Novel Ruthenium(II) Carbonyl Compounds

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Several new ruthenium(II) carbonyl compounds have been prepared by the replacement of chlorine atoms of $Ru(CO)_2(2,2'$-bipyridyl or 1,10-phenanthroline)Cl_2 with chelating ligands such as salicylaldehyde, β-diketones, 2-hydroxy aromatic ketones and 8-hydroxyquinoline. It has been observed that the geometry of the products remained essentially the same (hexacoordinated, octahedral) as in the starting chloro compounds, the ligand acting as monodentate.

Introduction

Ruthenium and rhodium carbonyl complexes, being effective catalysts for hydrogenation reactions, have been intensively studied. Ruthenium carbonyl derivatives containing bidentate nitrogen donor ligands such as $Ru(CO)_2Cl_2[2,2'$-bipy or 1,10-phenan] were first prepared by Wilkinson *et al.* [1]; complexes of the type $[Ru(bipy)_2(CO)Cl]^+ClO_4^-$ and $[Ru(bipy)_2(CO)_2][PF_6]_2$ have been studied more recently [2, 3]. Selective mono-decarbonylation of some ruthenium complexes $Ru(CO)_2X_2L_2$ has been reported by Black *et al.* [4]. We report here the preparation of a series of six coordinate complexes of Ru(II) of the type $Ru(CO)_2(2,2'$-bipy or 1,10-phenan)L_2 where LH is a monobasic bidentate chelating ligand; these compounds are formed by the replacement of chlorine atoms in $Ru(CO)_2(2,2'$-bipy or 1,10-phenan)Cl_2 with a bidentate chelating ligand. The reactions carried out may be outlined as follows:

$$RuCl_3 \xrightarrow[6\text{ hr}]{CO,\ EtOH} \text{`Red carbonyl solution'}$$

$$\xrightarrow[2\text{ hr}]{2,2'\text{-bipy or }1,10\text{-phenan}} Ru(CO)_2(2,2'\text{-bipy or }1,10\text{-phenan})Cl_2$$

$$\xrightarrow[2\text{ hr}]{2NaL} Ru(CO)_2(2,2'\text{-bipy or }1,10\text{-phenan})L_2$$

where LH is one of the bidentate chelating ligands mentioned in Table I.

Experimental

Experiments were done in a dry, oxygen-free nitrogen atmosphere.

Sodio Derivative of Salicylaldehyde

Sodium methoxide prepared from sodium metal (0.046 g; 2 mmol) and methanol (5 ml), was refluxed in benzene (20 ml) with salicylaldehyde (0.244 g; 2 mmol) for 30 minutes. The solvent was then removed (along with excess methanol) under reduced pressure, product washed with hexane and kept *in vacuo* at 60° to obtain the sodio derivative as a dry, free flowing powder. The sodio derivative could also be prepared from sodium hydride and salicylaldehyde in 1:1 molar proportion in ether medium.

$Ru(CO)_2(bipy)(salicylaldehydo)_2$

The sodio derivative of salicylaldehyde [prepared as in (a)] was suspended in tetrahydrofuran (25 ml) and $Ru(CO)_2(bipy)Cl_2$ (0.384 g; 1 mmol) added and refluxed for 3 hr. The contents were then centrifuged and the product obtained as a solution in tetrahydrofuran was kept *in vacuo* to get a dry mass. This was extracted with cold methanol, and the extract concentrated under reduced pressure. The brown crystalline solid obtained was washed with benzene or chloroform, and dried. Yield 0.135 g (75% of theory).

Other ruthenium compounds were prepared similarly (Table I).

Results and Discussion

The new ruthenium compounds are dark brown in colour and they melt with decomposition. They are stable in dry air and are sparingly soluble in chloroform, benzene and hexane.

Monomeric $Ru(CO)_2(2,2'$-bipy or 1,10-phenan)-Cl_2 complexes have octahedral stereochemistry with

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TABLE I. New Ruthenium(II) Carbonyl Compounds.

