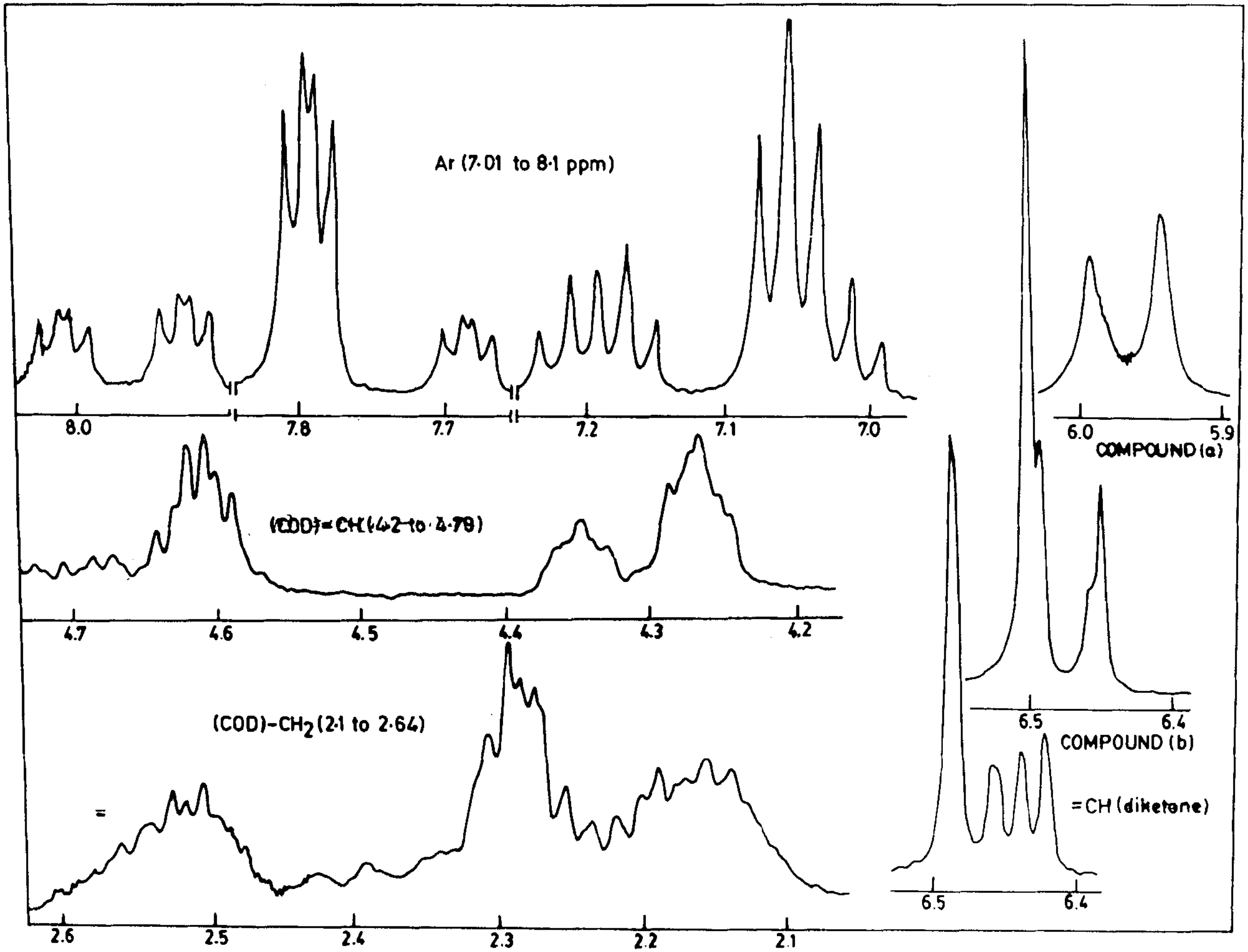


Fig. 3. ^{1}H NMR (400 MHz) spectrum of compound (c).

TABLE 3

C/H Analysis and M.P. of some new (COD)Ru$[R^1C(O)CHC(O)R^2]_2$ complexes

Compound	Formula	C/H Calculated C	C/H Calculated H	C/H Found C	C/H Found H	M.P. °C
(a)	$C_{28}H_{28}O_4F_2Ru$	59.25	4.93	59.50	5.10	108
(b)	$C_{28}H_{24}O_4F_6Ru$	52.58	3.75	52.75	4.12	115
(c)	$C_{30}H_{22}O_4F_{12}Ru$	46.45	2.83	45.87	2.31	127

Preparation of 1,3-diketones All the 1,3-diketones were prepared by the method of Joshi et al. [9] .

Preparation of (COD)Ru(1,3-diketone)$_2$ complexes The (1,5-cyclooctadiene)ruthenium chloride (0.27 g, 1 mmol) was heated to 140 °C with the respective diketones (0.3 g) in dimethyl formamide (3 ml) in the presence of anhydrous Na_2CO_3 (1 gm, excess) until it dissolved to form a deep orange solution. The mixture was filtered and the residue washed with cold methanol, water added dropwise to the filtrate for precipitation of the complex. It was recrystallised from methanol. The compounds were purified by column chromatography over florsil column using cyclohexane and solvent ether as solvents. The compounds showed satisfactory carbon and hydrogen analysis (Table 3).

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