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SYNTHESIS OF SOME 1,5-CYCLOOCTADIENE—RUTHENIUM(II) COMPLEXES

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Summary

The polymeric, halogen-bridged complex [(diene)RuX$_2$]$_n$ (where diene = 1,5-cyclooctadiene) reacts with acetylacetone, benzoylacetone, salicylaldehyde, 2-mercaptopyridine, 8-hydroxyquinoline and 2-mercaptobenzthiazole in hot dimethylformamide in the presence of sodium carbonate, to give chelate complexes [(diene)ruthenium(chel)$_2$]. Two geometrical isomers of 1,5-cyclooctadiene bis(benzoylacetonato)ruthenium(II) have been characterised.

Diene bis(dimethyldithiocarbamato)ruthenium(II) complexes [diene = 1,5-COD or bicyclo[2.2.1]hepta-2,5-diene] are also described.

Introduction

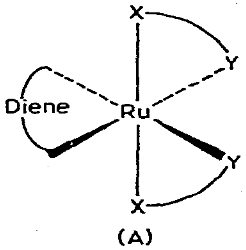
Although the polymeric, halogen-bridged complexes [(diene)RuX$_2$]$_n$ [where diene = 1,5-cyclooctadiene, (I), or bicyclo[2.2.1]hepta-2,5-diene, (II)] have been known for many years [1,2], only a few of their reactions have been reported. One reason for this is their extreme insolubility in most common organic solvents. *p*-Toluidine causes fission of the halogen bridges to yield [RuX$_2$(diene)(*p*-toluidine)$_2$] [1]. Bis-π-enyl-1,5-cyclooctadiene-ruthenium(II) complexes result when (I) reacts with allyl Grignard reagents [3].

Pannetier et al. prepared bis(acetylacetonato)(1,5-cyclooctadiene)ruthenium(II) [4] and the corresponding norbornadiene derivative [5] by a two-step procedure involving (diene)(oxalato)ruthenium intermediates. A more direct method of making the bis(acetylacetonato) complexes is reported here, and its extension to the preparation of several new compounds [(diene) ruthenium (chel)$_2$] described. (Where chel = benzoylacetonato, salicylaldehydato, pyridine-2-thiolato, oxinato-, benzthiazole-2-thiolato, and dimethyldithiocarbamato-).

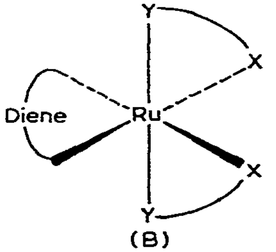
Results and discussion

When [(1,5-COD)RuCl$_2$]$_n$ is heated for a few minutes with acetylacetone in dimethylformamide, in the presence of anhydrous sodium carbonate, bis (acetylacetonato)(1,5-cyclooctadiene)ruthenium(II) is formed. Similar reactions of (I) with salicylaldehyde, 2-mercaptopyridine, 2-mercaptobenzthiazole and 8-hydroxyquinoline smoothly afford the compounds (1,5-COD)ruthenium(chel)$_2$, where chel = OC_6H_4CHO (VII); SC_5H_4N (VIII); OC_9H_6N (IX) and SC_7H_4NS (X).

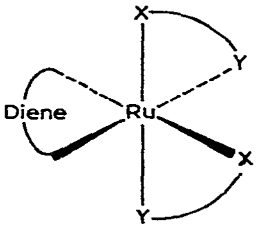
The PMR spectra of some samples of (1,5-cyclooctadiene)bis(salicylaldehydato)ruthenium(II) indicated the presence of geometrical isomers, particularly before thorough recrystallisation. The analytical sample showed only one sharp resonance (τ 1.06 ppm) in the -*CH*O region, indicating that the two salicylaldehydato ligands are symmetrically disposed to each other, as in (A) or (B). In the spectra of some specimens, two weaker additional lines at τ 0.95 and 1.29 ppm appeared, showing that isomer (C) was also present.



(A)



(B)



(C)

With 2-mercaptopyridine, compound (I) afforded an orange cystalline product, (VI), in 80% yield. The sample had a sharp melting point, was monomeric in chloroform solution, and behaved as a single substance on thin layer chromatography. These results suggest the presence of only one isomer. The related compound $(Ph_3P)_2Ru(2\text{-}C_5H_4NS)_2$ has recently been shown by X-ray diffraction to have a *trans* arrangement of sulphur atoms, with the two Ph_3P ligands *cis* to each other [6].

We had hoped to obtain tentative evidence for the structures of our compounds using vibrational spectroscopy in the 200 - 500 cm^{-1} region. Unfortunately attempts to obtain Raman spectra were unsuccessful owing to sample decomposition in the laser beam. Far IR spectra were measured, but the observed bands could not be assigned with any confidence to Ru—N, Ru—O or Ru—S vibrations.

As mentioned above there are three possible geometrical isomers of a complex such as (COD)Ru(X—Y)$_2$. Liquid chromatography showed that the crude product from the reaction of benzoylacetone with (I) did contain three such components, one present in very low proportion. By recrystallisation and column chromatography it was possible to separate two of the isomers [compounds (V) and (VI)] (see Table 1). The PMR spectrum (V) m.p. 176°, shows only one sharp resonance, assigned to equivalent *CH*$_3$ groups of the two benzoylacetonato ligands, at τ 7.71 ppm. In the spectrum of (VI), m.p. 84°, two resonances of equal intensity at τ 7.72 and 7.98 ppm indicate non-equivalent methyl groups, consistent with a structure of the type (C).