No.	Reaction		Product	M.p. (°C)	Analysis Found (calc.)	
					C	H
	$Ru(CO)_2(1,10\text{-phenan})Cl_2$ with	(a)	a = $Ru(CO)_2(C_{12}H_8N_2)Cl_2$	220	41.82(41.15)	2.10(1.96)
1	Salicylaldehyde		$Ru(CO)_2(C_{12}H_8N_2)(C_7H_5O_2)_2$	98	58.44(58.00)	3.54(3.11)
2	Acetylacetone		$Ru(CO)_2(C_{12}H_8N_2)(C_5H_7O_2)_2$	80	53.33(53.80)	4.91(4.10)
3	Benzoylacetone		$Ru(CO)_2(C_{12}H_8N_2)(C_{10}H_9O_2)_2$	78	61.66(61.88)	3.67(3.94)
4	Dibenzoylmethane		$Ru(CO)_2(C_{12}H_8N_2)(C_{15}H_{11}O_2)_2$	75	67.87(67.40)	3.47(3.83)
5	8-Hydroxyquinoline		$Ru(CO)_2(C_{12}H_8N_2)(C_9H_6NO)_2$	160	62.00(61.41)	3.53(3.19)
6	2-Hydroxyacetophenone		$Ru(CO)_2(C_{12}H_8N_2)(C_8H_7O_2)_2$	200	59.58(59.27)	3.35(3.62)
7	2-Hydroxybenzophenone		$Ru(CO)_2(C_{12}H_8N_2)(C_{13}H_9O_2)_2$	190	65.25(65.63)	3.14(3.55)
8	2-Hydroxy-4-methoxy benzophenone		$Ru(CO)_2(C_{12}H_8N_2)(C_{14}H_{11}O_3)_2$	180	63.27(63.69)	3.43(3.79)
	$Ru(CO)_2(bipy)Cl_2$ with	(b)	b = $Ru(CO)_2(C_{10}H_8N_2)Cl_2$	>250	37.13(37.48)	2.44(2.08)
9	Salicylaldehyde		$Ru(CO)_2(C_{10}H_8N_2)(C_7H_5O_2)_2$	155	56.02(56.16)	3.18(3.14)
10	Acetylacetone		$Ru(CO)_2(C_{10}H_8N_2)(C_5H_7O_2)_2$	110	51.24(51.63)	4.12(4.30)
11	Benzoylacetone		$Ru(CO)_2(C_{10}H_8N_2)(C_{10}H_9O_2)_2$	140	60.16(60.41)	4.00(4.09)
12	Dibenzyolmethane		$Ru(CO)_2(C_{10}H_8N_2)(C_{15}H_{11}O_2)_2$	105	66.17(66.33)	3.47(3.95)
13	8-Hydroxyquinoline		$Ru(CO)_2(C_{10}H_8N_2)(C_9H_6NO)_2$	140	59.34(59.83)	3.67(3.32)
14	2-Hydroxyacetophenone		$Ru(CO)_2(C_{10}H_8N_2)(C_8H_7O_2)_2$	>200	57.27(57.57)	3.33(3.77)
15	2-Hydroxybenzophenone		$Ru(CO)_2(C_{10}H_8N_2)(C_{13}H_9O_2)_2$	>200	64.15(64.44)	3.44(3.67)
16	2-Hydroxy-4-methoxy benzophenone		$Ru(CO)_2(C_{10}H_8N_2)(C_{14}H_{11}O_2)_2$	>200	62.24(62.53)	4.22(3.91)

cis carbonyl, *cis* ligand and *trans* chlorine atoms. Their IR spectra (in cm^{-1}) show only one ν(Ru–Cl) at 330 (in vaseline) suggesting *trans* disposition of chlorine atoms [5]. The bipyridyl compound is reported to have two strong ν(CO) at 2070 and 2007 (in chloroform) since the two CO groups occupy *cis* positions [6]. The IR spectra of both the dichlorides (in nujol) have been found by us to furnish ν(CO) at 2030 and 1980. In the spectrum of $Ru(CO)_2(bipy)(salicylaldehydo)_2$, the ν(O–H) and ν(Ru–Cl) are absent as expected when the chlorine atoms are replaced by salicylaldehyde. In this chlorine-substituted product, ν(CO) appears in the lower frequency region. The band at 1980 is shifted to 1930 indicating stronger dπ–pπ interaction in the product, probably as a result of low π acceptor ability of salicylaldehyde oxo-anion as compared to chloride. The reduction in the ν(CO) value may also be correlated with the total electronegativity of the substituent group. The ν(C=O) of salicylaldehyde is seen at 1655, indicating the non-coordinating unidentate nature of the ligand in this complex. The ν(Ru–N) remains unchanged at 280 [5].

Similar features are also seen in the cases of other ligands (Table II).

Hence it may be concluded that while the chlorine atoms are replaced either with salicylaldehyde or any other similar ligand, the geometry of the substituted product remains the same as the starting chloro compound as shown in the following diagram.

TABLE II. IR Absorption Frequencies in cm^{-1} for Ruthenium(II) Carbonyl Compounds.

No.*	ν(CO)		Ligand ν(C=O)
(a)	2030	1985	–
1	2030	1950	1665
2	2000	1940	1650
3	2015	1940	1640
4	2005	1940	1645
5	2030	1930	1585**
6	2010	1930	1650
7	2020	1940	1645
8	2015	1930	1630
(b)	2030	1980	–
9	2030	1940	1660
10	2000	1940	1650
11	2015	1940	1655
12	2015	1940	1655
13	2020	1935	1585**
14	2010	1940	1655
15	2010	1930	1630
16	2010	1930	1635

*Sr. No. same as in Table I. **ν(C=N).

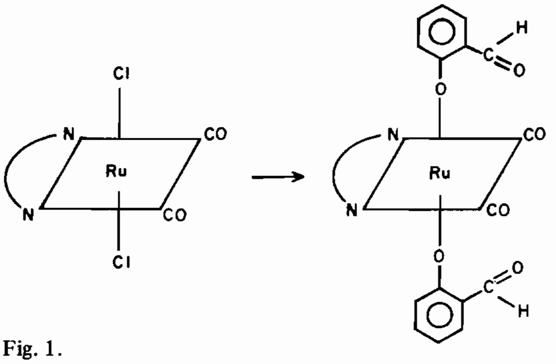

Fig. 1.

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