$[(1,5\text{-COD})RuCl_2]_n$ and $[(Nbd)RuCl_2]_n$ react with sodium dimethyldithiocarbamate in hot dimethylformamide to yield the bis(dimethyldithiocarbamato)(diene)ruthenium (II) derivative. The infrared spectra indicate bidentate dithiocarbamate ligands [ν(CN) 1520 cm^{-1}, s] [7]. At room temperature

TABLE 1

ANALYTICAL DATA FOR THE RUTHENIUM COMPLEXES

Compound	M.p. (°C)	Recryst. solvent	Found (calcd.) (%)			Mol.wt.found (calcd.)
			C	H	S	
(III) (COD)Ru(Acac)$_2$	151—152	Acetone or aq. acetone	53.4 (53.1)	6.2 (6.4)		
(IV) (nbd)Ru(Acac)$_2$	101—102	Aq. acetone	52.5 (52.5)	5.4 (5.7)		
(V) (COD)Ru(Bzac)$_2$	175—176	Methanol	63.3 (63.3)	5.8 (5.7)		
(VI) (COD)Ru(Bzac)$_2$	82— 84	Aq. methanol	63.3 (63.3)	5.6 (5.7)		
(VII) (COD)Ru(Sal)$_2$	163—165	Aq. acetone	58.6 (58.5)	4.9 (4.9)		
(VIII) (COD)Ru(C_5H_4NS)$_2$	219—220	Methanol	50.6 50.1 (50.3)	4.7 4.9 (4.7)	14.1 (14.9)	399(430)
(IX) (COD)Ru(Ox)$_2$	290—295 dec.		62.7 (62.8)	4.9 (4.9)	N=5.7 (N=5.6)	490(498)
(X) (COD)Ru(Mbt)$_2$	Darkens 260° dec.	Dimethyl formamide	49.0 (48.8)	3.8 (3.7)	23.6 (23.7)	
(XI) (COD)Ru(S_2CNMe_2)$_2$	218—220	Aq. methanol	37.7 (37.4)	5.3 (5.4)	28.4 (28.5)	446(449)
(XII) (nbd)Ru(S_2CNMe_2)$_2$	238—239	Aq. methanol	36.3 (36.0)	4.6 (4.6)	29.5 (29.6)	

the proton NMR spectra show inequivalence of the methyl groups of the dithiocarbamato ligands, but on warming the two resonances coalesce (at about 57°) to a single line. Similar behaviour has been reported for a number of dithiocarbamato complexes [8 - 10].

Experimental

Melting points were determined in open capillaries on a Gallenkamp apparatus and are uncorrected. Elemental analyses and molecular weight measurements (Vapour pressure osmometry in chloroform) were by A. Bernhardt, Elsbach über Engelkirchen, West Germany and by the School of Pharmacy, London. PMR spectra in $CDCl_3$ were recorded on Varian EM360 and HA-100 spectrometers.

Bis(acetylacetonato)(1,5-cyclooctadiene)ruthenium(II)

(1,5-cyclooctadiene)ruthenium(II) chloride (0.27 g, 1 mmol) was heated to ca. 140° with acetylacetone (0.3 ml) in dimethylformamide (5 ml) in the presence of anhydrous sodium carbonate (1 g, excess) until it dissolved to form a deep orange solution. (about 5 min). The mixture was filtered and the sodium salts washed with methanol. Water was added slowly to the combined filtrate and washings until the product separated as yellow microcrystals. Recrystallisation from aqueous methanol afforded bis(acetylacetonato)(1,5-cyclooctadiene)ruthenium(II), 0.23 g (56%), m.p. 101 - 102°. (Lit. [4] m.p. 97°.)

Bis(benzoylacetonato)(1,5-cyclooctadiene)ruthenium(II)

The crude mixture of isomers was similarly prepared from (1,5-cyclooctadiene)ruthenium(II) chloride (0.82 g, 3 mol) and benzoylacetone (1.05 g). Crystallisation of this product from methanol afforded orange-yellow crystals of isomer (V), (0.35 g) m.p. 164 - 169°, raised to 175 - 176° after two further recrystallisations from methanol.

Addition of water to the mother liquors from the crystallisation of the crude mixture of products gave a yellow precipitate (0.890 g) which was chromatographed on Florisil. 10% Diethyl ether in cyclohexane eluted first a yellow band containing isomer (V), followed by the main orange band. Further elution gave low yields of two red compounds (not identified). Thin-layer and liquid chromatography showed that the main fraction mainly consisted of one component [isomer (VI)] which was purified by three recrystallisations from aqueous methanol to m.p. 82 - 84°.

Procedures similar to that described above for compound (III) were followed in the preparation of compounds (VII) - (X). Compounds (VIII) and (IX) crystallised from the dimethylformamide solution on addition of methanol. Compound (X) is soluble in hot dimethylformamide, but separates on cooling.

Bis(dimethyldithiocarbamato)(1,5-cyclooctadiene)ruthenium(II)

$[(1,5\text{-COD})RuCl_2]_n$ (0.28 g) was added over 3 min to a hot solution of sodium dimethyldithiocarbamate (0.26 g) in dimethylformamide (8 ml). It rapidly dissolved to give a brown solution and a white precipitate of sodium chloride. The reaction mixture was cooled and water (ca. 10 ml) slowly added. The precipitate was filtered off and recrystallised from aqueous acetone to give yellow-brown plates (0.315 g) (70%). The corresponding norbornadiene complex was prepared similarly.

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